ELECTRO-PLATING

SURVEY OF MODERN PRACTICE

INCLUDING THE ANALYSIS OF SOLUTIONS

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PREFACE TO FIFTH EDITION

A NEW edition appearing during the rapidly progressive period of industrial activity associated with unparalleled war production, must necessarily contain some reference to the newer methods which have been introduced into the science and art of electrodeposition which has now found so wide application in engineering and industry generally.

The time has not come to do justice to the somewhat unusual methods which have been called for. Some indications, however, are possible, and are to be found in their respective sections of the book.

Of these more recent improvements on older processes and those of recent initiation, it may at once be assumed that they have not been put into service in any haphazard manner. Modern progress calls for intensive research and exploration of the practical possibilities prior to any ~~attempt to apply~~ them in any type of mass production.

Some improvements of older processes are naturally to be expected as newer processes are developed, but there is today more need than ever for them to be put on a sound practical basis before the layout of the capital and plant required for their large-scale application.

That these newer processes will have a determining influence on the future of the industry, there can be little doubt, though it may not be possible as yet to forsee with exactitude how these developments will mature.

Of previous innovations it is generally recognized that chromium plating had a far greater effect toward the general improvement of plating processes than could have been most sanguinely anticipated, and it is now safe to assume that during this present period, when the scarcity of some formerly essential materials has had to be compensated for by alternative methods, these latter may find continued application in developing peace-time industry.

In the present edition these newer features will be mainly of a practical character and are at present only briefly indicated. Details must be reserved for later publication.

We again gladly and gratefully acknowledge our indebtedness to those responsible for the loan of many of the illustrations which serve so excellent a purpose. Among them may be mentioned: The Westinghouse Brake and Signal Company, Limited, British Drug Houses, Imperial Chemical Industries, Messrs. Grauer and Weil, Limited, and Electro-Chemical Engineering Company, Limited.

S. F.
A. D. W.

PREFACE TO FIRST EDITION

THE methods of the electrodeposition of metals have in recent years been considerably advanced. This has been to some extent due to the organized research which has been initiated and carried out in America at the Washington Bureau of Standards, and in this country by the Department of Scientific and Industrial Research. Concomitantly there has been a growing sense of co-operation evidenced by the various associations of electro-platers in America, and in this country in the recently established Electro-platers' and Depositors' Technical Society, the journal of which has been freely consulted by the authors. Many private firms, too, have been responsible for much organized research on the subject due, in part, to the increasing applications of electrodeposition in several departments of engineering.

Very definite progress has accrued from these efforts. Not only has our knowledge of the fundamentals been largely increased, but quite new aspects of the deposition of metals have passed the experimental stage and become established practice with every promise of greater advances yet to come.

These advances have, so far, only found expression in the larger treatises and in many original papers.

It has, therefore, been thought advisable briefly to review these advances in a simple form which will, it is hoped, appeal to the practical plater.

Such a brief account is necessarily very incomplete, as the authors well appreciate. It is hoped, however, that, within the compass of this book, there will be found sufficient to indicate the nature of the advances, and to stimulate the desire for access to the numerous facilities now available for widened knowledge of the subject.

The new scientific knowledge of electrodeposition is now permeating the workshop, and must continue to do so until the numerous problems at present existing, with those which are sure to arise with the increasing applications of electrolysis to the adaptation of metals, are all referred to fundamental principles. Only through such channels can any hope exist for the extension of the processes and the production of deposits calculated to embrace the special properties now being called for.

Grateful acknowledgment is here made for the loan of illustrations from The Westinghouse Brake and Signal Company Limited, and Messrs. Grauer and Weil, Ltd.

S. F.
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such as silver and gold markedly depreciate the conductivity of copper. In many cases malleable metals are made brittle; ductile metals lose their characteristic power of being drawn satisfactorily into wire. Soft metals are made harder. Nowadays there is every argument for the production of the purest form of metal with the subsequent *addition* of any small amounts of other metals which may be beneficial.

While these examples concern the physical or mechanical properties of the metals, their chemical properties are equally altered, and this is a matter of moment to the metal colourer in view of the very different effects which are forthcoming when, for example, samples of pure and commercial metal are treated similarly in a colouring solution. As a general rule, the lighter browns produced on electrolytic copper are darkened on the commercial metal. There may easily be a considerable difficulty in matching up colours of two parts of a copper article containing both the electrolytic and commercial forms of the metal. This is a difficulty which the metal colourer frequently meets, and the divergencies of colour invariably increase with an increase of the impurity or, more generally, we may say, the added metal.

Yet some of the changes of properties occasioned by the presence of impurities are definitely advantageous. Copper in silver and in gold sensibly hardens these relatively soft metals, and it seems reasonable therefore that some additions of metals can be made and increased in order to develop really useful properties in metals which in their pure form are devoid of them. This is, in fact, the simple story of the production and application of what are called alloys or mixed metals. For this purpose we may regard carbon as a metal and recall that even the smallest quantity in iron increases its hardness and strength so that further controlled additions give rise to the long series of carbon steels which constitute the most important raw material of the engineering industry.

On the metal depositing and colouring sides, too, these alloys show properties widely different from those of their constituent metals. Slight variations of composition often bring marked changes in colouring properties increasing the complexity of the problem of the metal colourer to reproduce the same shades on different batches of work of slightly different composition.

Alloys. While electrolytic methods for the refining of metals have put on to the market a number of industrial metals in an exceedingly pure form, these do not necessarily exhibit properties of the greatest service in industry. It is common knowledge that certain mixtures of metals or alloys exhibit properties which are in advance of those of the pure metals individually, and hence the extensive use of the alloys in many departments of industry.

These alloys are used for several reasons. They are usually stronger than the single metals. They have increased hardness and therefore resistance to wear. Frequently they exhibit better working properties and are therefore more easily fashioned. Many have lower melting points and are applicable as solders. Others, too, are less liable to corrosion.

These alloys are exceedingly numerous and therefore varied in composition and properties. There are some more or less standard compositions which have general acceptance, but there is always the tendency for manufacturers to deviate from the standard mixtures in order to obtain slightly enhanced properties for which some special proprietary claim may be made, and hence there can be no dependence that any two samples of brass, for example, are of the same composition unless they have been guaranteed to conform to some accepted specification.

Action of Air on Metals. Few metals are capable of withstanding long exposure to atmospheric or other similar corrosive conditions. A piece of steel rusts quickly on exposure to damp air. Intensive investigation during the past two decades has considerably enlarged our knowledge of both the facts and their interpretation.

One estimate of the ravages of rust puts the annual loss as of the order of £500,000,000, and rust has been aptly called the "rat that eats steel." Rusting is strictly a chemical process and thus constitutes an eternal and flameless fire. Initially much labour is expended in extracting iron from its ore, but immediately the metal is put into service, unless definitely prohibited, it degenerates again to rust.

Research has of recent years produced a number of stainless and therefore rustless metallic products. These are relatively costly, so that we are far from realizing a "rustless" age. Chemical industry is concerned with fighting the enemy rust, and this is done by the application by one or other of several methods of chemically durable coatings. Paints and varnishes and less corrosive metals are examples, while a further alternative is that of producing on the surface of the corrosive metal a uniform and adherent layer of a stable compound, and this is the principle followed in metal-colouring processes.

Rate of Corrosion. Corrosion proceeds at very different rates with different metals and also with the same metal under differing conditions. This can readily be illustrated by submerging or partly submerging a number of clean iron nails in a variety of liquids. A good deal of suggestive information is forthcoming from even such simple experiments. For example, iron rusts in ordinary water, but the action is less marked in distilled water. If the distilled water is kept free from air the action on iron is only very slight, while a trace of alkali in water suffices to maintain the original brightness of the iron. Again, as may be anticipated, a small addition of hydrogen peroxide—which readily parts with oxygen—accelerates corrosion. These are results which are capable of simple explanation and from which some evidence is forthcoming upon which can be based a simple conception of the chemical changes concerned with the rusting of iron.

Atmospheric Conditions. Before proceeding to a study of the action of air on metals some recognition of the constituents of the atmosphere must be made. In different parts of the country—and, where international service conditions are under consideration—of the world, the conditions of the atmosphere vary considerably. There are, for example, different degrees of humidity at different times, differences of temperature, the presence or absence of rain which may wash away soluble products of the action of the atmosphere on the metal, and lastly, the presence of impurities arising from a difference in local industries with their respective outputs of gaseous and other impurities into the air.

One of the difficulties of comparison of results from different workers has been allowances for these different atmospheric conditions. As a result, it becomes necessary to state exactly the atmospheric conditions at the point at which an investigation has been carried out. In addition, there will be a certain amount of divergence in the recording and interpretation of the results which accrue to the investigation. It is apparent, therefore, that the results of such work are not subject to the same rigid classification which obtains in cases in which the conditions can be definitely stated, and also consistently maintained.

The atmosphere contains many constituents which might contribute to the staining, corrosion, and rusting of metals. Sulphuric acid is a common impurity. It results from the combustion of coals containing sulphur. Of this sulphur, probably one half finds its way into the air in the form of sulphuric acid and a slight appreciation of the following equation—

$$S + O_2 + O + H_2O = H_2SO_4$$

impresses the fact that 32 parts by weight of sulphur produce 98 parts by weight of pure sulphuric acid. Hence 100 tons of coal containing 1 per cent of sulphur, during burning, adds to the atmosphere $\frac{1}{2} \times \frac{98}{32} = 1\frac{1}{2}$ tons of sulphuric acid, and an easy calculation shows the amount of acid added to the air, by a power station consuming 2,000 tons of coal per day, unless steps are taken—and these *are* taken in some modern power stations—to remove the sulphur constituents from the flue gas before it finds its way into the air.

Another constituent of the air which makes a large contribution to corrosion is carbonic acid gas (CO_2). In the case of iron the following cycle of operations is generally agreed upon—

CO_2 and moisture form a very weak acid, carbonic acid (H_2CO_3). This attacks iron

$$Fe + H_2CO_3 = FeCO_3 + H_2$$

Ferrous carbonate ($FeCO_3$) is a known, though not large, constituent of rust. It is unstable, and in moist air changes thus—

$$2FeCO_3 + O + 3H_2O = Fe_2O_3 . 3H_2O + 2CO_2$$

Hydrated ferric oxide is the nearest approximation to the composition of rust, while CO_2 is liberated and therefore set free to continue cyclically its pernicious work. Everyday experience goes to show this. Painting over rusty iron is useless because of this continued action with the further production of rust which, underneath the coating of paint, causes it to peel in large patches. Nevertheless, carbonic acid

TABLE VIII

Behaviour of Metals with Air

Metal	Colour	Effect at Ordinary Temperature	Effect at High Temperature
Aluminium	White	Remains bright.	At red heat burns with white light, giving Al_2O_3.
Antimony	White	Remains bright.	Oxidizes at M.P., producing Sb_2O_3 (white).
Cadmium	White	Remains bright in air free from CO_2.	Burns to CdO (brown).
Chromium	Steel grey	Remains bright.	Superficial oxidation to Cr_2O_3.
Cobalt	Grey-white	Unacted on by dry air. Slowly oxidized by moist air.	
Copper	Red	Unacted on by dry air. CO_2 and water cause tarnishing, as also does H_2S.	Forms Cu_2O and CuO at low temperature. Burns at high temperature.
Gold	Yellow	Does not oxidize.	Does not oxidize.
Iron	White-grey	Dry air [illegible] action. Rusts in moist air.	Oxidizes to Fe_3O_4 (black).
Lead	Bluish white	Tarnishes.	First forms PbO (yellow), then Pb_3O_4 (red lead).
Manganese	Steel grey	Oxidizes to Mn_3O_4.	Oxidizes to Mn_3O_4.
Mercury	White	No action.	At nearly its B.P. forms HgO (red).
Nickel	White	Little action	Forms NiO.
Platinum	White	No action	Unaffected.
Silver	White	Unaffected. Turns black if H_2S is present.	Not oxidized, but melted metal occludes oxygen.
Tin	White	No action.	Oxidizes to SnO_2 (mixed with SnO).
Zinc	Bluish white	Slight oxidation.	Burns bluish flame forming ZnO.

gas plays some decorative part in the air in its production of those beautiful green antique effects common to statuary bronze. Here the acid first attacks the bronze and the resulting compounds are transformed to green basic carbonates which, being insoluble, provide a permanent and pleasing coating.

Sulphuretted hydrogen (H_2S) in the air provides another staining and corrosive agent. It results from the combustion of coal gas. The gas attacks silver thus—

$$2Ag + H_2S = Ag_2S + H_2$$

The silver sulphide (Ag_2S) constitutes the coloured tarnish upon all unlacquered silver goods. A similar action takes place with copper goods, the sometimes pleasing coloured stain being copper sulphide (Cu_2S). Both of these metallic sulphides are soluble in a weak solution of potassium or sodium cyanide, and these reagents are used in the cleaning of these metals, though they are, of course, far too poisonous to constitute a household remedy.

Corrosion and Rusting. Before leaving this brief account of the action of air on metals, it may be well to more carefully distinguish between the terms corrosion and rusting. The terms have so far been used somewhat vaguely, intentionally. A clear definition is now desirable. In the case of iron, the metal is in the first case very slightly dissolved by the acid constituents of the air. This attack (and other similar chemical effects) constitutes corrosion. Under some circumstances a metal may suffer such an attack and still remain clean. This happens in the usual dipping processes where the soluble products are washed away by [illegible] of rinsing waters. Formed slowly by the moist air, they are not, in the absence of rain, washed away before they undergo the second change into insoluble and therefore more permanent products. This second stage constitutes rusting, the term being most usually applied in the case of the corrosion of iron and its numerous variations in the form of steels. Finally, the accompanying table (VIII) gives a statement of the action of air on a number of metals at both ordinary and elevated temperatures.

CHAPTER II

ELECTRICITY AND ELECTROCHEMISTRY

VOLTAIC cells—Electrical units—Electrical work—Constitution of electrolytes—Current—The process of electrolysis—Degree of dissociation—Resistance of metals—Resistance of electrolytes—Mixed electrolytes—Relative ionic speeds—Absolute speeds of ions

Voltaic Cells. It was at the end of the 18th century that electrical current was first generated by the now very well-known method of immersing plates of zinc and copper in dilute sulphuric acid. The current generated was reputed to flow from the zinc to the copper inside the cell, and from the copper to the zinc outside the cell. For a long time this was the only source of current available for much important pioneering work in electrodeposition. The method, welcome as it then was, was nevertheless very faulty. Zinc dissolves in the acid and when current is being produced the corresponding hydrogen is set free at the copper plate. Thus very fine bubbles of gas collected on the copper plate and set up a very high resistance, considerably reducing the effect of the cell. This phenomenon was for a long time, and sometimes still is erroneously, called polarization. It could be minimized by continuously brushing off the gas bubbles, quite an inconvenient task. Later, Smee largely overcame the difficulty by substituting for the copper plate one of silver which had been platinized or coated with a thin film of platinum. This film, while apparently smooth, is microscopically rough, and from the fine points of the deposit the hydrogen bubbles are detached in much the same way as a liquid drops from a point. This was the principle of the Smee cell which provided an automatic method of eliminating the hydrogen and its detrimental effects.

The introduction of the Daniell cell in 1832 provided a chemical and much more satisfactory method of overcoming the difficulty. In one of a number of forms, this cell comprises a plate or rod of amalgamated zinc immersed in dilute sulphuric acid in which also stands a porous pot containing a solution of copper sulphate with an immersed copper plate or rod. The varied forms of this cell can be found from other sources. The chemical reactions are of more importance here.

In a simple manner it may be stated that the zinc dissolves in the acid—

$$Zn + H_2SO_4 = ZnSO_4 + 2H$$

The hydrogen does not appear at the zinc plate, but in th ionic form migrates towards the copper plate and, in contac with copper sulphate, reacts thus—

$$CuSO_4 + 2H = H_2SO_4 + Cu$$

The blue colour of the solution thus slowly disappears copper is deposited on the original copper plate withou hydrogen and there offers no addition to the resistance of t cell. The efficiency of the cell is therefore largely depend upon the presence of copper sulphate or, what is equivalen copper ions. The cell thus maintains a steady current ove long periods and finds considerable application in directions other than electrodeposition. The cell is of particular interest to us in that, if the current generated were used for th deposition of copper, as much of that metal would be deposited within the cell as in a copper depositing outfit fed by the current. Further, it was from the observations made on this internal copper deposit that the modern art of electro-typing found its origin. This development was due to the keen observation of Spencer and Jordan in England and Jacobi in Russia. A simple observation was fraught with an important industrial application. The Daniell cell provides us with many principles parallel to those applied in electrodeposition.

Electrical Units.—[illegible] of electricity along a conduct is, in many respects, comparable with that of water throug pipe. Thus in Fig. 1, the flow of water is effected by the pump, while the heights of water in the tubes A, B, and C indicate the pressure of the water at the base of these tubes. Similarly, in Fig. 2, the conductor AB is carrying electricity, this result being due to the cell or accumulator C. Simple conceptions and units are important. We measure quantity of water in pounds or gallons. Similarly we measure electricity [illegible] coulombs, and we define the coulomb as the quantity of electricity which will deposit 0·001118 gm. of silver, 0·000329 gm. of copper, or 0·00001035 gm. of hydrogen.

Next, we measure the rate of flow of water in pounds or gallons in minutes or hours, rate involving both quantity and time. Similarly current is the rate of flow of electricity. When the rate is such that one coulomb passes a given point er second, the rate of flow of electricity or current is called the mpere, a single term embodying both quantity and time. can therefore measure current by allowing it to deposit pper or silver. Thus, if in 30 minutes, 1·5 gm. of copper are posited, then the average current is—

$$\frac{1{\cdot}5}{0{\cdot}000329 \times 30 \times 60} = 2{\cdot}54 \text{ amperes}$$

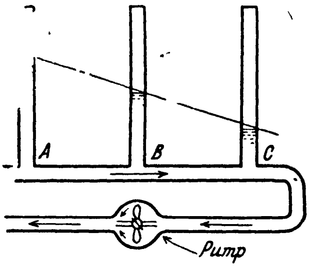

FIG. 1. FLOW OF WATER

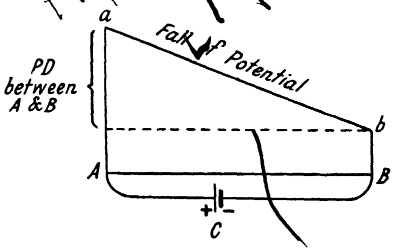

FIG. 2. FLOW OF ELECTRICITY

Why this apparently unusual unit came to be adopted need not be explained in detail, but it may be said that it is exactly one-tenth of a unit of current derived from electro-magnetic henomena and based on the c.g.s. (centimetre, gram, second) ystem of units.

Next, in **Fig. 1, water only moves because there is a difference of pressure** between the points A and C. The greater this difference of pressure the greater the rate of flow of the water. Similarly, in Fig. 2, electricity flows from A to B because there is also a difference of (what is here called) potential. The greater this difference of potential, the greater the rate of flow of coulombs or, in other words, the greater the current. Whence arises this difference of potential? In the case of water, the pressure is applied at the pumping station (in most cases). In the electrical simile the force is developed in the cell, accumulator or generator. This force is called Electromotive Force (E.M.F.). The difference of potential between the points *A* and *B* determines the force expended in driving the coulombs along the wire.

The unit of electromotive force is the volt which is also the unit of P.D. It is the unit driving power behind the electricity. Now all conductors offer some opposition or resistance to the flow of electricity. This resistance is measured in terms of ohms. The ohm is the resistance offered by a column of mercury 106·3 cm. long and a cross-sectional area of 1 square millimetre at a temperature of 0° C. This may appear to be a curious choice, but the derivation of these three important units was not made according to their convenient definitions. They had other origins which do not concern us here.

Now the volt is that difference of potential required to maintain a current of one ampere in an ohm resistance. This simple relationship is algebraically expressed in the form

$$\frac{\text{E.M.F. (volts)}}{R\ \text{(ohms)}} = \text{Current } (I)\ \text{(amperes)}$$

The rule applies for the whole or parts of a circuit, and is universally known as Ohm's Law, and is illustrated in Fig. 3 in which voltmeter and ammeter are shown connected to a wire having a resistance of one ohm between the points *A* and *B*. With this constant resistance any increase in the P.D. between the two points effects a corresponding increase in the current or, in other words, in a constant resistance, current is proportional to the P.D. With the acceptance of this law, ammeter and voltmeter readings provide a method of determining the resistance. If, for example, between the points *A* and *B* with a different wire resistance there is a P.D. of 2 volts and the ammeter reading is 10 amperes, then—

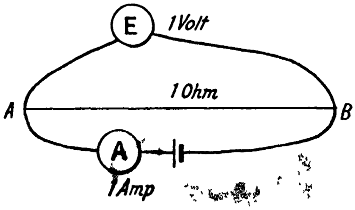

FIG. 3. ILLUSTRATING OHM'S LAW

$$R = \frac{E}{I} = \frac{2}{10} = 0{\cdot}2 \text{ ohm.}$$

In much the same way if the voltmeter reading across a plating bath is 2·5 volts and the current 20 amperes, then the equivalent resistance of the bath is 2·5 ÷ 20 = 0·125 ohm. The relationship of these three values will have many applications in the interpretation of the instrument readings across a plating tank, although there are occasions when some slightly different interpretation will have to be placed upon the readings.

Electrical Work. When metals are being deposited from solutions, work is being done, and this, varying with the conditions, must be capable of quantitative expression. Now electrical work is expressed as joules, the joule being the amount of work done when a current of one ampere is produced under a P.D. of one volt for one second. Thus with a bath pressure of 3 volts and a current of 40 amperes, the work done per hour

$$= 3 \times 40 \times 60 \times 60 = 432{,}000 \text{ joules.}$$

On the mechanical side, work is expressed in terms of the foot-pound which is equivalent to the work done in raising a pound weight to a height of one foot. Thus a hundredweight raised to a height of 10 feet represents an expenditure of work of 112 × 10 = 1120 foot-pounds.

We frequently, however, express the rate of doing work. Thus, when work is done at the rate of 33,000 foot-pounds per minute or 550 foot-pounds per second the rate is called one horse-power.

In electrical work, when work is done at the rate of one joule per second the rate is expressed as a single term, the watt. Watts are therefore amperes × volts. Both the watt and joule are small units, and are conveniently replaced for much work by larger units. Thus the kilowatt = 1000 watts, and the kilowatt-hour represents 1000 × 60 × 60 = 3,600,000 joules. This unit—the kilowatt-hour—is called the Board of Trade unit (B.o.T.U.) and is the unit used in the measurement of power consumption by the electrical supply companies.

A comparison of the usual mechanical units with those used in electrical work is also of interest. Careful experiment has revealed the fact that—

$$1 \text{ joule} = 0{\cdot}7372 \text{ ft.-lb.}$$

1 watt is therefore equal to 0·7372 ft.-lb. per sec.

Hence $1 \text{ ft.-lb. per sec.} = 1 \div 0{\cdot}7372 \text{ watt}$

and $550 \text{ ft.-lbs. per sec.} = \dfrac{550}{0{\cdot}7372} = 746 \text{ watts.}$

Hence 1 horse-power = 746 watts and this is usually designated E.H.P. to represent the fact that electrical power is being expressed.

Similarly, $1 \text{ kW.hr.} = \dfrac{1000}{746} = 1\tfrac{1}{3} \text{ E.H.P.}$

These are units which are frequently required when it becomes necessary to express the work done in any large-scale deposition. For small work, however, we are not frequently concerned with the quantities. Other factors in the deposition are of greater moment.

Constitution of Electrolytes. By the term *electrolysis* is meant, in general, the decomposition of chemical substances by the aid of electrical energy. The term is, however, equally applicable to operations in which electrical energy is used in the production of chemical materials.

An *electrolyte* is a substance amenable to this electrical decomposition. The term is sometimes applied to substances either in the solid form or in the form of a solution. A closer study of the subject, however, demands some differentiation between these two forms of the same substance. In the solid form the substance may be a non-conductor. Even in some solvents it may fail to conduct the electrical current. In neither of these forms is it susceptible to the type of decomposition which is called electrolysis. In another solvent, usually water, the substance may conduct electricity and then be subject to electrolysis. In this form it is an electrolyte, which may therefore be regarded as a conducting medium in which the current effects chemical changes in accordance with well-defined laws, which must be stated. These laws are those usually associated with the name of Faraday.

The electrical energy is applied to these electrolytic solutions by two electrodes which conduct electricity metallically (that is without decomposition), the chemical changes taking place within the solution and on the immersed portions of the electrodes.

These electrolytic substances are, when dissolved in water (the usual solvent), subject to a type of change which is called *electrolytic dissociation*, the products being called *ions* and the process being reversible. Common salt (NaCl) is such a substance. Dissolved in water it becomes in part resolved into ions as follows—

$$NaCl \rightleftharpoons Na^{\cdot} + Cl^{-}$$

These ions are charged atoms or radicals (groups of atoms which exist in combination but are not obtainable in the free form). A further example illustrates this when—

$$CuSO_4 \rightleftharpoons Cu^{\cdot\cdot} + SO_4^{--}$$

These ions carry electrical charges either positive or negative; hydrogen, the metals, and basic radicals being positively charged, while the acidic radicals are negatively charged. By this negative charge may be understood the addition of an "atom" of negative electricity or *electron* as it is termed, while the positive charge may be taken as meaning the loss of an electron. Thus the chlorine ion is a chlorine atom carrying an electron, while the sodium ion is the sodium atom minus an electron. These negative electrons are the fundamental charges in virtue of which all these electrolytic processes are made possible.

There are some exceptions to this general rule of dissociation. Mercuric chloride solution, for example, is only very slightly ionized. It is a very feeble conductor and other evidences point to the same conclusion of slight ionization.

In some cases ionization proceeds in two or more stages. Thus the usual constituent of the silver plating solution is $AgCN.KCN$.

This dissociates as follows—

First Stage. $AgCN{\cdot}KCN \rightleftharpoons K^{\cdot} + Ag(CN)^{-}_2$.

Second Stage. $Ag(CN)_2^{-} \rightleftharpoons Ag^{\cdot} + 2CN^{-}$.

The second stage, however, is usually very slight, there being only a very small amount of silver in the solution as silver ions ($Ag^{\cdot}$). The ion $Ag(CN)_2^{-}$ is called a *complex ion*, being capable of further resolution into more simple ions.

Substances which dissociate largely at low or moderate dilutions are called *strong* electrolytes, while others, like acetic acid, which are only slightly dissociated at low or moderate dilutions are termed *weak* electrolytes.

The atoms, and therefore the ions, are exceedingly small. Some idea of their dimensions may be gathered from the fact that the copper deposited by 1 ampere in one hour (1·182 gm.) results from the conversion of no fewer than 11,000,000,000,000,000,000,000 copper ions into atoms which have then to be obtained in a form carrying the properties desired in the copper deposit.

Current. These ions respond to electrical influences. The function of the electrical generator is to keep the electrodes charged, thus attracting ions carrying opposite charges. The negatively charged ions or *anions* are attracted to the positively charged electrode which is called the *anode*, while the positively charged ions or *cathions* pass through the solution to the negatively charged electrode or *cathode*. This orderly motion of ions towards the electrodes is called the migration of ions. According to the older conception of current in electrolytes, the anode was the electrode by means of which current entered the solution, the cathode similarly being the electrode by which the current left the solution. In conformity with modern conceptions the anode is the electrode by which electrons separated from the migrated anions leave the cell, while the cathode provides the entrance for electrons to neutralize the positive ions which by migration reach the cathode. There is thus a definite change in the conception of the direction of the current, but it is easy to adapt our notions to the more up-to-date scheme.

Further, current in the metallic conductor comprises the passage of electrons from atom to atom or molecule to molecule without the movement of these atoms or molecules. In the electrolyte, however, current is this orderly motion of two streams of oppositely charged ions in opposite directions. Current is therefore developed *in* the electrolyte by the electrical potentials produced and maintained at the electrodes by the generator. It is not an external motion of electricity which is, then, passed *through* the solution. Many phenomena in electrolysis would be altogether unintelligible apart from this more modern conception of the mechanism of electrolysis.

The Process of Electrolysis. A simple idea of what is happening in an electro-plating solution is essential in order to appreciate the conditions which make for successful deposition.

Take the case of copper sulphate. It is well recognized that, in solution, this substance is partly dissociated into ions, thus

$CuSO_4 \rightleftharpoons Cu^{\cdot\cdot} + SO_4^{--}$. These ions are electrically charged. With an applied P.D., they migrate to their respective electrodes, and thus the metal ions find their way to the cathode. There they gain electrons and become converted into atoms, and are deposited. Copper ions are blue, but the deposited copper is red. At the anode, the SO_4^{--} ions are not discharged. With a copper anode, more copper passes into the ionic form, and this, in company with the SO_4 ions, constitutes the new copper sulphate, which takes the place of that which has been decomposed to supply the deposited copper. Other compounds used in electro-plating behave similarly, producing ions as shown in Table IX.

TABLE IX

ELECTROLYTES AND IONS

Substance	Formula	Ions	
		Anion	Cathion
Copper sulphate	$CuSO_4$	SO_4^{--}	$Cu^{\cdot\cdot}$
Silver nitrate	$AgNO_3$	NO_3^{-}	$Ag^{\cdot}$
Nickel sulphate	$Ni\,SO_4$	SO_4^{--}	$Ni^{\cdot\cdot}$
Copper potassium cyanide (1)	$Cu\,K(CN)_2$	$Cu(CN)_2^{-}$	$K^{\cdot}$
,, (2)		$2CN^{-}$	$^2Cu^{\cdot}$
Silver potassium cyanide	$AgK(CN)_2$	$Ag(CN)_2^{-}$	$K^{\cdot}$
Potassium carbonate	K_2CO_3	CO_3^{--}	$2K^{\cdot}$
Caustic soda	$NaOH$	OH^{-}	$Na^{\cdot}$
Sulphuric acid	H_2SO_4	SO_4^{--}	$2H^{\cdot}$
Zinc sulphate	$ZnSO_4$	SO_4^{--}	Z[illegible]·
Cadmium sulphate	$CdSO_4$	SO_4^{--}	$Cd^{\cdot\cdot}$

If the anode is not freely soluble, then water is ionized, leading to the retention of the hydrogen ions in the solution, which, with the SO_4^{--} of a sulphate forms sulphuric acid, well known to be produced with insoluble or imperfectly soluble anodes, while oxygen is evolved at the anode.

According to this view, the undissociated copper sulphate, being neutral, takes no direct part in the plating process, and does not add to the conductance of the solution. In the ordinary plating solution, which also contains sulphuric acid, only about one-fifth of the blue salt is dissociated. The addition of acid for the purpose of conductance actually reverses, in part, the dissociation of the copper compound.

Degree of Dissociation. Different substances vary very considerably in the extents to which they dissociate in solution. Some dissociate considerably while others in a similar state of dilution, to only a very slight degree. The methods by which this information has been acquired need not be given. The results are of far greater importance. To take an example, a solution of copper sulphate containing 125 gm. of the blue salt per litre contains only one-quarter of its material in the ionized form, the remaining three-quarters being in the molecular or undissociated form. The degree of dissociation is therefore (expressed as a fraction) only 0·25. This is an approximate figure. For every four molecules of the salt put into a solution of this concentration, there are three molecules of the undissociated salt while the dissociated molecule has produced one each of Cu and SO_4 ions. Of all this material, only the ions conduct and therefore, from the conducting point of view, the three-quarters of the material is inactive. If the solution is diluted to one-tenth of this strength the degree of dissociation increases to about two-fifths. It is an invariable rule that dissociation increases with dilution.

With the acids usually regarded as strong, the degree of dissociation is considerably greater. Thus with hydrochloric acid containing 36·5 gm. HCl per litre, the degree of dissociation is of the order of four-fifths, while by dilution to one-tenth of the strength the dissociation increases to over nine-tenths.

Relevant figures are given in Table X.

TABLE X

DEGREE OF DISSOCIATION

Electrolyte	Gm. per Litre	Oz. per Imp. Gal. approx.	Degree of Dissociation	Gm. per Litre	Degree of Dissociation
Sulphuric acid . .	49	8	·52	4·9	·59
Hydrochloric acid .	36·5	6	·79	3·65	·925
Acetic acid. . .	60	10	·0038	6	·013
Caustic potash . .	56	9	·77	5·6	·89
Copper sulphate . .	124·8	20	·225	12·48	·395

A simple illustration of this principle is seen in the fact that sulphuric acid and boric acid may be made of the same molecular strength. The sulphuric acid exhibits all the usual properties of acids, while boric acid is obviously very harmless. The acid properties in both cases are due to the presence of hydrogen ions, which are abundant in the case of sulphuric acid and only very few in the case of boric acid. Boric acid is therefore only a feeble conductor of electricity and its presence in the nickel solution is evidently not for the purpose of imparting conductance.

Resistance of Metals. The electrical resistance of metals is relatively small. That of the centimetre cube is called the *specific resistance* or *resistivity.* In the case of metals it is so small that it is more conveniently expressed in millionths of an ohm or *microhms.* Values for the more common metals are given in Table XI

TABLE XI

RESISTANCE OF METALS AND ALLOYS

Metal	Sp. R. Microhms per $Cm.^3$	Relative Conductance
Silver	1·6	100
Copper	1·6	100
Gold	2·06	78
Aluminium	2·9	55
Zinc	5·75	28
Platinum	8·9	18
Iron	9·6	16·7
Nickel	12·4	13
Lead	20	7·5
Antimony	35	4·6
Mercury	100	1·6
Bismuth	130	1·1
Nickel silver	32	5·0
Platinoid	42	3·9
Manganin	53	3·0

Resistance of Electrolytes. The resistance of electrolytes is considerably greater than that of metals and is expressed in ohms. That of sulphuric acid containing 49 gm. H_2SO_4 per litre (the normal or equivalent solution) is about 5 ohms, that is, over 3,000,000 times that of copper. This is usually considered a good conducting solution. The values of other electrolytes are found in Tables XII and XIII.

TABLE XII

SPECIFIC RESISTANCE OF ELECTROLYTES

Electrolyte	Grammes per litre	Sp. R ohms	Conductivity $= \frac{1}{\text{Sp. R}}$
H_2SO_4	49	5·05	·198
HCl	36·5	3·32	·301
HNO_3	63	3·226	·310
$HC_2H_3O_2$	60	757	·00132
KOH	56	5·43	·184
$NaOH$	40	6·37	·157
NH_3 (Soln). . .	17	1121	·00089
K_2CO_3	69	14·14	·0707
Na_2CO_3	53	21·98	·0455
KCl	74·5	10·18	·0982
$NaCl$	58·5	13·45	·07435
NH_4Cl	53·5	10·31	·097
$CuSO_4.5H_2O$ . .	124·8	38·7	·0258
$AgNO_3$	170	14·79	·0676

TABLE XIII

RESISTANCE OF ELECTROLYTES

Electrolyte	Specific Resistance*	Conductivity†
Copper sulphate (sat)	29·3	·0341
,, ,, (normal) . .	38·8	·0258
Zinc sulphate (sat)	33·7	·0296
,, ,, (normal)	32·1	·0311
Sodium chloride N.	13·4	·07435
Potassium chloride N. . . .	10·18	·0982
Sulphuric acid (Sp. Gr. 1·2) .	1·35	·74
,, ,, N.	5·05	·198
Nitric acid (Sp. Gr. 1·36) . .	1·4	·714
,, ,, N.	3·226	·310

* Specific Resistance . . . ohms per cm.^{3}
† Conductivity . . . amperes per volt per cm.^{3}

The method of determining the specific resistances of electrolytes does not call for immediate treatment and is well beyond the scope of this work. Nevertheless two simple though inadequate methods may be described to give a greater appreciation of the meaning of the term and importance of the property. Imagine a cell as shown in Fig. 4 with opposite and parallel copper electrodes in a solution of copper sulphate of normal strength, that is, containing 124·8 gm. of the blue salt per litre. Voltmeter and ammeter are attached and a current is produced in the cell. In addition to the voltmeter and ammeter readings, we have by simple measurement the inter-electrode distance which is the length of the electrolyte, and also the sectional area (the product of the breadth and depth of the solution and electrodes). Assume the following readings—

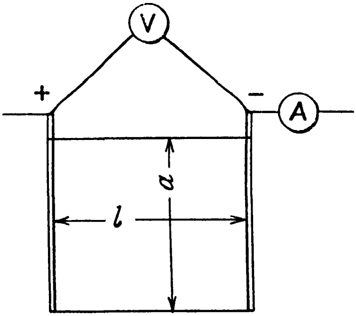

FIG. 4. RESISTANCE OF ELECTROLYTE

$$\begin{aligned} \text{P.D.} &= 4{\cdot}65 \text{ volts} \\ I &= 0{\cdot}15 \text{ ampere} \\ l &= 20 \text{ cm.} \\ a &= 25 \text{ sq. cm.} \end{aligned}$$

The total resistance of the solution is therefore $E \div I$ or

$$4{\cdot}65 \div {\cdot}15 = 31 \text{ ohms}$$

As resistance is proportional to length and inversely proportional to sectional area or

$$R = \frac{\text{Sp. R.} \times l \text{ (cm.)}}{a \text{ (cm.}^2\text{)}}$$

the specific resistance is obtained by dividing the total resistance by the length in centimetres and multiplying by the area in sq. cm. The specific resistance is therefore—

$$\frac{31 \times 25}{20} = 38{\cdot}8 \text{ ohms.}$$

This method, while apparently simple, has little application for electrolytes as there are a number of circumstances which militate against its accuracy. These include changes in the concentration of the electrolyte around the electrodes, and also, where insoluble or imperfectly soluble anodes are being used, changes in the chemical composition of the solution.

To some extent, the errors due to these slight changes of concentration and a slight polarization can be eliminated by a modification of the apparatus used. A glass tube (Fig. 5) is fitted with stoppers and two small copper electrodes which practically fill the section of the tube. The tube is filled with electrolyte—an acid copper solution—and connected in series with a suitable accumulator (*A*), variable resistance (*VR*), and current detector (*G*), and an easily observed reading taken. The cathode is now withdrawn through a measured length further from the anode. This increases the resistance and reduces the current. The current is now brought back to its original value by taking out resistance from *VR*. This reduced resistance is equal to that added in the electrolyte by the movement of the cathode. Thus an increase of 10 cm. length of electrolyte in a tube of 2 cm. diameter gave an increase in resistance of 17 ohms. Then—

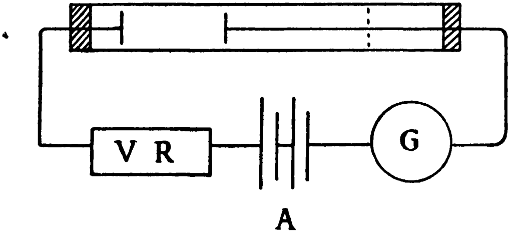

FIG. 5. RESISTANCE OF ELECTROLYTES

$$\text{Area of tube} = \pi r^2 = \frac{22}{7}\ \text{sq. cm.}$$

Further—

$$\text{Specific resistance} = \frac{R \times a}{l}$$

$$= \frac{17}{10} \times \frac{22}{7} = \frac{374}{70}$$

$$= 5{\cdot}3\ \text{ohms}$$

For electrolytic resistances, however, alternating current methods are employed as these do not occasion any permanent change in the electrolyte undergoing test.

Now as resistance is proportional to length and inversely proportional to sectional area, it is obviously desirable, as far as is practicable, to keep down the distance between the electrodes and have these as large as possible. Where electrodes of large sizes are placed close together, the resistance may be very small indeed.

In the case of an acid copper solution containing 150 gm. of the blue salt and 50 gm. of acid per litre, the specific resistance (see Table XIV, page 38) is 5·3 ohms.

With square foot electrodes placed 4 in. apart the electrolyte immediately between the plates will have a resistance of—

$$\frac{5{\cdot}3 \times (4 \times 2{\cdot}54)}{(12 \times 2{\cdot}54)^2} = 0{\cdot}058 \text{ ohm.}$$

These conditions only infrequently obtain in electrodeposition practice owing to the irregular shape of the work under treatment. Where large scale deposition is concerned, these are matters which call for consideration, as reduced bath resistance means reduced P.D. to produce the desired current and thus reduced electrical work, most of which is converted into heat in the solution. As such, it cannot be regarded as entirely wasted. In fact, in some processes this constitutes a convenient method of warming the solution and maintaining a moderate temperature.

Usually, however, the sectional area of the solution exceeds that of the surface of the electrodes, and the resistance is thereby further reduced.

Mixed Electrolytes. Usually electro-depositing solutions are supplied with some constituent which adds conductance without impairing the required chemical properties. Illustrative of this is the addition of sulphuric acid to the copper sulphate bath, the marked reduction of the resistance of which is shown, though not to an exact scale, in Fig. 6.

At the same time it may be pointed out that where an added substance, in this case the acid, has an ion common with one of the original substance, in this case the SO_4 of the copper sulphate, each substance suppresses the dissociation of the other. Thus it is that the addition of copper sulphate to sulphuric acid does not add to its conductance. The reverse, and to some extent unexpected, result is observed. In any case the resistance of the mixed electrolyte is greater than that which might be calculated by the addition of the two individual conductances. This is illustrated by the data embodied in Table XIV.

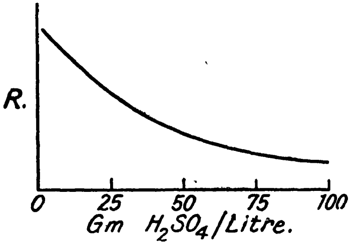

Fig. 6. Decreasing Resistance of Copper Sulphate with Additions of Acid

TABLE XIV

Resistance of Mixed Electrolytes

$CuSO_4.5H_2O$		H_2SO_4		Sp. Resistance of mixture	
Grams per litre	Sp. R.	Grams per litre	Sp. R.	Calc.	Found.
0		50	4·8	4·8	4·8
50	65	50	4·8	4·48	4·9
100	45	50	4·8	4·34	5·1
150	29	50	4·8	4·07	5·3
200	24	50	4·8	4·0	5·5

Other additions for the improvement of conductance are a number of neutral salts in the nickel bath and of carbonates in the usual cyanide solutions, though it often happens that these additions serve other advantageous purposes.

Conductance, too, is usually improved by elevation of temperature, and hence the use in some cases of warmed solutions. This increase in conductance varies with the different solutions and generally may be taken to be of the order of 1·5 to 2·5 per cent per degree centigrade over the value at ordinary temperatures.

Relative Ionic Speeds. The steady motion of ions towards their respective electrodes, with the accompanying transportation of the electrical charges they carry, constitutes current in the solution. Some ions move rapidly, others more slowly. Hydrogen provides the most rapidly moving ion. Ionic speed contributes to the conductance and, in electrolytes, current is not something manufactured outside the solution and then passed through, but is the steady motion of the ions, developed by the attraction of the charged electrodes. Again, some substances are more freely ionized than others. For the best conductance the substance should ionize freely and produce rapidly moving ions. This condition is realized with sulphuric and similar acids, hence the addition of sulphuric acid to the feebly conducting copper sulphate solution.

The relative rates of migration can readily be determined. They are usually obtained in pairs. Chemical analysis of the solution around the anode and cathode in a solution of copper sulphate without free acid shows that the two ions, $Cu^{\cdot\cdot}$ and SO_4^{--}, migrate at relative rates represented by the figures 0·375 and 0·625. The copper is the slower ion. The simpler proportions are as 3 : 5. Put another way, this means that three-eighths of the total current is concerned with the transport of copper ions towards the cathode and five-eighths with the motion of SO_4^{--} towards the anode. Put in still another way, it means that of the total current depositing 8 gm. of copper, only sufficient current is in the direction of the cathode to transport 3 gm. of copper. For every 8 gm. of copper deposited there will be a deficiency of 5 gm. around the cathode, the solution here becoming rapidly weaker and inefficient unless, by some method of stirring or circulation, the solution strength is maintained around the cathode. The bearing of this on continued deposition needs no further emphasis. Practical methods of dealing with the difficulty will be touched upon later.

Relative rates of migration of the several pairs of ions are shown in Table XV.

From these figures it will be seen that H ions move nearly five times as fast as Cl ions. Similarly, as H ions move $0·822 \div 0·178 = 4·6$ times as fast as SO_4 ions, and these in turn move $0·625 \div 0·375 = 1·66$ times as fast as copper ions,

TABLE XV

Relative Rates of Migration of Ions

Electrolyte	Anion	Cathion
Copper sulphate	·625	·375
Silver nitrate	·529	·471
Sodium chloride	·604	·396
Sulphuric acid	·178	·822
Caustic soda	·825	·175
Hydrochloric acid	·167	·833
Nitric acid	·159	·841
Cadmium sulphate	·616	·384
Ammonium chloride	·508	·492
Magnesium sulphate	·619	·381

it follows that under the same electrical conditions, H ions move 4·66 × 1·66 = 7·7 times as fast as copper ions. Thus it is possible to draw up a list of ions in the order of their relative speeds of migration. Such a list is given in Table XVI

TABLE XVI

Relative Ionic Speeds

Cathions		Anions	
H (hydrogen)	100	OH (hydrion)	61·8
K (potassium)	19·6	SO_4 (sulphion)	21·7
NH_4 (ammonium)	19·3	Cl (chlorion)	20
Ba (barium)	16·1	NO_3 (nitrion)	18·9
Cd (cadmium)	15·1	$C_2H_3O_2$ (acetion)	11·8
Ag (silver)	14·9		
Na (sodium)	13·1		
Cu (copper)	13		

in which H ions, which move the fastest of all ions, are given a speed of 100. Usually the metal ions move slowly, and this results in the cathode layer of solution becoming weak in metal and leads to the necessity for stirring of some form to maintain uniform concentration and supply the needful metal to the cathode.

Absolute Speeds of Ions. The *absolute rate of migration* of ions depends also upon the P.D. applied. The rate is very small and is usually expressed as centimetres per second when the P.D. is 1 volt per centimetre.

Some of the important values are shown in the following Table (No. XVII). From them it will be appreciated that in practical electrodeposition we cannot be entirely dependent upon this migration for the supply of ions to the cathode. Illustrating this it may readily be calculated that with copper electrodes 10 cm. (4 in.) apart, and with a P.D. of 1 volt, the time taken for a copper ion to migrate from the anode where it is formed to the cathode where it is required is—

TABLE XVII

ABSOLUTE SPEEDS OF IONS

cm/sec/volt/cm at 18° C.

Cathions		Anions	
H	·00326	OH	·00180
K	·000668	SO_4	·000703
Ag	·00056	Cl	·000681
Cu	·000476	NO_3	·000631
Na	·000457	$C_2H_3O_2$	·000356

$$\frac{10 \times 10}{0{\cdot}000476 \times 3600} = 58{\cdot}3 \text{ hours.}$$

This slow migration, however, is usually amply compensated for by the disturbance to the solution due to the addition and withdrawal of work, by the convection currents of warmed solutions, or by designed circulation or agitation.

CHAPTER III

ELECTROCHEMISTRY

FARADAY'S Laws—Current efficiency—Coulometers—Ampere-hour meters—Current density—Current density meters—Correcting current density by P.D.—Supplementary anodes—Shields—Bi-polar electrodes—Polarization—Electro-chemical series—Electrode potentials—Potential diagrams—Overvoltage—Applications of electrochemical series—Production and discharge of ions

Faraday's Laws. The quantities involved in electrolysis were thoroughly explored in experiments by Michael Faraday, whose results are embodied in two simple yet all-important laws. First we recall that unit current is called the ampere, while unit quantity of electricity, the ampere-second, is termed the coulomb. *Faraday's First Law* states that the quantities of substances involved in electrolytic changes (including therefore the metals deposited) are proportional to the number of coulombs passed. Thus, under similar conditions, 10 A. in 2 hours deposit twice as much metal as 2½ A. in 4 hours. *Faraday's Second Law* states that the quantities of chemical substances concerned in electrolysis (including, therefore, metals deposited) are proportional to their chemical equivalents. These are quantities with which we must be familiar to appreciate quantities of metals deposited by various currents. Some knowledge of chemistry is required for this purpose. Chemical equivalents mean the weights (which may vary very considerably) of chemical substances which do the same amount of chemical work. For example, it will soon be appreciated that 49 gm. of sodium cyanide do the same amount of work in a solution as 65 gm. of potassium cyanide. They are equivalent quantities. Similarly 32·5 gm. of zinc and 9 gm. of aluminium both displace 1 gm. of hydrogen from hydrochloric acid. They, too, are equivalent quantities, and such quantities as are related to 1 gm. of hydrogen, or more exactly 8 gm. of oxygen, are called *chemical equivalents.*

At this stage it may be well to add a more comprehensive definition of the term electrolysis as implying "the production of chemical changes by ionic migration and discharge in accordance with Faraday's laws."

A few other interesting quantities may be noted. The *electro-chemical equivalent* (E.C.E.) is the amount of substance concerned with 1 coulomb. This is usually a very small amount, and is therefore expressed in milligrams. This amount multiplied by 3600 (seconds per hour) gives the weight of metal deposited per ampere-hour, a useful figure in all computations of weights deposited. Further useful figures are the weights in pounds avoirdupois per 1000 Ah. while, where we are concerned with estimations of thickness of deposits, it is easy to calculate the thickness of deposit for definite current densities and time. From these figures many others of interest are easily obtained.

Many of these quantities are embodied in Tables XVIII and XIX.

TABLE XVIII

QUANTITATIVE DATA

Element	Symbol	Chemical equivalent	E.C.E. mg.	Gm. per Ah.	Lb. (av.) per 1000 Ah.	Mils. per hr. per 10 A. per sq. ft.
Cadmium	Cd	56	·58	2·088	4·6	1
Chromium	Cr	8·75	·091	·3276		*
Copper						
(sulphate)	Cu	31·8	·329	1·182	2·61	·56
(cyanide)	,,	63·6	·658	2·364	5·22	1·12
Cobalt	Co	29·5	·305	1·098	2·42	·53
Gold						
(chloride)	Au	65·6	·676	2·436	78 oz. tr.	
(cyanide)	,,	197	2·03	7·308	235 ,,	
Hydrogen	H	1	·0104	·0376	—	
Iron	Fe	28	·29	1·044	2·3	
Lead	Pb	103·5	1·071	3·86	8·51	1·45
Nickel	Ni	29·3	·303	1·090	2·40	·534
Oxygen	O	8	·0828	·298	—	
Silver	Ag	108	1·118	4·024	129 oz. tr.	1·63
Tin	Sn	59·5	·615	2·21	4·87	1·28
Zinc	Zn.	32·5	·338	1·22	2·6	·74

* See Chapter XIX.

From this table it will be found that to deposit $\frac{1}{10}$ in. of copper with a current density of 20 A. per square foot will require 89 hours, this assuming that the current is producing its full amount of metal.

TABLE XIX

Theoretical weights of metals deposited

	Gm. per Ah.	Oz. per 100 Ah.	Mils per hr. with CD = 100
Copper (ic)	1·182	4·16	5·65
,, (ous)	2·364	8·32	11·3
Silver	4·024	12·9 (troy)	16·2
Iron	1·044	3·68	5·5
Nickel	1·090	3·84	5·34
Cobalt	1·098	3·87	5·5
Lead	3·86	13·6	14·8
Cadmium	2·09	7·36	10·4
Tin (ous)	2·21	7·78	14·0
,, (ic)	1·00	3·89	7·0
Zinc	1·22	4·3	7·3

The calculation is as follows—

Take the case of a current density of 10 A. per square foot in the copper sulphate solution. Consider 1 sq. ft. and a deposit of one hour. The deposit may be expressed in terms of the dimensions and also from the known weight calculated from the ampere hours. Now 1 cub. in. = 16·4 c.c. and the density of copper is 8·9. Let the thickness of the deposit be called *t* inch.

Then weight of deposit is—

(1) $12 \times 12 \times t \times 16{\cdot}4 \times 8{\cdot}9 = 21{,}020t$ gm.

(2) $10 \times 1{\cdot}182 = 11{\cdot}82$ gm.

Then $21{,}020 \times t = 11{\cdot}82$

$$t = 11{\cdot}82 \div 21{,}020$$
$$= 0{\cdot}00056 \text{ in.}$$
$$= 0{\cdot}56 \text{ mil.}$$

This calculation can be made in other ways, the resulting useful expressions being shown in Table XX.

TABLE XX

Calculations on thickness of Deposits

(1)

Thickness (in.) of metal deposited per hour with given C.D. $= \dfrac{\text{C.D.} \times \text{gm. per Ah.}}{144 \times 16{\cdot}4 \times \text{Sp. Gr. of metal}}$

Example

Thickness of copper from acid bath per hour with 18 A per sq. ft.

$$= \frac{18 \times 1{\cdot}182}{144 \times 16{\cdot}4 \times 8{\cdot}93}$$

$$= \frac{21{\cdot}3}{21090}$$

$$= {\cdot}001'' \text{ approx.}$$

(2)

Time (hr.) to deposit t inches of metal with known C.D. $= \dfrac{144 \times t \times 16{\cdot}4 \times \text{Sp. Gr.}}{\text{gm. per Ah.} \times \text{C.D.}}$

Example

Hours to deposit ·001″ Zinc at 10 A per sq. ft.

$$= \frac{144 \times {\cdot}001 \times 16{\cdot}4 \times 6{\cdot}9}{1{\cdot}21 \times 10}$$

$$= 1{\cdot}35 \text{ hours}$$

(3)

C.D. required to deposit t inches of metal in given time $= \dfrac{144 \times t \times 16{\cdot}4 \times \text{Sp. Gr.}}{\text{gm. per Ah.} \times \text{hours}}$

Example

C.D. required to deposit ·00063 inch silver in one hour

$$= \frac{144 \times {\cdot}00063 \times 16{\cdot}4 \times 10{\cdot}5}{4{\cdot}024}$$

$$= \frac{15{\cdot}5}{4{\cdot}024}$$

$$= 3{\cdot}85 \text{ A per sq, ft.}$$

Again, as the electrical work (in joules) done in a bath is the product of the volts, amperes and seconds (units of P.D. current and time), then the consumption of electrical energy in the acid copper bath, with a P.D. of 1·5 volts, per ton of copper is obtained as follows—

$$\text{Ampere-hours per ton} = \frac{\overset{\text{(lb. per ton)}}{2240} \times \overset{\text{(gm. per lb.)}}{451}}{1{\cdot}182 \text{ (gm. Cu per Ah.}} = 860{,}000$$

$$\text{Watt-hours per ton} = \frac{2240 \times 454 \times 1{\cdot}5\ (\text{volts})}{1{\cdot}182} = 1{,}310{,}000$$

$$\text{Kilowatt-hours per ton (units)} = \frac{2240 \times 454 \times 1{\cdot}5}{1{\cdot}182 \times 1000} = 1310$$

This does not seem to be a large consumption of energy. It would be expensive at 1d. per unit. Large scale deposition of copper, for example in electrolytic refining, is carried out with 0·3 volt. The energy consumption is therefore $\frac{1310 \times {\cdot}3}{1{\cdot}5} =$ 262 units, and this, at a farthing per unit, amounts to 65·5d., a surprisingly small amount.

Current Efficiency. The term *current efficiency* denotes a matter of considerable importance in electrodeposition. In Table XVIII (p. 43) we have recorded the amounts of the several metals which should be deposited at the cathode or dissolved from the anode by 1 ampere-hour. From these figures others can easily be calculated. One important point about these figures must be noted. They represent quantities obtained only under the very best conditions of deposition. Generally speaking, they would only be obtained with comparatively strong solutions with low current densities and with the electrolyte moving. Now these quantitative conditions are not always realized in practice. There is consequently a falling off in the amount of metal deposited per ampere-hour and also, in some cases, of that dissolved at the anodes. We thus get an idea of what is called the *cathode efficiency*, this being expressed thus—

$$\text{Cathode efficiency} = \frac{\text{wt. metal deposited} \times 100}{\text{wt. calculated from the ampere-hours}}$$

This is a figure in many cases not far from 100, though in some cases, particularly the warm cyanide solutions, it may be much less.

Similarly there is an *anode efficiency*

$$\text{Anode efficiency} = \frac{\text{wt. dissolved from anode} \times 100}{\text{wt. calculated from ampere-hours}}$$

This is usually nearly 100. Occasionally it falls below 100, while in other cases it may go above 100. In cyanide solutions, particularly, the anodes are apt to dissolve chemically in addition to electrochemically, and thus more metal dissolves from the anode than that calculated from the ampere-hours.

Now the ideal condition would be that of 100 per cent efficiencies at both the anode and cathode. There would then be no secondary reactions at the electrodes, no gases evolved, and no change in the metal content of the solution. Seldom is this ideal condition realized.

Failing this, the next best thing is for the anode and cathode efficiencies to be equal, even if below 100. This, at least, would guarantee an unvarying metal content of the bath, a very desirable condition. If the cathode efficiency is greater than the anode efficiency the bath becomes poorer in metal On the other hand, if the anode efficiency is greater than the cathode efficiency the bath becomes enriched in metal. These are not the only changes, for with a change in the metal content there must also be changes in the content of other constituents which combine with or react with the additional metal entering or leaving the solution.

Another convenient term is *electrode efficiency* which represents the relative efficiencies at the anode and cathode so that

$$\text{Electrode efficiency} = \frac{\text{anode efficiency} \times 100}{\text{cathode efficiency}}$$

This may also be represented with the 100 omitted, and therefore as a proportion and not as a percentage. The cadmium bath provides an example in which the electrode efficiency is more than 100 per cent, and to avoid the concentration of metal in the solution in this and other similar cases it is common practice to add inert anodes which take a proportion of the current without contributing any metal to the solution.

The chromium bath is an outstanding example in which a chromium anode efficiency is always likely to be 100 while the cathode efficiency rarely exceeds 10 to 15 per cent. If we take the figure at 12½ per cent, it means that eight times as much metal would dissolve from the anode as would be deposited at the cathode. The solution becomes syrupy owing to excessive concentration of chromic acid, and this is one reason for the use of insoluble lead anodes in this example of metal deposition.

Coulometers. There are occasions when the measurement of current used in electro-deposition needs to be somewhat accurately made. Ordinarily the maintenance of a uniform current is a difficult matter and it is equally difficult to take note of all the variations as recorded on the ammeter and deduce from them anything like an accurate average.

In such cases the current may be measured by " passing it " through an electrolytic cell in which the products of electrolysis are quantitatively produced and accurately measured. For quantitative deposition the conditions must be such as ensure a cathode efficiency of 100 per cent while the products must be capable of accurate measurement.

Such a cell is called a *coulometer.* The terms *silver coulometer* and *copper coulometer* will be sufficiently expressive. Where silver is to be deposited it must be from the nitrate solution, usually with platinum electrodes. In the copper coulometer the ordinary acid sulphate solution is employed with the addition of about 50 gm. of alcohol per litre. In both cases current density must be kept within limits in order to ensure full cathode efficiency.

Gas coulometers comprise electrodes in either an acid or alkaline electrolyte, the collected products being either the hydrogen evolved at the cathode, or, in some cases, the mixed gases from both electrodes. Alkali solutions with nickel electrodes are frequently employed for this purpose, as the reactions at the anode are more simple and are not beset with the production of other oxidized products which consume oxygen, this being the chief defect when some acid electrolytes are used.

In any case the average current is computed from the quantity of product obtained and the time of deposition, 1 ampere-hour of silver being 4·024 gm., and of copper 1·182 gm. while a simple calculation shows that 1 ampere-minute produces 10·35 c.c. of mixed hydrogen and oxygen measured at normal temperature and pressure.

This method of determining the average current over a run is employed to advantage in many examples of research work.

Ampere-hour Meters. If the coulometer is of use in small scale deposition, as indeed it is, there would seem to be need for a similar instrument to measure ampere-hours on the larger scale of industrial work Such instruments are called ampere-hour meters. By them, the current is totted up with the time, so that at the end of any period there is recorded the product of the amperes and hours. A more accurate measure of the average current used over the period is thus attained. Whatever changes take place during the operation of the bath they are usually proportional to the ampere-hours passed through. Such changes will include drag-out which is proportional to the square feet of work passed through, and this in turn with the current and time. changes of metal concentration, acidity, carbonates, free cyanides and other possible variations. These changes can only be obtained in the first place by the periodic analysis of the solution, but soon it will be found that they are proportional to the ampere-hours passed through. Such a record will provide an automatic warning when necessary additions should be made to keep the bath up to constant strength.

Another variable which is not always easy to trace by analysis is the addition agent (see page 129), and here again a record of the ampere-hours passed through will provide a guide for further additions without actually waiting for the deposit to deteriorate for want of this essential to good plating.

Above all these considerations, however, is the accurate guide to the amount of metal deposited, but this necessitates an idea of the current efficiency of deposition at the normal current density in use. This again is a matter of experience, but the value of the instrument will be appreciated in the deposition of such metals as silver and gold, while many of the baser metals could with advantage be under control by the same method.

Lastly, if a new process is being operated under the terms of a royalty, the ampere-hour meter will provide the best indicator as to the extent to which the process has been applied and for which the royalty is due.

Current Density. The rate at which metals are deposited is all-important, and these rates vary considerably. In any case an excessive rate leads to the production of rough, powdery or "burnt" deposits. Some simple method of comparison is desirable and even essential. The system adopted is usually the current (amperes) per unit area (sq. ft. or sq. dm.). This provides a simple method of indicating the current to be used. Thus a current of 10 A. on a surface of 4 sq. ft. means a current density of 2½ A. per sq. ft. Now 1 sq. ft. = 9·2 sq. dm. and the metric units are frequently used abroad. Hence a current of 18·4 A. on a surface of 2 sq. ft. represents a current density of 1 A. per sq. dm.

Approximate computations of the area receiving a deposit are readily available for the regular though differing shapes.

Thus the area of a square is found by squaring the length of its side. A square of 1 ft. side will therefore present a surface of 1 sq. ft. or 144 sq. in. on one face, this needing to be doubled if both faces are receiving the deposit.

For a rectangle the area is the product of the length and breadth, both measurements being made in the same units. Thus a sheet 2½ ft. by 1½ ft. presents on both sides a surface of—

$$2\tfrac{1}{2} \times 1\tfrac{1}{2} \times 2 = 7\tfrac{1}{2} \text{ sq. ft.}$$

The area of a circle is given by the expression πr^2 or $\frac{\pi d^2}{4}$, where π is approximately $\frac{22}{7}$ or the circumference divided by the diameter. With these few simple rules many computations of area are possible, while more irregular shapes can be mentally compared with the similar regular form and reasonably accurate estimates made.

A piece of wire, for example, is a very elongated cylinder, the circular ends of which may be neglected. As an example, a yard of 16G wire (0·064 in. diameter) offers a surface of—

$$\frac{22}{7} \times 0{\cdot}064 \times 36 = 7{\cdot}2 \text{ sq. in.}$$

Current density figures vary very considerably with the different metals, and even with the same metal under different conditions. Thus it may only be possible to deposit copper from a comparatively weak solution at the rate of 10 A. per sq. ft., while in a much stronger solution, which is kept in motion, this rate might be increased to 200 or even 300 A. per sq. ft. The different rates of deposition largely control the nature of the deposit and the special property required in the deposit will, therefore, have something to do with the permissible rate of deposition.

It is often very desirable that rates of deposition which have, in some cases, been found to be satisfactory should be capable of easy reproduction. If all work were flat and the surface, therefore, easily computable, this would prove a simple matter. Usually, however, the work handled by the electro-plater is of very irregular shape and size. Any even approximate computation of the area is out of the question. The control of the current to realize some desired average value can then be obtained by the control of the P.D. across the bath terminals. This is explained in another paragraph.

Current Density Meters. Some attempt, however, to get over the difficulty has been made in the introduction of current density meters. These comprise some form of cathode, usually cylindrical, which, when immersed to a given mark, presents a definite surface. On them is mounted a small ammeter through which the current passes on its way to the hook supporting the meter on the cathode bar. Imagine this meter to present one-quarter of a sq. ft. in the solution and the current passing on to it is 1 A. The current density is therefore 4 A. per sq. ft. The small ammeter is marked or calibrated, so that instead of reading the actual current passing on to this cathode, in this case 1 A., it reads 4 A., so that this and similar readings represent the C.D. at once. The use of such an instrument necessitates its immersion to the same depth every time.

It would appear more reasonable to use for this purpose a cathode comprising a flat sheet rather than one which is cylindrical, as the former probably more nearly approximates to the nature of much work which is subject to electrodeposition. In any case there will always be some difficulty in reconciling the standard area of the meter cathode surface with that of the very variably shaped work which has to be plated. Again, even with flat work, experiments with a single flat cathode at once reveal the fact that the outer parts of a cathode surface receive thicker deposits than those nearer the centre, while with cathodes comprising projecting and depressed areas this difference will be even more marked so that the projections may be receiving a matt deposit while the depressed parts remain bright.

Another difficulty attaches to the use of the device. Its reading is the current density on this particular cathode, and not necessarily that on even the adjacent piece of work of totally different shape and probably different distance from the anode. If used, these qualifications must be remembered.

Again, where a variety of work is suspended from a single cathode rod, the end pieces will usually receive the thicker deposit, and to avoid this it is a not uncommon practice to hang dummy cathodes in these end positions to take the excessive current and with it the usually rough deposit.

It will be remembered, too, that, to use a common expression, the current takes the shortest cut across the solution, that s, the path of least electrical resistance. Hence the outer portion of a small cathode receives the thicker deposit while with the use of a large cathode and small anode, "burning" may be made to take place in the centre of the cathode.

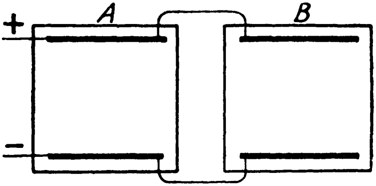

FIG. 7. SIMILAR BATHS IN PARALLEL

A little thought will show that some discretion needs to be exercised in the disposition of the anodes and cathodes for the production of uniform deposits. An old-time rule stipulated a large anode surface. This contained a suggestion of truth when anodes were imperfectly soluble and increase in anode area reduced the anode current density and so increased anode efficiency. Nowadays, however, anodes are much more perfectly soluble and this eliminates the need for excessive anode area.

Correcting Current Density by P.D. In order to adjust approximately the C.D. on different and irregular articles which are not amenable to computation by measurement, the P.D. across the terminals of the bath may be used. Suppose a bath is giving the required deposit with a current of 10 A. per sq. ft. and the P.D. is 2 volts. Generally speaking, as the area of the work increases so also must the current to maintain the same C.D. It will then be found that the P.D. is practically constant and a constant P.D. is an easier method of regulation of the current than any attempt to compute area and adjust the current to it. This rule of constant P.D. to maintain constant C.D. is, however, only an approximate one, true only under certain ideal conditions not easily realized in ordinary plating baths.

Consider the baths in Fig. 7. In *A* both anode and cathode are of the same dimensions. The resistance of the bath is due to the column of liquid between them. Another similar bath *B* is placed side by side and paralleled. The resistance of the two baths in parallel is one-half that of a single bath,

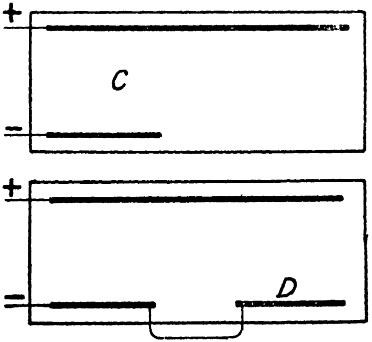

Fig. 8. Correcting C.D. by P.D.

and the same P.D. produces sufficient current for the doubled cathode surface. In Fig. 8, *C*, a bath of the ordinary type, the anodes are already in parallel. With one cathode the current does not take the path of liquid between the cathode and that part of the anode immediately opposite to it. It extends to the whole of the anode and thus the resistance of this bath is less than that of *A*. For the same current, *C* takes a smaller P.D. than *A*. Putting in a further cathode *D* reduces the resistance to that of the paralleled baths *A* and *B* in Fig. 7, but this does not now exactly halve the resistance of the bath shown in *C*. To produce double the current for twice the area, therefore, necessitates raising the P.D. slightly above its original value. It thus becomes a general rule that when working with only a voltmeter, or even when an ammeter is in circuit but the cathode areas are not easily computable, a slightly increased P.D. is required to maintain the same C.D. on increasing areas of work. This is a good workshop rule.

Supplementary Anodes. Where very irregularly shaped work is being undertaken and with it wide variations in the current density on the different areas, a more uniform distribution of current is obtained by the use of small anodes so disposed that current has greater access to the more remote cathode areas. Such added anodes are called *supplementary anodes.*

Shields. In some cases it becomes desirable to divert the current from very exposed portions of the cathode thereby distributing it more uniformly on the less prominent parts. This is effected by interposing shields of some suitable non-conducting material which will withstand the action of the solution. Glass is obviously the most adaptable material for this purpose and this method of manipulation of the current finds some application.

Bi-Polar Electrodes. Fig. 9 represents a copper sulphate bath arranged with a plate of copper (*a*), which is not metallically connected with either the anode or cathode, but through which the current must pass either wholly or in part. The side facing the anode receives a deposit of copper, while the side facing the cathode functions as an anode. Such an electrode is called a bi-polar or secondary electrode. The interposition of this secondary electrode makes practically no difference to the ammeter and voltmeter readings. Generally speaking, the plate does not vary in weight as metal is deposited as rapidly as it is dissolved away. These conditions arise in examples of electrodeposition, sometimes by design and at times by accident. By design, the system is used in the so-called "series" system of suspending the plates in copper refining tanks. Accidentally, it may occur in the case of work which is not properly connected with the cathode rod. Portions of this work may pick up current from the anode and pass it on to adjacent parts of a properly connected cathode. This is a condition which obviously should not arise.

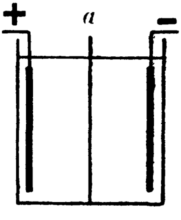

FIG. 9. BI-POLAR ELECTRODE

Assume next that the interposed plate is of lead. It will receive a deposit of copper on the side facing the anode and, the other side being insoluble, will become peroxidized with the evolution of oxygen and the production of sulphuric acid in the solution. These are results which can safely be anticipated. With a plate of lead, however, there will be a marked alteration of the ammeter and voltmeter readings as an appreciable E.M.F. will be required on the anode side of the secondary electrode in order to bring about the chemical change expressed in the relevant equation—

$$CuSO_4 + H_2O = Cu + H_2SO_4 + O$$

This is a condition which frequently happens without design in work which is being plated in a lead-lined tank and which is badly arranged with respect to the lining of the tank. The condition is shown in Figs. 10 and 11, from which will be seen the

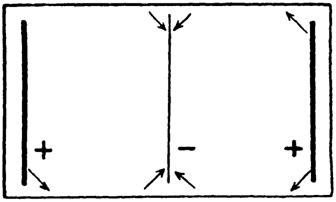

FIG. 10. LEAD LINING AS BI-POLAR ELECTRODE

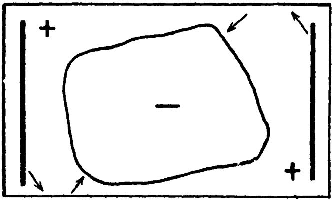

FIG. 11. LEAD LINING AS BI-POLAR ELECTRODE

possibility of current leaving the anode and passing to an adjacent portion of the lead lining with deposition of metal, leaving it at a point adjacent to some part of the cathode, with a localized peroxidation of the lining. This condition usually arises from badly disposed work which is large, and in which case the current may find an easier passage through the good conducting lining of the vat than through an appreciable distance of a poorly conducting solution. Insulating linings of wood or glass serve to prevent this undesigned operation of the lining as a bi-polar electrode.

Polarization. This term frequently arises in electrodeposition. Briefly, it refers to the tendency of the products of electrolysis to revert to their original condition. A more detailed and scientific definition is possible, but this simple one will here suffice. As an example, the electrolysis of water sets free hydrogen and oxygen at, say, two platinum electrodes. These gases linger on the electrodes and having, as it were, been dragged away from each other are anxious to recombine. This tendency to revert to their original form of water is measurable as an E.M.F. in a direction opposite to that which disengaged them.

In copper sulphate solution with copper electrodes this tendency does not exist, as there is no ultimate decomposition taking place. The copper which is deposited on the cathode is replaced by that dissolved from the anode. In a nickel solution, however, in which there may be imperfect solution of the anode, oxygen and sulphuric acid are formed at the anode and these with the nickel deposited on the cathode show a marked tendency to re-form nickel sulphate according to the following equation—

$$\mathrm{Ni} + \mathrm{O} + \mathrm{H_2SO_4} = \mathrm{NiSO_4} + \mathrm{H_2O}$$

On taking off the current from such a bath there will still be a reading on the voltmeter which expresses this tendency to recombination. This type of polarization is known as *chemical polarization* arising from a change of chemical composition of the solution around the electrodes.

In greater detail, imagine a copper sulphate bath with a copper anode and cathode. With varying currents the P.D.'s associated with each are noted. The copper anode is removed and replaced by one of lead of exactly the same area and distance from the cathode, and the P.D.'s to generate the same currents in the bath noted. Typical figures are shown in the accompanying Table (No. XXI).

TABLE XXI

POLARIZATION

Copper Anode			Lead Anode				
E volts	I amperes	$R = \frac{E}{I}$ ohms	E volts	I amperes	$\frac{E}{I}$	$E - e$	$\frac{E - e}{I} = R$ ohms.
·8	10	·08	2·15	10	·215	·9	·09
1·15	15	·076	2·45	15	·163	1·2	·08
1·5	20	·075	2·8	20	·140	1·55	·077
1·9	25	·076	3·25	25	·130	2·0	·08
2·3	30	·077	3·65	30	·122	2·4	·08
3·1	40	·077	4·35	40	·109	3·1	·077

Several points are readily observed from this table. First, the P.D.'s with lead anodes are appreciably higher than those with the copper anode. Secondly, by calculating the resistance of the bath with a copper anode we get a tolerably uniform set of figures which, averaged, represent the resistance of the bath. Applying the same process with the lead anode figures, a constant value of the resistance is not obtained. These figures are shown in the table. Next the figures may be made to reveal more of their meaning by plotting them as shown in Fig. 12.

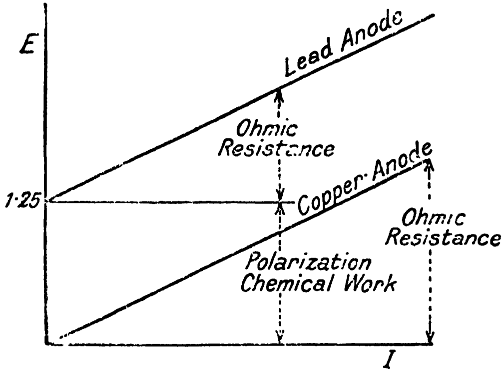

FIG. 12. CHEMICAL POLARIZATION

It will then be observed that the line connecting the points in the case of the lead anode cuts the P.D. line at 1·25 volts, meaning that with this voltage there is no appreciable current. This is hardly true in practice, there being slight deviations of which note cannot be taken at this stage. This definite voltage is what is called *polarization*. It represents the part of the P.D. decomposing the copper sulphate, depositing copper on the cathode, producing sulphuric acid and giving off oxygen at the anode according to the chemical equation

$$CuSO_4 + H_2O = Cu + O + H_2SO_4$$

This reaction does not occur with the copper anode, copper dissolving at the anode at the same rate as that deposited at the cathode, thus maintaining the metal content of the solution. If we deduct this polarization (*e*) from the total voltage with the lead anode the volts remaining now give, with the current, a uniform set of figures for the resistance of the solution and these agree with those with the copper anode. Polarization is thus a state of the electrodes which sets up a P.D. in the reverse direction to the main P.D. In other words, polarization is the tendency of the products of electrolysis to revert to their original condition. The main P.D. has, therefore, to overcome this polarization P.D. before it can generate any current. If the main P.D. is withdrawn the polarization becomes obvious, and the bath may be used as an accumulator, except that its capacity is small. The lead accumulator is a more perfect piece of apparatus to utilize the same principle.

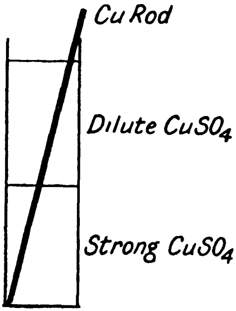

FIG. 13. CONCENTRATION POLARIZATION

Now lead as an anode in the copper bath is quite insoluble. Such insoluble anodes are, however, sometimes used, as for example in copper-depositing processes in which the aim is to extract the copper from the solution without putting more in. Further, the chromium bath is another illustration. At one time, nickel baths showed the effect very obviously, though more recently with the better types of anodes now available this polarization is less noticeable. It was this P.D. of polarization which was responsible for the reversal of the polarity of dynamos which were in use and not correctly designed to avoid this trouble. In practically all plating solutions in which soluble anodes are used, this polarization should not be present appreciably. If it is, it is usually due to anodes not dissolving correctly, and the trouble should be located and attended to. There is, however, another type of polarization which is usually not so pronounced.

Take the case of a copper bath with copper electrodes. The migration of the copper ions is relatively slow. There is, therefore, a concentration of copper sulphate in the anolyte and a diminution of strength around the cathode. There is a definite tendency for these to equalize by the solution of copper from the cathode to strengthen up the catholyte, and at the same time the deposition of copper on the anode to reduce the concentration there. These effects are small, but nevertheless there. They may readily be illustrated in a simple experiment in which a copper rod stands in a cell containing layers of strong copper sulphate solution and a weaker solution above. This is depicted in Fig. 13. The matter is emphasized by the substitution of weak sulphuric acid in place of the weak copper sulphate. After a time, the rod is removed and is observed to have received a deposit from the stronger solution and to have dissolved anodically from the upper portion. While this theoretically should go on until the two layers attain the same concentration, this would take a long time. This type of effect is called *concentration polarization.* It is present in every plating solution, but does not appreciably influence the plating process.

When deep work hangs in a stationary solution there is a tendency to stratification of the solution with thickening of the deposit in the lower parts of the work. This is, in part, due to concentration polarization. The defect is readily remedied by stirring or agitation.

Electrochemical Series. An even rapid survey of the metals considerably used in industry at once shows that they possess very different degrees of corrodibility. Some metals are very active. They dissolve quickly in acids and are far from permanent in air. Others are moderately stable in air and these are relatively slow in their action with acids. The active metals are necessarily difficult to extract from their naturally occurring compounds. A large consumption of energy is involved in separating them from the elements with which they are combined. Magnesium, aluminium, and sodium, and to a smaller degree, zinc, exhibit this chemical activity. Gold, platinum, and to a lesser degree silver, are relatively permanent in acid atmospheres. They not infrequently occur in nature in the free form.

The term "noble" in Chemistry implies a permanence under corrosive conditions rather than mere price.

From such a general survey of the chemical properties of the metals, reinforced by quantitative data where this is possible, it becomes easy to arrange the metals in an order in which these properties are relatively expressed. Such an approximate order is given in Table XXII.

TABLE XXII

ELECTRO-CHEMICAL SERIES

Sodium
Magnesium
Aluminium
Zinc
Iron
Nickel
Tin
Lead
Copper
Arsenic
Antimony
Silver
Platinum
Gold

The active and inactive ends of this series will be quickly recognized. The earlier mentioned and active metals are, in the nomenclature of electrochemistry, said to be *electro-negative,* while those at the opposite end of the series and which are relatively stable in air are *electro-positive.* These terms, which constitute a reversal of the earlier method of indication, derive their origin from the fact that metals like sodium, aluminium, and zinc readily pass into solution either in water or acid. They then form cathions with a positive charge, leaving the plate from which they have been formed electro-negatively charged. On the other hand, solutions of copper, silver, and other electro-positive metals readily give up their cathions, charging the plate upon which they form, electro-positively.

In any case the list is only approximate in its order. For example, tin, which is more stable in acid solutions than is iron, becomes very much more active in alkali solutions than iron, while some metals which ordinarily tend to come out from the ionic form to the metallic form are very much slower or even opposite in their behaviour in contact with cyanide solutions.

Nevertheless, the list is very useful in giving some indication of the probable behaviour of the metal under corrosive conditions.

An example is that of the displacement of a metal from a solution of its salts by other metals. This is commonly called simple immersion. Approximate results are given in Table XXIII.

Electro Pdeotentials. This subject can, however, be treated a little more exactly from another and more important point of view. We have come to recognize that when a metal dissolves in an acid for example, forming a soluble ionized

TABLE XXIII

SIMPLE IMMERSION

	Zn	Pb	Cu	Fe	Ni	Sn	Hg
Zinc sulphate . .	n	n	n	n	n	n	n
Lead acetate . .	d	n	n	n	n	n	n
Stannous chloride . .	d	d	n	n	n	n	n
Silver potassium cyanide	d	n	d	n	n	n	n
Copper sulphate .	d	n	n	d	n	d	n
Silver potassium cyanide	d	n	d	n	n	n	n
Mercuric nitrate .	d	d	d	d	d	d	n
Silver nitrate . .	d	d	d	d	d	d	n
Platinum chloride	d	d	d	d	d	d	d
Gold chloride .	d	d	d	d	d	d	d

d = deposition n = no deposition

salt, the metal has, in fact, passed from the solid to the ionic state in much the same way as a solid with a characteristic odour is recognized because some of it evaporates into the air without passing through an intermediate liquid form. Those metals which dissolve readily are those whose salts ionize readily. This tendency of the metal to form ions is denoted by the term "electrolytic solution pressure." This, in the case of zinc in the Daniell cell, finds expression in its contribution towards the E.M.F. of the cell. Other metals have a much smaller electrolytic solution pressure, so slight that they are unable to effect the production of more metal ions in a solution already containing them. On the other hand, there may be, and indeed often is, a tendency of the ions to fall out from the solution into the metallic form. This happens to be the case with the copper ions from a copper sulphate solution, and this process makes its contribution towards the recognized E.M.F. of 1·09 volts of the Daniell cell.

Thus the action in the Daniell cell may be represented as—

$$Zn + CuSO_4 = ZnSO_4 + Cu$$

Written ionically this becomes—

$$\underset{\text{metal}}{Zn} + \underbrace{Cu^{\cdot\cdot} + SO_4^{--}}_{\text{ions}} = \underbrace{Zn^{\cdot\cdot} + SO_4^{--}}_{\text{ions}} + \underset{\text{metal}}{Cu}$$

Or it may be expressed still more simply—

$$\underset{\text{metal}}{Zn} \rightarrow \underset{\text{ions}}{Zn^{\cdot\cdot}} = \cdot 48 \text{ volt}$$

$$\underset{\text{ions}}{Cu^{\cdot\cdot}} \rightarrow \underset{\text{metal}}{Cu} = \cdot 61 \text{ volt}$$

Each of these two processes provides its quota towards the ultimate E.M.F. of the cell. These contributions were originally determined to have the values above assigned to them and thus was deduced the surprising, but by no means impossible, idea that the larger share of the 1·09 volt came from the copper end of the cell and not from the zinc.

The methods of this determination need not be entered upon here. They are to be found in treatises on the more theoretical side of the subject. We are now concerned with their application in the electro-depositing process.

What was done for zinc and copper was also possible and done for all other metals and their solutions. For each of these metals there is what we will continue to call an electrolytic solution pressure, while in the respective solutions there will be a pressure of the metal ions present and this can simply be called the ionic pressure or metal ion pressure. If the electrolytic solution pressure exceeds the ionic pressure the metal tends to pass into solution as ions, while on the other hand if the ionic pressure exceeds the electrolytic solution pressure ions tend to pass back into the metallic form.

These processes provide the origin of the differences of potential which occur when metals stand in solutions of their salts. These P.D.'s are determinable both in magnitude and direction. The following values were originally assigned to them—

Zinc	— ·48 v.	Nickel	+ ·06 v.	Hydrogen	+ ·28 v.
Iron	— ·15 ,,	Tin	+ ·14 ,,	Copper	+ ·61 ,,
Cadmium	— ·12 ,,	Lead	+ ·15 ,,	Mercury	+ 1·17 ,,

The interpretation of these values is as follows—

The negative sign attached to zinc and similar metals means that these metals readily ionize, and, producing positive ions in the solution, become themselves negatively charged. The positive sign as in the case of copper means that positive metal ions more readily pass from the solution on to the metal, delivering their positive charge to the metal plate. The figures originally attached to these metals were different from those now given. They were determined by a direct method of, however, a not altogether satisfactory type. It was later regarded as much more satisfactory to transfer these values to a new scale which had all the advantages of experimental accuracy but of a comparative nature only. On the old scale the value for hydrogen was + ·28 volt, while that of copper was + ·61 volt and that of zinc — ·48 volt. These figures had an absolute value. On the new or hydrogen scale the hydrogen value is taken as zero. The copper value thus becomes + ·61 — (+ ·28) = + ·33 volt, while that of zinc becomes — ·48 — (+ ·28) = — ·76 volt. Originally the values were for metals standing in normal solutions of their salts regardless of their degree of dissociation and therefore ionic strength of the solution. On the hydrogen scale, the more recently determined values refer to metals standing in solutions of normal metal ionic strength. More detail of these figures and their meaning can be obtained from other works. Their simple application to electrodeposition can, however, be indicated. The generally accepted values of these electrode potentials are as follows—

TABLE XXIV

ELECTRODE POTENTIALS

Magnesium	$Mg \rightarrow Mg^{\cdot\cdot}$	— 1·55	volts
Aluminium	$Al \rightarrow Al^{\cdot\cdot\cdot}$	— 1·34	,,
Zinc	$Zn \rightarrow Zn^{\cdot\cdot}$	0·76	,,
Iron	$Fe \rightarrow Fe^{\cdot\cdot}$	— 0·43	,,
Cadmium	$Cd \rightarrow Cd^{\cdot\cdot}$	— 0·40	,,
Nickel	$Ni \rightarrow Ni^{\cdot\cdot}$	— 0·22	,,
Tin	$Sn \rightarrow Sn^{\cdot\cdot}$	— 0·14	,,
Lead	$Pb \rightarrow Pb^{\cdot\cdot}$	— 0·13	,,
Hydrogen	$H \rightleftharpoons H.$	0·00	,,
Copper	$Cu \rightarrow Cu..$	+ 0·33	,,
Mercury	$Hg \rightarrow Hg.$	+ 0·79	,,
Silver	$Ag \rightarrow Ag.$	+ 0·80	,,
Gold	$Au \rightarrow Au.$	+ 1·5	,,

This order of metals provides a more exact expression of the electro-chemical series than that afforded by a general survey of the chemical properties of the metals.

The Daniell cell provides a convenient starting point. In it zinc forms positive ions which migrate towards the copper plate. A P.D. of — 0·76 volt is developed. Copper ions migrate towards the copper plate and are there deposited, yielding a further 0·33 volt. These are the respective contributions of these processes towards the recognized value of 0·76 + 0·33 = 1·09 volts of this cell. Similarly in a zinc plating solution of the sulphate type, the production of zinc ions at the anode is attended by the production of approximately 0·76 volt at the anode. The similar deposition of zinc ions at the cathode necessitates the consumption of 0·76 volt. These two P.D.'s balance one another when anode and cathode efficiencies are ideal or 100 per cent. Usually they vary slightly but with no very great difference. Nevertheless, the usual voltmeter reading takes into account both of the so-called "electrode potentials" together with the fall of potential due to the ohmic resistance of the bath, a somewhat complex result as has been previously indicated (see p. 57).

With the copper sulphate solution somewhat different conditions are met. Here anode solution involves the consumption—not the generation—of something of the order of 0·33 volt, while the deposition at the cathode involves the production of a like difference of potential. Under ideal conditions these electrode potentials are equal and opposite and the voltmeter then records the fall of potential due to the resistance. Only under these ideal conditions can we obtain even an approximate idea of the resistance of an electrolyte by the use of direct current (see page 36).

Nothing further than this very bare outline of the conception of the origin of potential differences between metals and their solutions in which they are partly immersed can be ventured upon here. It must suffice to say that a more thorough treatment can be found in the more theoretical treatises, and that the applications in electrodeposition are far-reaching, throwing considerable light on these problems.

Potential Diagrams. This information is more strikingly represented in the diagrams of Fig. 14 in which (*a*) represents the potential changes in the Daniell cell; (*b*) shows the electrode potential changes in a zinc sulphate solution; and (*c*) indicates those occurring in the usual acid copper sulphate solution.

In each case only a very small current is assumed to be flowing so that the fall of potential due to ohmic resistance is slight. This is shown by the almost horizontal line.

Overvoltage. This is a further idea upon which a few words of explanation may prove helpful. It may not appear at first that the variation of the metal which constitutes the cathode in a depositing process will seriously influence the deposition of the metal, except, of course, in those cases in which the metal is more electro-negative than that to be deposited and in which cases deposition takes place by "simple immersion." It was, however, found that a higher E.M.F. was required to maintain the deposition of hydrogen on a cathode of smooth platinum than on one of platinized platinum. The substitution of other cathodes revealed larger differences. For example, it requires 0·78 volt more to deposit hydrogen against a mercury cathode than against one of platinized platinum. This additional or excess voltage is called "overvoltage," and has important applications in many cases of electrodeposition. The following table shows the overvoltages required by the various cathode metals for the maintenance of hydrogen deposition—

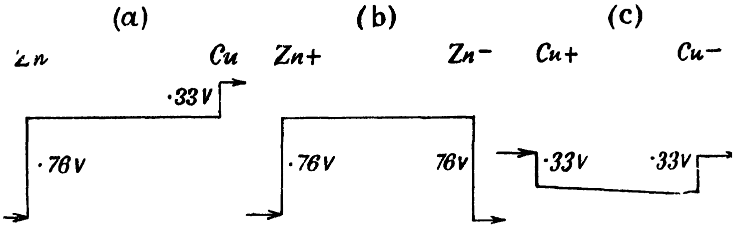

FIG. 14. POTENTIAL DIAGRAMS

TABLE XXV

HYDROGEN OVERVOLTAGE

Platinized platinum	00 volt	Copper	·23 volt
Gold	·02 ,,	Cadmium	·48 ,,
Polished platinum	·09 ,,	Tin	·53 ,,
Silver	·15 ,,	Lead	·64 ,,
Nickel	·21 ,,	Zinc	·70 ,,
		Mercury	·78 ,,

These figures are only to be used approximately as they are variable according to such conditions of deposition as current density and temperature.

Of lesser importance to the electro-depositor is a similar phenomenon with oxygen deposition but of some interest is the occurrence of overvoltage in connexion with metal deposition. This is a matter upon which there is at present little data available.

Applications of Electrochemical Series. Some applications of the principle involved in the electro-chemical series may be briefly referred to. The negative or active metals are usually plated with the more positive metals in order to give them a greater degree of permanence. Iron and steel, so largely used in industry, are usually coated with either zinc or tin in numerous applications. A note of importance here arises. The permanence of metals is not dependent entirely upon their chemical characteristics. It is to some extent dependent upon the properties of the compounds formed by exposure to corrosive conditions. In the order in the list we might anticipate more rapid corrosion of the zinc coating of "galvanized" iron or steel than of the base metal itself. By exposure, however, zinc forms in a relatively dry atmosphere a thin film of oxide, which is adherent and protective. Aluminium does the same and this thin protective film accounts for the relative permanence of metals which from their chemical properties might be expected to be readily attacked by a corrosive atmosphere. In an acid atmosphere containing, say, sulphuric acid, a common impurity in an industrial atmosphere arising from the burning of coals containing an appreciable quantity of sulphur, zinc forms a basic sulphate, which again is insoluble and therefore forms a protective layer.

FIG. 15. ZINC PROTECTING IRON

FIG. 16. TIN CORRODING IRON

Still further, when by abrasion the iron of the galvanized metal becomes exposed, the electrochemical difference between the two metals is such that the zinc corrodes away in preference to the iron. This is sacrificial corrosion, shown in Fig. 15.

Again, with tinned iron, while the tin coating is continuous the tin is very little attacked by the air and the product remains bright. With exposure of the iron this base metal rusts badly, encouraged as it is by the electrochemical difference which is responsible for small currents set up between the two metals from the iron through the corrosion medium to the tin, thus corroding and rusting the iron rather more rapidly in the presence of tin than in its absence. This is shown in Fig. 16. Similar effects are observed with copper on iron—an undesirable combination; while nickel on iron or steel would act more like zinc and thus provide a beneficial combination.

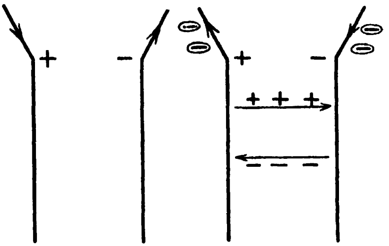

FIG. 17. FLOW OF ELECTRICITY IN ELECTROLYTE

Yet again, the electro-negative metals readily deposit by simple immersion the electro-positive metals from solutions of their salts, for which reason, therefore, iron and zinc cannot be successfully copper plated from the sulphate solution, even apart from the presence of free acid, this necessitating recourse to the much more stable cyanide solution.

Production and Discharge of Ions. A few words relative to the processes of extracting metals from their ionic form and replacing them by new ions formed at the anode will here be appropriate. At the cathode end of the story we shall consider that the metallic and similar ions, having migrated there under the influence of the applied P.D., lose their positive charge—by which is meant that they pick up an electron for each valency—and are then either deposited in the case of some, though not all metals—for example aluminium—or suffer some further secondary change affecting the chemical composition of the catholyte.

Taking the simple case of the deposition of the metal, these ions having been discharged are now in the form of atoms which, by controlled deposition, pile themselves together in a form which constitutes the deposit. In this process of discharge of the ion some metals absorb energy, while others develop energy. There are, therefore, potential differences set up between the film of electrolyte and the cathode, of which in ordinary electro-plating measurements we have little indication.

Again, at the anode, which will be assumed to be passing into solution efficiently, metal is, as it were, evaporating into the form of ions in the electrolyte. In doing so the metal atom loses an electron for each valency; these negative charges passing away from the anode into the "outer" circuit while the ions assume a positive charge. Again, there are energy changes and differences of potential. This more modern conception is illustrated in contrast with the older view of current in Fig. 17.

With ideal anode and cathode efficiencies these potential differences are of equal value and opposite character. They therefore balance each other, and the reading on the voltmeter is that of the loss of potential as the current "passes" through the solution. If anode and cathode efficiencies are not equal—and this happens, for example, in every case in which, as is frequent, the anode is not dissolving as rapidly as metal is being deposited—then the voltmeter reading includes not only the potential fall through the solution but also these electrode potential differences, which are known as the *anode potential* and *cathode potential.*

The voltmeter reading, therefore, is quite frequently the total of three values, the two electrode potentials and also the fall of potential across the solution. Where anode and cathode efficiencies are high, and more especially when the anode value is nearly 100 per cent, the voltmeter reading gives a good indication of the resistance of the solution. When the anode efficiency, particularly, is less than 100 per cent, chemical changes take place which lead to the absorption of energy, this being recorded by a substantially increased voltmeter reading.

Voltmeter readings therefore, while indicative of the conditions of operation, need to be interpreted with care.

CHAPTER IV

PRINCIPLES OF CHEMICAL ANALYSIS OF ELECTRO-DEPOSITING SOLUTIONS

INTRODUCTION—Types of chemical analysis—Gravimetric analysis—Volumetric analysis—Colorimetric methods—Gravimetric methods—Electrolytic analysis—Volumetric methods—Standard solutions

Introduction. With the increase in the application of scientific methods to the processes of electrodeposition, there comes the need for greater control in the composition of the solutions used. To-day it is recognized that every constituent of a solution should justify its presence by some definite function, and that this purpose should be assured by the presence of the required substance in the right amount. This usually necessitates chemical analysis. In fact, while the so-called addition agents are in many cases regarded as desirable, there is some tendency to omit them on account of the difficulty of quantitatively estimating them, it being felt that such materials should not be present unless they can be controlled by chemical or other types of analysis.

It is, however, not suggested that chemical analysis provides the only method of control of the composition of depositing solutions. In cases in which there is a single constituent, the determination of the density may go far towards general control, but there are few such examples in modern electro-plating. In other cases it may be possible that a quick determination of the resistance of the solution will afford a clue to the working conditions. Such a method is not without possibilities in the case of the chromium solution, an effective chemical analysis of which is not altogether a simple matter. For the greater part, however, chemical analysis will be necessary.

Types of Chemical Analysis. Such analyses can usually be run on several different lines each with its special appeal and also limitations. In adapting these methods to workshop requirements a number of conditions have to be met which do not arise in the analytical laboratory. These concern the apparatus available. The simpler this is, the better the chance of its installation in the workshop. Further, there is the time involved in the analysis. Again, the quicker this can be effected, the better, while still further, accuracy must claim attention. Among the various types of analysis are those known as Gravimetric and Volumetric analysis.

Gravimetric Analysis. Very simply it may be stated that these are the more accurate but involve longer time. They involve the conversion of the constituent to be determined into some known substance of definite composition, which is obtained in a perfectly pure form and weighed. They are not the methods of the greatest use in the workshop, but some of the workshop problems need to be referred to the laboratory in which these gravimetric methods can be more accurately carried out.

Volumetric Analysis. In this type of analysis, most of the measurements are made with definite volumes of solutions known as standard solutions. They are as a rule quickly carried out, but lack the accuracy of the gravimetric methods. This, however, is not always of vital importance. The analytical chemist may occasionally be concerned with a result to the fourth significant figure. Quite commonly, he will be concerned with the third, so that, for example, he may want to know whether the result is 5·41 or 5·42. This order of accuracy is almost never required in the general analysis of plating solutions. Assume for a moment that it is required to maintain the silver content of a plating solution of 2·5 oz. per gallon. Without specifying exactly the permissible variation from this figure for the production of equally good deposits, it will be at once appreciated that a wider variation is allowable in this analysis than would ordinarily appertain to general chemical analysis. A similar remark might be made not only to the amount of free cyanide but to a number of other constituents. There are, however, examples in which a greater degree of accuracy would be necessary.

For the general control of plating solutions, volumetric methods are of wide application. Applied only in the roughest manner, they would have obviated a plater from attempting to deposit silver from a solution which contained no more metal than would just whiten the work, and the copper-depositor from wondering at his solution being slow and showing tendency to overheating when it contained no free acid, or the chromium-plater from being concerned at the resistance of his bath in spite of its high hydrometer reading when actually it contained no free chromic acid owing to the accumulation of trivalent chromium and iron. These are examples taken from experience and generally concern the type of analysis which requires to be frequently undertaken in order to maintain baths in working order. A greater degree of accuracy would of course be required where a large quantity of silver-containing materials is being disposed of for the recovery of the precious metal, if such term can be used in view of the ruling low price.

Colorimetric Methods. There are then methods of analysis which are based on a system of matching colours of solutions of the compounds concerned with those of standard solutions of known strength. They have their limited degree of application, much depending on the permanence of the standard colours and also the interference of other substances which may be present in the solution. The usual pH determination can be regarded as some example of this type of analysis.

Gravimetric Methods. This type of method obviously refers to the application of methods of weighing as the medium of measurement. Generally the term ought to cover all methods employing either direct or indirect weighing as an important operation in the analysis. For the present purpose, however, we can delete such methods as those of the hydrometer. Concerning the methods which involve some chemical manipulation we recognize a general principle. Here, for example, is a nickel-plating solution of which the content of the nickel salt is required. Now it is obviously impossible to extract the salt and weigh it. It is equally impossible to extract most of the constituents of plating solutions in a weighable form.

An alternative route is possible. Take the case of a silver-plating solution. It contains the double cyanide of silver and possibly potassium, together with free cyanide and carbonates. Now it is possible to convert this soluble silver compound into one which is completely insoluble, the chloride for example. This solid is then separable from substances in solution by filtration, and by washing, the last traces of soluble salts are removed. If now the chloride and paper are thoroughly dried, they can be weighed and, deducting the weight of the paper, the weight of silver chloride is thus obtained. Of silver chloride we know the exact composition and thus we can readily calculate the silver obtained in the form of chloride from a given volume of the silver-plating solution. The only or chief difficulty in this case is the complete drying of the chloride without the risk of decomposition, but it can be got over by manipulative methods which are best explained in individual examples as they arise. This is only a bare outline of the sequence of operations through which gravimetric analysis is conducted. It is clear that there is more chemical work than in volumetric methods. Gravimetric methods are capable of great accuracy and are of considerable refinement when the circumstances warrant excessive care.

Electrolytic Analysis. There is, however, one special phase of gravimetric analysis which should make an instant appeal to the electro-chemist. This concerns the possibility and practicability of actually plating out the whole of the metal from the solution on to a suitable weighed cathode without recourse to the more tedious methods usually associated with gravimetric analysis. Such procedure is known as electrolytic analysis. It has some application in industrial work but its applicability to the analysis of plating solutions is limited. One or two points may here be briefly referred to.

This example of electrodeposition involves the use of a solution with gradually decreasing metal content; in fact, toward the end of the operation the metal content is reduced to nearly zero. The production of a weighable deposit might then become a problem. Ordinarily, these deposits would become powdery and useless from a commercial point of view. By selecting the material of the cathode and by the addition of other materials to the solution, these deposits can be procured in a weighable form and the procedure provides a welcome method of analysis. Unfortunately the metal most used for this purpose is platinum, which is costly, but there are possibilities of substituting other and cheaper metals in certain cases. The charm of the process is that, once started, the deposition proceeds with very little attention almost to completion, there being the occasion for some testing towards the end of the process. Finally, the solution is removed, the deposit washed, dried, and weighed.

Volumetric Methods. A brief outline of the methods of volumetric analysis involve a discussion of (1) the apparatus commonly used and (2) the types of solutions used as standards.

VOLUMETRIC APPARATUS. Types of apparatus in general use include—

(*a*) Measuring flasks (Fig. 18) which are usually made to contain 1 litre, 500 c.c., 250 c.c. or other definite volumes and are provided with a long narrow neck with a ground stopper.

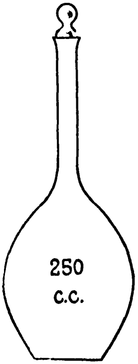

FIG. 18. MEASURING FLASK

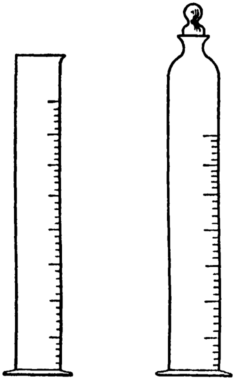

FIG. 19. GRADUATED CYLINDERS

On the neck is a circular mark which indicates the level of the volume of the liquid specified on the flask. These flasks are made to *contain* the specified volume, not to deliver it. When the latter condition is also required, a higher level on the neck of the flask will be found to which liquid must reach if, on pouring out, the specified volume of liquid is to be delivered. This, however, is unusual. Measuring flasks are of chief use in making up definite volumes of solutions.

(*b*) Graduated cylinders (Fig. 19) are used for a similar purpose except that whereas flasks have only one or at the most two marks and refer only to one or two volumes of liquid, cylinders are graduated throughout their length so that they are capable of indicating many definite volumes. Against this convenience, however, must be set the fact that the markings on a wide cylinder cannot be used so accurately as those on the comparatively narrow neck of the flask. From these graduated cylinders volumes may be poured with approximation.

(*c*) Pipettes. For transferring liquids in definite volumes from one vessel to another, pipettes are commonly used. Their form is indicated in Fig. 20, the upper narrow portion carrying the mark representing the volume of liquid which is delivered. Common capacities are 5 c.c., 10 c.c., 25 c.c. and 50 c.c. although any other volume can be similarly dealt with. Thus a 25 c.c. pipette holds up to the mark rather more than 25 c.c. but delivers accurately this volume. In use, the liquid is drawn into the pipette to a point above the mark and held there by the quick application of the finger or thumb. A little experience is of more value than any amount of description. The finger or thumb is then released allowing the liquid to fall to the exact level of the mark, after which the liquid is allowed to fall into the vessel into which it is to be transferred. Before

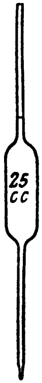

Fig. 20. Pipette

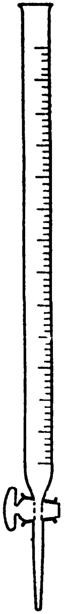

Fig. 21. Burette

Fig. 22. Meniscus

drawing up the volume of liquid into the pipette it will be obvious that a small quantity, preferably two small amounts, should first be drawn into the pipette to rinse it, these small quantities being scrapped. Otherwise drawing a liquid into a wet pipette will lead to its dilution by the water contained in the pipette. The pipette has but one mark and delivers one volume of liquid.

(*d*) Burettes, which are depicted in Fig. 21, serve the purpose of delivering any small volume of liquid up to the capacity of the burette. They comprise accurately graduated tubes fitted with stopcocks. The graduations usually read downwards, the markings representing small but definite volumes, usually tenths of a cubic centimetre. Before use, they are rinsed with the liquid which is to be introduced into them and then filled above the zero mark. The excess is then run out to zero, this process serving to ensure that the bottom of the burette below the graduations is filled with the liquid as it obviously will be after any other volume has been run out.

There is, or should be, no difficulty in reading the level of the liquid in the burette. The surface is deeply curved, the most conspicuous feature of the surface being the lower part of the "meniscus." This is shown in Fig. 22. A piece of white paper may be supported on the burette to provide a background against which the reading is more easily taken, and readings to 0·05 c.c. or 0·02 c.c. or even 0·01 c.c. may be taken with a little experience.

Illustrative of the application of these pieces of apparatus, assume that 5 gm. of silver nitrate are dissolved in distilled water in a litre flask the solution being diluted in the flask up to the mark representing 1000 c.c. After the preparation of any solution in this manner, shaking is essential to ensure uniformity of the strength of the solution. Otherwise some parts will be stronger than others and for the purposes of measurement this is equivalent to a ruler with "inches" of different length. Every 25 c.c. of this solution withdrawn by means of a pipette brings out $\frac{25 \times 5}{1000} = 0{\cdot}125$ gm., a quicker operation than weighing such an amount time after time. Again if run from a burette, 12·2 c.c. would represent $\frac{12{\cdot}2 \times 5}{1000} = 0{\cdot}061$ gm. of silver nitrate. Small and accurately measured quantities of the dissolved substance can thus be taken from a large bulk of solution, the preparation of which has involved only one weighing of the salt.

Burettes are usually made from tubes carefully chosen for their correct diameter and uniform bore. These factors can never be taken beyond any shadow of doubt. Graduation is effected by machine ruling and it is not unusual to find that successive ten cubic centimetres differ slightly from each other. These variations would not be sufficiently large to seriously affect the type of analyses with which we are concerned. For more accurate work, however, it becomes necessary to check these volumes by weighing successive "equal" volumes of water and allowing for the density of the water at the temperature of the experiment. Without going to this extreme, it is possible markedly to limit possible errors in a burette by always using the same, usually the top, portion of the scale so that the successive readings are measured from zero. If any error is involved, it more or less cancels out with successive readings, or at the worst, gives a small but constant error which may be permissible.

STANDARD SOLUTIONS

These are solutions of known and usually definite chemical strengths used in volumetric analysis. They are what might be called chemical "rulers." It is, however, sometimes possible to compare the strengths of two solutions with the use of what is commonly called a standard solution in much the same way as it is possible to compare two lengths by reference to a "bit of wood" of which the length is not exactly known. In linear measurements we more often use a piece of wood of standard length. In volumetric work we use solutions of definite and known strength. These are our standard solutions.

Some simple basis of solution strength is obviously necessary and this finds its origin in the chemical equivalents which are at the bottom of all quantitative work in Chemistry. A solution which contains the gramme equivalent, that is, the chemical equivalent weight in grammes per litre, is called a normal solution and denoted by N. Thus a normal solution of sulphuric acid contains $98 \div 2 = 49$ gm. H_2SO_4 per litre. An alternative (although not much used) designation is "E," meaning equivalent.

Solutions of one-half, one-tenth, or one-hundredth of this strength are called semi-normal, deci-normal, and centi-normal respectively, and represented $\frac{N}{2}$, $\frac{N}{10}$ and $\frac{N}{100}$.

The great advantage attaching to this system is that equal volumes of solutions of the same "normality" will exactly react with each other. Thus 10 c.c. of any normal acid will be neutralized by 10 c.c. of any normal alkali, while 5 c.c. N . H_2SO_4 will be neutralized by 50 c.c. of decinormal NaOH. The strengths of some common volumetric solutions are given in Table XXVI, and it will be easy to see how the respective quantities of the different reagents have been derived.

One point of considerable importance, however, must be observed. In the preparation of these standard solutions, the chemical equivalent must be determined from the reaction which is involved. This point may be stressed by an example.

TABLE XXVI

STRENGTHS OF STANDARD SOLUTIONS

Solution	Grams per Litre		
	N	$\frac{N}{2}$	$\frac{N}{10}$
H_2SO_4	49	24·5	4·9
HCl	36·5	18·25	3·65
HNO_3	63	31·5	6·3
Na_2CO_3	53	26·5	5·3
NaOH	40	20	4
$AgNO_3$	170	85	17
$Na_2S_2O_3 . 5H_2O$	248	124	24·8

Usually potassium cyanide precipitates silver nitrate according to the following equation—

$$AgNO_3 + KCN = AgCN + KNO_3$$

when 170 parts by weight of silver nitrate are equivalent to 65 parts by weight of potassium cyanide. This reaction is not used analytically by the addition of KCN to $AgNO_3$. Frequently, however, the mixture is made in the reverse direction and the addition of silver nitrate to an excess of potassium cyanide follows the course represented by the equation—

$$AgNO_3 + 2KCN = AgCN . KCN + KNO_3$$

There is no permanent precipitation until the whole of the KCN has been absorbed in producing soluble double cyanide or silver and potassium. Then, and not till then, a permanent precipitate is formed by the interaction of $AgNO_3$ with the AgCN . KCN according to the following equation—

$$AgNO_3 + AgCN . KCN = 2AgCN + KNO_3$$

By the time of the first appearance of a permanent precipitate or turbidity, the first reaction will have been completed and the second just commencing. The first permanent turbidity therefore marks or indicates the completion of the first reaction. If then silver nitrate is run into potassium cyanide solution, the first permanent turbidity is the indication that 170 parts by weight of silver nitrate have reacted with 130 parts by weight of potassium cyanide and the equivalent of potassium cyanide in this reaction is not 65 but twice that amount.

Solutions of exact normalities are difficult to prepare in that they involve weighing out very exact quantities of the substance. Other standard solutions which are not exactly equivalent but are nevertheless very definite may be more easily made, and are serviceable for most cases of analysis, while, as will be seen later, it is sometimes convenient to make standard solutions of such strength that the required answer can be expressed, by the choice of quantities taken, as the figure read from the burette or some value simply related to it, thereby avoiding a final calculation.

CHAPTER V

SOME MATERIALS USED IN ELECTRO-PLATING

SULPHURIC acid—Nitric acid—Hydrochloric acid—Aqua regia—Acetic acid—Determination of strengths of acid solutions—Estimation of mixed acids—Caustic potash—Caustic soda—Ammonia—Estimation of alkalis—Standard sulphuric acid—Simple alkali determination—American potash—Mixed alkalis—Alkali cyanides—Specifications for cyanides—Analysis of cyanides—Standard silver nitrate—Evaluation of a sample of KCN—Alternative standard solution—Comparison of potassium and sodium cyanides—Estimation of chlorides—Alternative method—Estimation of carbonates—Antidotes against cyanide poisoning

Sulphuric Acid (Oil of Vitriol). The general properties of this acid are fairly well known. The more common name was derived from the fact that its earliest production was by the distillation of ferrous sulphate, then (and still) known as green vitriol, other vitreous or glassy (crystalline) substances also commonly known being blue vitriol (copper sulphate) and white vitriol (zinc sulphate). This process of distillation of iron sulphate is still practised for the production of various types of rouge (iron oxide).

In the modern manufacturing processes the acid is made from either iron pyrites or sulphur (brimstone). For the purer qualities of acid and that required for accumulator purposes, brimstone is invariably used on account of its relative purity. When pyrites is used there pass into the acid a number of impurities (arsenic is one) which are detrimental to some of the uses of the acid, especially the manufacture of a number of foodstuffs and also the electrolyte of the lead accumulator.

Manufacturing methods comprise the chamber process in which oxides of nitrogen provide the catalyst to accelerate the conversion of SO_2 into the acid. The process is carried out in large lead-lined chambers and hence the name, chamber acid. The other process utilizes finely divided platinum to bring the SO_2 and oxygen into that more intimate contact which is necessary for speedy chemical change. Hence the name, "contact" process.

Acid produced in the chamber does not exceed 70 per cent strength, as above that figure the lead of the chambers is attacked. Higher concentrations are obtained by a simple process of evaporating off some of the water either in large silica basins or by dropping the acid down towers up which pass the hot gases from either a coke fire or the pyrites burners, on their way to the chambers. The contact process produces acid of practically 100 per cent strength.

In any case in the purchase of the acid there should be some knowledge of its strength and some simple method of determining this. For general purposes the use of the hydrometer will suffice, with subsequent reference to the well-recognized

TABLE XXVII

SPECIFIC GRAVITY OF SULPHURIC ACID SOLUTIONS

Specific Gravity	Percentage of H_2SO_4	Grams H_2SO_4 per Litre
1·0064	1	10·06
1·013	2	20·26
1·019	3	30·57
1·0256	4	41·02
1·032	5	51·60
1·039	6	62·34
1·0536	8	84·29
1·068	10	106·8
1·083	12	130
1·114	16	177·2
1·144	20	229
1·182	25	295
1·223	30	367
1·264	35	442
1·306	40	522·4
1·351	45	608
1·398	50	699
1·448	55	796
1·501	60	900·6
1·557	65	1012
1·615	70	1130·5
1·675	75	1256
1·734	80	1388·2
1·786	85	1519
1·822	90	1639·8
1·8376	95	1746
1·8426	100	1842·6

tables which correlate density with percentage strength, the works method of expressing the proportion of real H_2SO_4 in the liquid. In this connection Table XXVII shows not only the densities and percentage strengths of a number of acid concentrations but also the number of grammes of the acid per litre, so that with any strength of acid the approximate composition is a matter of quick determination. From the table it is seen, for example, that 60 per cent strength corresponds to a Sp. Gr. of 1·501. A litre of this acid therefore weighs 1501 gm. of which 60 per cent or 900 gm. is H_2SO_4. There should hardly be the occasion to give the reminder about adding the acid carefully to water and not water to the acid.

Nitric Acid (*Aqua Fortis, meaning "Strong Water"*). This acid is largely used in admixture with sulphuric acid as a dip for the copper alloys. It is chemically made by the action of oil of vitriol on Chili saltpetre (sodium nitrate).

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

In the older process the acid and nitrate are mixed in cast iron retorts, the acid coming over and being condensed in acid-proof stoneware bottles. There are, of course, other methods of making the acid which received prominence during the late war. The pure acid is colourless while the colour of the commercial type is due to impurities, chiefly oxides of nitrogen.

In the process of manufacture the use of relatively weak sulphuric acid results in the production of relatively weak nitric acid which can be concentrated up to 70 per cent strength by simple boiling. At that strength, both acid and water come over together, so that no further concentration is possible. The stronger varieties of acid are therefore made with stronger sulphuric acid, or concentrated from the 70 per cent acid by first mixing with sulphuric acid which, as it were, hangs on to the water allowing the HNO_3 to be distilled off to a strength of 100 per cent. The densities and strengths of nitric acid are shown in Table XXVIII.

Hydrochloric Acid (*Spirits of Salt, Muriatic Acid*) finds some application in electro-deposition. It is produced practically as a by-product in the manufacture of sodium carbonate, the first stage of which involves the conversion of common salt (rock salt) into sodium sulphate (salt cake)—

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$$

TABLE XXVIII

SPECIFIC GRAVITY OF NITRIC ACID SOLUTIONS

Specific Gravity	% HNO_3	Gm. HNO_3 per litre
1·53	100	1530
1·495	90	1345
1·46	80	1168
1·423	70	996
1·374	60	824
1·317	50	658
1·251	40	500
1·185	30	355
1·120	20	224
1·089	15	163
1·067	11·4	122

Formerly the acid fumes were allowed to escape into the atmosphere. Stricter regulations then necessitated their absorption in water and incidentally opening up the acid to a number of industrial uses. It must be remembered that whereas both sulphuric and nitric acids are, when pure, liquids, hydrochloric acid is a gas, the commercial acids being solutions of the gas in water. The various strengths of this acid are shown in Table XXIX.

TABLE XXIX

SPECIFIC GRAVITY OF HYDROCHLORIC ACID SOLUTIONS

Specific Gravity	Percentage of HCl	Gm. HCl per litre
1·197	40	479
1·174	35	411
1·154	31	358
1·141	28·5	325
1·118	24	268
1·098	20	219
1·074	15	161
1·054	11	116
1·032	6·5	67
1·02	4	41

Aqua Regia. This is a mixture of strong nitric and hydrochloric acids which when warmed react, and evolve chlorine which at the moment of its production is capable of attacking such noble metals as platinum and gold, dissolving them thus—

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$
$$Pt + 4Cl = PtCl_4$$
$$Au + 3Cl = AuCl_3$$

This chlorine when originally evolved is in the atomic form in which it is particularly active. It is then said to be "nascent." Other gases behave similarly. Thus atomic or nascent hydrogen (H) achieves many chemical changes not possible with ordinary or molecular hydrogen (H_2).

Acetic Acid is produced by the fermentation of alcohol—a process which involves oxidation—

$$C_2H_6O + O_2 = H . C_2H_3O_2 + H_2O$$

This process is followed in the production of malt vinegar. On the industrial scale, acetic acid is obtained from the watery distillate of heating wood in the production of charcoal. When pure and strong the liquid acid freezes at 16·5° C. In cold weather the liquid freezes. Such strong acid is called glacial acetic acid.

Determination of Strength of Acid Solutions

This is a matter which need not be considered in detail for each of the three acids referred to. The matter can be dealt with more generally.

The acids as purchased require considerable dilution prior to analysis. The estimations of acid strength are conveniently made with N/2 Na_2CO_3. The acids must therefore be diluted down to this order of strength.

$$\begin{aligned} \text{Now 1 c.c. N/2 } Na_2CO_3 &= 0{\cdot}0245 \text{ gm. } H_2SO_4 \\ &= 0{\cdot}0315 \text{ gm. } HNO_3 \\ &= 0{\cdot}01825 \text{ gm. } HCl \end{aligned}$$

Sulphuric Acid. The strongest acid contains, as reference to Table XXVII shows, approximately 1800 gm. H_2SO_4 per litre: To reduce it to N/2 (containing 24·5 gm. per litre) necessitates dilution to about 80 times its volume. Roughly, measure out 10 to 12 c.c. of the acid into a small weighed glass vessel.

Weigh to give the exact weight of the acid. Carefully dilute. Transfer to a litre flask, taking all precaution that the acid is thoroughly washed into the flask. Dilute to 1000 c.c. and shake. Take 25 c.c. of this solution by means of a pipette into a conical flask. Add two drops of methyl orange solution. In the acid solution the colour changes to pink. Run in the semi-normal sodium carbonate from a burette until the colour just changes to yellow. This should be repeated and the titrations averaged in order to ensure a more accurate result.

Example—

Weight of acid = 20·5 gm., diluted to 1000 c.c.
25 c.c. diluted acid require 20·1 c.c. N/2 Na_2CO_3.
Hence percentage of H_2SO_4 in the sample

$$= \frac{20\cdot 1 \times \cdot 0245 \times 1000 \times 100}{25 \times 20\cdot 5} = 96.$$

Nitric Acid. Reference to Table XXVIII shows that the usual type of strong acid of 1·4 sp. gr. contains 70 per cent HNO_3, or approximately 1000 gm. per litre. The semi-normal acid contains 31·5 gm. per litre. The strong acid therefore requires dilution about 30 times. Weigh out accurately about 30 c.c. of the strong acid. Dilute to 1000 c.c. and titrate 25 c.c. with N/2 Na_2CO_3.

Example—

Weight of acid = 28·4 gm. diluted to 1000 cc.
25 c.c. diluted acid require 15·8 c.c. N/2 Na_2CO_3.
Hence percentage HNO_3 in the sample

$$= \frac{15\cdot 8 \times \cdot 0315 \times 1000 \times 100}{25 \times 28\cdot 4} = 70$$

Hydrochloric Acid. The usual strong acid contains 35 per cent HCl or approximately 410 gm. per litre. Semi-normal acid contains 18·25 gm. per litre. Before titration the strong acid requires dilution about 20 times.

Example—

Weight of acid = 50·5 gm. diluted to 1000 c.c.
25 c.c. diluted acid require 20·2 c.c. N/2 Na_2CO_3.
Hence percentage strength of the acid sample

$$= \frac{20\cdot 2 \times 0\cdot 01825 \times 1000 \times 100}{25 \times 50\cdot 5} = 29\cdot 2$$

ESTIMATION OF MIXED ACIDS

Mixtures of acids are frequently used in electrodeposition. It should be possible to determine their quantitative composition with some degree of accuracy. Obviously specific gravity methods will be of little use. Chemical methods involving both volumetric and gravimetric must be employed.

The first step will be that of the determination of what is called the "normality" of a suitably diluted sample, and for the purpose of dilution some approximate idea of the strength of the mixed acid must first be gained. By way of illustration, take a mixture of sulphuric and nitric acids as commonly used in the dipping of brass articles. A little of the acid can be quickly and roughly diluted down and tested with N/2 sodium carbonate to ascertain its approximate strength. Upon the basis of this experience a larger and suitable quantity is weighed out and diluted to 1000 c.c. Measure out with a pipette 25 c.c. of this acid and titrate with N/2 Na_2CO_3 with methyl orange as indicator.

Example—

Weight of acid 39·78 gm. diluted to 1000 c.c.
25 c.c. diluted acid require 28 c.c. N/2 Na_2CO_3.

The diluted acid is obviously stronger than the N/2 sodium carbonate. It is in fact $28 \div 25 = 1{\cdot}12$ times semi-normal or 0·56N.

Now $N.H_2SO_4 = 49$ gm. per litre.

$\therefore \quad 0{\cdot}56\ N.H_2SO_4 = {\cdot}56 \times 49 = 27{\cdot}4$ gm. H_2SO_4 per litre.

Similarly—

$N.HNO_3 = 63$ gm. per litre
${\cdot}56N.HNO_3 = 0{\cdot}56 \times 63 = 35{\cdot}3$ gm. HNO_3 per litre.

If this diluted acid were sulphuric acid without any nitric acid, its strength would be 27·4 gm. H_2SO_4 per litre. Similarly if the acid were nitric acid without any H_2SO_4, its strength would be 35·3 gm. per litre. Both these acid solutions have the same normality, that is, the same power of neutralizing sodium carbonate or other alkali. The titration does not give us any indication of the relative quantities of the two acids present. It therefore becomes necessary to determine one of these gravimetrically. The sulphuric acid can readily be estimated in the following manner. Take 25 c.c. of the diluted acid. Dilute further with distilled water. Heat to boiling and add an excess of boiling barium chloride solution, that is, till there is no evidence of more ppt. forming. The following reaction occurs—

$$H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl$$

The white ppt. is $BaSO_4$ which, to put it briefly, is filtered through a paper of known ash and thoroughly washed until the washings give no evidence of the presence of chlorides. The ppt. is then dried and the paper containing it folded and placed in a porcelain crucible which has previously been cleaned and weighed. This is heated to redness until the whole of the carbon from the paper is burnt off. By this time the $BaSO_4$ can be assumed to be dry and the crucible now contains $BaSO_4$ together with the small ash of the filter paper. Deduct the weight of this ash. (This will usually be indicated upon the packet.) Assume the weight of $BaSO_4$ obtained to be 0·9 gm.

Now $$\frac{BaSO_4}{233} = \frac{H_2SO_4}{98}$$

Hence $$H_2SO_4 \text{ per litre} = \frac{98}{233} \times \frac{0{\cdot}9}{25} \times 1000 = 15{\cdot}1 \text{ gm.}$$

Now 15·1 gm. H_2SO_4 per litre $= \frac{15{\cdot}1}{49} = 0{\cdot}308$ N.

$$\begin{aligned} \text{Total normality of mixed acid} &= 0{\cdot}56 \\ \text{Normality due to } H_2SO_4 &= 0{\cdot}308 \\ \therefore \quad \text{Normality due to } HNO_3 &= 0{\cdot}252 \\ \therefore \quad \text{Gm. } HNO_3 \text{ per litre} &= 0{\cdot}252 \times 63 \\ &= 15{\cdot}9 \end{aligned}$$

Hence 39·78 gm. original strong acid contain

$$15{\cdot}1 \text{ gm. } H_2SO_4 = \frac{15{\cdot}1}{39{\cdot}78} = 38\%$$

and $$15{\cdot}9 \text{ gm. } HNO_3 = \frac{15{\cdot}9}{39{\cdot}78} = 40\%$$

With a mixture of sulphuric and hydrochloric acids the total normality will first be determined by titration with sodium carbonate, after which the titration in the neutral solution can be continued with standard silver nitrate (using K_2CrO_4 as indicator) to determine the hydrochloric acid, this latter titration only being made in neutral solution.

The procedure for other mixtures will follow on similar lines.

ALKALIS

Caustic Potash (*Potassium Hydroxide, KOH*). This constitutes one of the chief alkalis used in the industry. A usual variety is that known as American potash while another type is that known as Montreal potash. The origin of the term "potash" is interesting, being derived from the fact that quantities of wood are burnt in large pots in America and elsewhere for the ashes which they leave. This ash (pot-ashes) contains a large proportion of potassium carbonate which can be dissolved from it and by evaporation of the solution yields a purer type commercially known as pearl ash.

By treating this potash (potassium carbonate) with slaked (lime) $Ca(OH)_2$, the carbonate is converted either wholly or partially into caustic potash thus—

$$K_2CO_3 + Ca(OH)_2 = 2KOH + CaCO_3$$

The calcium carbonate is separated off and the liquid evaporated, the resulting product containing both carbonate and caustic in varying proportions. A number of examples of this type of potash yielded on analysis the following results—

TABLE XXX

ANALYSES OF AMERICAN POTASH

Sample	KOH	K_2CO_3	Total
1	26·3	29·7	56
2	15·8	34·5	50·3
3	41·6	26·2	67·8
4	14	34·5	48·5

These vary very considerably in their composition although a better grade of the same type of material gave an analysis of—

K_2CO_3	41·7%	K_2SO_4	4·0%
KOH	49·6%	KCl	2·0%
Na_2CO_3	1·4%		

A simple method of determining the quantities of carbonate and caustic will be given later. At present we have only need to point out that these types of potash are largely (still largely, we might say) used for the removal of grease prior to electro-deposition.

Better qualities of potassium hydroxide are made with purer materials by the electrolysis of potassium chloride.

Caustic Soda (*Sodium Hydroxide, NaOH*) finds considerable application in electro-deposition not only in the preparation of depositing solutions but also in special types of cleaners. It is made by the electrolysis of salt solution and also by causticizing sodium carbonate obtained from salt cake. The ordinary material for chemical use is marketed in sticks and flakes, but in larger quantities the massive lump form is more usual. Like caustic potash it will always contain a proportion of carbonate, this resulting from exposure to the atmosphere. Analytical examination follows that of the potash compound.

Ammonia. This is another alkali of common application. The commercial liquid is a solution of the extremely soluble gas, of which only a very small proportion enters into chemical combination with the formation of ammonium hydroxide thus—

$$NH_3 + H_2O = NH_4OH$$

this compound being altogether too unstable to obtain in anything more than a most dilute solution. The strongest solution of the gas has a specific gravity of 0·880 and hence the usual designation of 880 ammonia. The material is largely obtained as a by-product of gas manufacture being obtained by the distillation of the ammoniacal liquor with lime. The accompanying table (No. XXXI) shows the strengths and concentrations of solutions of this gas.

TABLE XXXI

Specific Gravity of Ammonia Solutions

Specific Gravity	Percentage of NH_3	Gm. NH_3 per litre
0·996	1	9·96
0·987	3	29·6
0·979	5	48·9
0·971	7	68
0·959	10	95·9
0·952	12	114
0·9414	15	141
0·925	20	185
0·911	25	228
0·898	30	269
0·880	36	317

Estimation of Alkalis

After what has been said in the section dealing with the estimation of acid strengths, the methods for alkalis can be more concisely stated. The first requirement is some standard acid of definite strength, and this is not a matter of direct preparation. It involves making an acid solution of approximate but rather greater strength than that required, standardizing this and exactly diluting it down to the required strength.

Standard Sulphuric Acid. Take 15 c.c. of the strong acid, dilute with water, transfer to a litre flask and make up to 1000 c.c. Titrate 25 c.c. of this acid with N/2 sodium carbonate with methyl orange as indicator.

Assume that 25 c.c. acid require 28 c.c. N/2 Na_2CO_3. The acid is obviously stronger than the carbonate. Further by the addition of $28 - 25 = 3$ c.c. water to each 25 c.c. of acid there will be 28 c.c. of mixture containing the acid originally in 25 c.c. of the diluted acid and therefore exactly balancing the alkali and thus being of exactly semi-normal strength. This is the usual procedure and then —

$$1 \text{c.c.N/2 acid} = 0{\cdot}020 \text{ gm. NaOH} = 0{\cdot}028 \text{ gm. KOH}$$
$$= 0{\cdot}0265 \text{ gm. } Na_2CO_3 = 0{\cdot}0345 \text{ gm. } K_2CO_3$$

Simple Alkali Determination. As a simple illustration of an alkali determination the percentage of Na_2CO_3 in washing soda may be taken. Weigh out 10 gm. of the soda, dissolve in water and make up to 250 c.c. in the appropriate measuring flask. Take out 25 c.c. into a conical flask, dilute somewhat with water, and add methyl orange. From a burette run in semi-normal acid until the yellow colour of the alkali changes to pink, indicative of the slightest acidity and therefore the completion of the neutralization. Assume that as a mean of several titrations the volume of acid used is 14·1 c.c. Then—

$$1 \text{ c.c. } N/2 \text{ acid} = 0{\cdot}0265 \text{ gm. } Na_2CO_3$$

Hence percentage of Na_2CO_3 in the original soda

$$= \frac{14{\cdot}1 \times 0{\cdot}0265 \times 250 \times 100}{25 \times 10} = 37{\cdot}4$$

Now the correct formula for washing soda is—

$$Na_2CO_3 . 10H_2O$$
$$106 + 180 = 286$$

and this formula is intended to express the fact that the substance contains $\frac{106 \times 100}{286} = 37\% Na_2CO_3$

The slightly higher figure in the estimation may readily be accounted for by loss of water by exposure.

American Potash. A somewhat similar test may be made with this material in order to determine its "causticity" or proportion of KOH. Weigh out 5 gm. of a sample, dissolve and make up to 250 c.c. Take out 50 c.c. and titrate with semi-normal acid using methyl orange as indicator. Assume the reading to be 22·5 c.c. Then—

$$1 \text{ c.c. } N/2 \text{ acid} = 0{\cdot}028 \text{ gm. KOH}$$

Hence percentage of KOH in the sample is—

$$\frac{22{\cdot}5 \times 0{\cdot}028 \times 250 \times 100}{50 \times 5} = 63$$

Now this figure assumes that the alkalinity is due entirely to KOH, and yet, during the titration, it will have been observed that CO_2 has been evolved, indicative of the presence of carbonate which is to be expected in this class of alkali. What we should like to know are the actual quantities of both of these alkalis.

Mixed Alkalis. Now there are differences in the sensitiveness of different indicators. Phenolphthalein is, for example, much more sensitive than methyl orange. This difference is illustrated by the fact that potassium (or sodium) bicarbonate is apparently acid to phenolphthalein and alkaline to methyl orange. A simple test will readily check this statement. Further, the neutralization of potassium carbonate takes place in two stages as follows—

(1) $K_2CO_3 + HCl = KHCO_3 + KCl$

this occurring without the evolution of CO_2. Then—

(2) $KHCO_3 + HCl = KCl + CO_2 + H_2O$

On the other hand, the neutralization of KOH can only take place in a single stage thus—

(3) $KOH + HCl = KCl + H_2O$

If then we titrate a mixture of caustic (KOH) and carbonate (K_2CO_3) using phenolphthalein as indicator, the disappearance of the violet colour indicates the completion of equations (3) and also (1). The addition of methyl orange still produces a yellow colour, and by continuing the titration till this changes to pink, the reaction represented by equation (2) will then be effected. Thus the first titration with phenolphthalein represents the neutralization of the caustic, while at the same time the carbonate is only at its half stage. Further, the second quantity of acid added to turn the methyl orange pink represents the second stage of the carbonate neutralization. Put in another and more usual manner, the first titration represents the caustic and half the carbonate, while the second titration figure represents the other half of the carbonate.

In an example, 50 c.c. of the American potash solution prepared as above (containing 5 gm. per 250 c.c.) gave with phenolphthalein 18·7 c.c. N/2 acid. A few drops of methyl orange then added and the titration continued resulted in the further addition of 3·8 c.c. of N/2 acid. Hence—

caustic + half the carbonate = 18·7 c.c. N/2 acid,
while half the carbonate = 3·8 c.c. N/2 acid.

Hence the KOH is represented by

$$18{\cdot}7 - 3{\cdot}8 = 14{\cdot}9 \text{ c.c. } \frac{N}{2} \text{ acid}$$

while the K_2CO_3 is represented by

$$2 \times 3{\cdot}8 = 7{\cdot}6 \text{ c.c. } \frac{N}{2} \text{ acid}$$

Now 50 c.c. of the potash solution contain 1 gm. of solid.

$$\text{Hence percentage of KOH} = 14{\cdot}9 \times 0{\cdot}028 \times 100 = 41{\cdot}7$$

$$\text{and percentage of } K_2CO_3 = 7{\cdot}6 \times 0{\cdot}0345 \times 100 = 26{\cdot}2.$$

We have thus a method of determining both the caustic and carbonate in a mixture by a single titration with two indicators, and this determination is also required in the analysis of many types of cleaning solution and also all depositing solutions in which caustic is an essential constituent, and which, in course of time, must in part be converted to carbonate by the absorption of carbonic acid gas from the air.

Alkali Cyanides. Potassium and sodium cyanides are important compounds in the electro-depositing industry, as a number of metals can only be successfully deposited from such solutions. For many years, however, there was considerable variation in the qualities of these materials which were available for this purpose. Further, each had some points of advantage over the other. Their methods of manufacture are not relevant here. Consider, however, their formulae—

$$\underset{65}{KCN} \equiv \underset{49}{NaCN}$$

These represent chemically equivalent quantities of the two pure substances, and bearing in mind the fact that potassium compounds are much more expensive than the corresponding sodium compounds, there may be some surprise at the large vogue which the potassium compound once had. With the late war there arose a dearth of potassium salts. Sodium cyanide had perforce to be used in place of the potassium compound. Subsequently in America the use of the sodium compound was still persisted in, while in this country there was a considerable reversion to the potassium salt as this became available again.

From the formulae it will be apparent that weight for weight the sodium compound does more work. There is the added advantage of greater cheapness. There must be some points in favour of the potassium salt which led to its continued use. Two advantages might be advanced. They are—

1. On dissociation, assuming the degree to be the same in

both cases, the potassium salt gives an ion of greater speed under similar electrical conditions. This is a small point.

2. All alkali cyanides are prone to decomposition in aqueous solution and by exposure. The changes are not too simple. Some of them are indicated in the following equations—

$$(a) \qquad NaCN + H_2O = NaOH + HCN$$

$$(b) \qquad 2NaOH + CO_2 = Na_2CO_3 + H_2O$$

$$(c) \qquad HCN + 2H_2O = H \cdot COOH + NH_3$$

The same type of reactions also take place with the potassium compound.

Obviously therefore these cyanide solutions soon deviate from their original composition with the accumulation of carbonates which have their advantages and also, to a much lesser extent, the formates which are also considered to be advantageous in the solution. Periodic additions of cyanides are therefore necessary in all cyanide baths leading to the increasing content of carbonates. Now there must be some limit to the usefulness of the carbonates, though the limits are by no means narrow. In the course of time, the solutions may become saturated with carbonates and this calls for their removal. Apart from this, they may crystallize out in the bath on the sides of the tank and also on the anodes, thereby considerably reducing their effective area and consequently their efficiency. Relevant to this point, the relative solubilities of the two carbonates are given in Table XXXII and from this it will be seen why the potassium salt commands great favour. Methods of removing these excesses of carbonates are given elsewhere.

In the metallurgy of gold, cyanides find an important application in dissolving out the finely divided metal which occurs so widely distributed in quartz. Solutions of cyanides of only 0·3 per cent effectively dissolve the gold according to the following equation—

$$2Au + 4\,NaCN + H_20 + 0 = 2\,AuCN \cdot NaCN + 2NaOH$$

In electro-deposition, cyanides find application for cleaning purposes and largely in the production of stable solutions of metals, the mineral salts of which are readily decomposed by contact with more active metals requiring to be plated. They also serve the purpose of providing solutions (that for the deposition of brass, for example) for the deposition of alloys the constituents of which are electro-chemically too different to allow of their co-deposition from solutions of their mineral salts.

TABLE XXXII

SOLUBILITIES OF POTASSIUM AND SODIUM CARBONATES

t° C.	100 Parts Water Dissolve Parts of	
	K_2CO_3	Na_2CO_3
0	89·4	7·1
5	104	9·5
10	109	12·6
15	110	16·5
20	112	21·4
25	113	28
30	114	38·1
40	117	46·2

Specifications for Cyanides. As has been stated, the earlier samples of these materials which were available to the electro-depositor were of indifferent composition and value. The common method of evaluating cyanides is by standard silver nitrate, which does not differentiate between the alkali cyanides (the sodium or potassium salts for example). By this method therefore it would be possible to prepare a mixture of NaCN (75·4%) and 24·6 per cent NaCl (to take an example of an indifferent impurity), so that, by the usual test the result might be expressed as 100 per cent KCN. This or its equivalent was quite the common experience, so that a mixture of NaCN with a fair amount of impurity could be passed off as almost pure KCN (judged solely by the silver nitrate test). The whole matter has now been regularized by the introduction, at the instigation of the Electro-depositors' Technical Society, of specifications issued by the British Standards Institution* which represent agreement among the chief manufacturers and users of these materials and provides assurance of composition and value to the purchaser and user.

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* B.S.I. Specification 622, 1935.

These specifications deal with two qualities of KCN, white and grey. The former, of 96–99 per cent, is to have a KCN content of at least 96 per cent with not more than 0·8 per cent of sodium (as Na). The grey variety single salt of 91–92 per cent KCN, is to have not less than 91 per cent KCN and sodium (as Na) not exceeding 0·8 per cent. The sodium salt (single NaCN) with a value of 128–130 per cent is to conform approximately to the formula NaCN with a cyanide content of not less than 97·0 per cent NaCN which is equivalent to 128·8 per cent KCN.

There are other details in the specifications and also the exact methods by which each is to be determined. Users of cyanides are advised to acquire a copy of these specifications and to see that they are adhered to in the materials purchased.

Some compositions of actual samples of cyanides in common use may be of interest, particularly as showing the other materials entering into the composition of these products.

Sodium cyanide 97—98% = 129—130% KCN

Sodium cyanide ($NaCN$)	97·5
Sodium carbonate (Na_2CO_3)	1·0
Sodium oxide (Na_2O)	1·5
	100·0

Sodium cyanide 74—76% = 98—100% KCN

Sodium cyanide ($NaCN$)	75%
Sodium carbonate (Na_2CO_3)	0 to 25%
Sodium chloride ($NaCl$)	25 to 0%

Potassium cyanide

Grey KCN		Pure white KCN	
KCN	91·5%	KCN	94%
NaCN	2·5	Na_2CO_3	0·5
K_2CO_3	2·5	K_2CO_3	3·5
Na_2O	3·5	KOH	1·5
		H_2O	0·5
	100·0		100·0

The "white" sample often therefore does not come up to specification, while the second sample of sodium cyanide represents a low grade material only used for cleaning purposes. The specific gravities of cyanide solutions do not find immediate application in electro-deposition but are given in Table XXXIII.

TABLE XXXIII

SPECIFIC GRAVITY OF POTASSIUM CYANIDE SOLUTIONS

Specific Gravity	% KCN	Gm. KCN per litre
1·213	35	425
1·181	30	354
1·149	25	287
1·119	20	224
1·089	15	163
1·061	10	106
1·048	8	84
1·036	6	62
1·025	4	41

ANALYSIS OF CYANIDES

Usually it will be necessary to know the cyanide, chloride, and carbonate content of a sample. Having in mind the requirements of modern specifications, there will be no occasion to give either in outline or detail the estimation of the relative proportions of the two compounds, those of sodium and potassium.

Principle of "Cyanide" Estimation. When potassium (or sodium) cyanide is added to silver nitrate there is an immediate ppt. of silver cyanide thus—

$$AgNO_3 + KCN = AgCN + KNO_3$$

This method of addition of the two substances does not find application in analysis. When, however, the mixture is made in the reverse direction the following reactions occur—

1. $AgNO_3 + 2KCN = AgCN . KCN + KNO_3$

2. $AgCN .KCN + AgNO_3 = 2AgCN + KNO_3$

Accordingly there is no permanent ppt. until the whole of the KCN has been absorbed in the production of the soluble double cyanide. As soon as reaction (1) is completed, the commencement of reaction (2) is indicated by the formation of a turbidity. The appearance of this turbidity is the indication of the completion of the first reaction.

By this method of addition—

$$\underset{170}{AgNO_3} \equiv \underset{130}{2KCN} \equiv \underset{98}{2NaCN}$$

Standard Silver Nitrate. A deci-normal solution is of convenient strength. It contains 17 gm. $AgNO_3$ per litre. 1 c.c. contains 0·017 gm. $AgNO_3$ 0·013 gm. KCN $\equiv$ 0·0098 gm., NaCN.

Evaluation of a Sample of KCN. Weigh out accurately 5 gm. of the sample and dissolve in water making up the volume of the solution to 250 c.c. Shake. Charge a burette with N/10 $AgNO_3$. Take 25 c.c. of the cyanide solution. Dilute to 100 c.c. (approx.) with water. Add a few drops of KI solution. [The purpose of this addition is to form more opaque and therefore more easily seen AgI at the completion of reaction (1) and thus sharpen the end point.] Warm slightly. Run in the $AgNO_3$ shaking after each addition until there is the first trace of a permanent turbidity. The titration is easy to carry out. Assume that, as an average of three titrations, the volume of $AgNO_3$ solution used is 36 c.c. Then—

Percentage KCN in sample

$$= \frac{36 \times 0{\cdot}013 \times 250 \times 100}{25 \times 5} = 93{\cdot}6$$

Sodium cyanide will be dealt with in the same manner except that there will be occasion to dissolve a proportionately smaller quantity of the sodium salt.

An Alternative Standard Solution. There is something to be said for the use of a silver nitrate solution of such strength that 1 c.c. = 0·01 gm. KCN. A simple calculation will show that this solution will contain $\frac{0{\cdot}01 \times 17}{0{\cdot}013} = 13{\cdot}08$ gm. $AgNO_3$ per litre.

If this solution had been used in the above test the volume of the weaker solution would have been $\frac{36 \times 17}{13{\cdot}08} = 46{\cdot}8$ c.c. which figure, doubled (as 25 c.c. of the cyanide solution contain 0·5 gm.) at once gives the percentage of KCN in the sample.

It should be noted that this method of estimation of either KCN or NaCN is given in its barest simplicity. The test is capable of being carried out with a good deal of precision and much more accurate methods are obviously necessary where large quantities of cyanides are being sold or bought under specification. These more accurate methods will be found in the British specification to which reference has already been made.

Comparison of Cyanides. It will be noted that, from the equivalent values of the two compounds KCN (65) and NaCN (49), any small quantity of the sodium salt in admixture with the potassium salt will tend to give a "good" figure in the estimation of KCN. Thus a mixture of 90 per cent KCN and 5 per cent NaCN would give a total result (as KCN) of—

$$90 + \frac{65}{49} \times 5 = 96{\cdot}6 \text{ per cent}$$

while in an extreme case a mixture of 75·4 per cent NaCN with 24·6 per cent of some inert compound, such for example as NaCl, would give a "KCN" value of

$$\frac{75{\cdot}4 \times 65}{49} = 100 \text{ per cent KCN}$$

Hence the restriction of the NaCN content of a substance which is supposed to be the potassium compound.

Estimation of Chlorides. These are frequently present in cyanide samples. They may be estimated as follows. Proceed with the KCN titration to completion when the following reaction will have been completed—

$$AgNO_3 + 2KCN = AgCN . KCN + KNO_3$$

The addition of a further equal volume of the silver nitrate solution will now complete the following reaction—

$$AgNO_3 + AgCN . KCN = 2AgCN + KNO_3$$

when the whole of the cyanide compound will be precipitated. A little K_2CrO_4 solution is now added and the titration carried on until there is a slight red coloration formed due to the pptn. of Ag_2CrO_4. This marks the completion of the pptn. of the chlorides in accordance with the equation—

$$KCl + AgNO_3 = AgCl + KNO_3$$

This last addition of $AgNO_3$ is a measure of the chloride present, and as 1 c.c. N/10 $AgNO_3$ = 0·00745 gm. KCl the percentage of KCl in the sample is readily calculated.

An Alternative Method involves decomposing the cyanides in a measured sample by the addition of HNO_3 and evaporating down to ensure the expulsion of all HCN. The solution could be neutralized and then titrated with $AgNO_3$ for the chloride content. A more reliable method, however, is that of the addition of an excess of N/10 $AgNO_3$ and then, using iron alum as an indicator, titrating back with N/10 ammonium thiocyanate as indicated in the estimation of silver in the plating solution in Chapter XIII (see page 258).

Estimation of Carbonates. This will be dealt with in detail in the estimation of carbonates in the silver plating solution to which reference can be made. The calculation requires only slight and obvious modification to adapt it to the estimation of carbonates in cyanide samples.

Antidotes Against Cyanide Poisoning. The excessively poisonous nature of the cyanides calls for the greatest care in their use. Constant use possibly makes the worker somewhat forgetful of their dangers. The attitude should be far from that of allowing familiarity to breed contempt. There are remarkably few cases of cyanide poisoning, having in mind the extensive use of these compounds. Precautions, however, must always be exercised and first aid remedies should always be to hand.

Every plating shop should be equipped with a list of instructions as to the treatment in case of unfortunate emergency. Those published by the Cassel Cyanide Company (I.C.I.) are conveniently framed for public display. Cyanide poisoning may occur through swallowing either the solid or liquid, or inhaling the gas. If from gas, the dangerous atmosphere must at once be left. If from solid or fluid a dose of cyanide antidote must at once be taken. This is compounded from two solutions: (1) 158 gm. of ferrous sulphate crystals dissolved in a litre of water and (2) 60 gm. anhydrous sodium carbonate dissolved in a litre of water. For a dose, mix 50 c.c. of each solution together and swallow immediately.

If the patient is unconscious, the antidote cannot be administered. He should be removed to a pure atmosphere, placed in a recumbent position (on no account walked about) and artificial respiration resorted to, keeping the patient warm with blankets and hot water bottles. A mixture of oxygen and carbon dioxide is given.

Medical aid, having at the first been summoned, can now give specialized treatment the nature of which is advised on the chart referred to. All plating shops should be provided with a chart of these urgent instructions.

CHAPTER VI

SOURCES OF CURRENT

INTRODUCTION—The lead accumulator—The dynamo—Methods of excitation—The motor generator—A.C. rectifiers—The lead-aluminium rectifier—The Westinghouse metal rectifier

Introduction. Only a brief survey of the possible sources of current can be attempted in a single chapter. Time was when it was usual to refer in detail to the principles of the usual types of voltaic cells, some of these having been used considerably in the early days of electro-plating. Now all this has changed. The dynamo, introduced as far back as 1867, opened up the way for large scale deposition, and while for many years cells were still in use by the electro-plater operating on a small scale, it might be difficult to find them in use to-day even in the smallest way in experimental work. Yet, many years ago, the Smee cell was largely used by electrotypers, while the Bunsen cell, with all its inconveniences and need of attention, was in considerable use by electro-platers. To-day the dynamo and motor generator are everywhere to be seen. In addition, there are now in use types of machines in which there is a more direct conversion of alternating current, which is the type so frequently generated at power stations and distributed for power work, to the direct form serviceable for electro-deposition.

The Lead Accumulator.—Throughout these changes in practice the lead accumulator has served a useful purpose, and is still in use where current is required over night periods when it is not convenient to run a machine.

The principle of the accumulator is simple. The two lead plates, usually set up in numbers in parallel, and known as the *positive* and *negative* plates respectively, hold in their structure lead compounds, that on the positive, when charged, being largely the brown oxide of lead (PbO_2), while the negative plate holds metallic lead in a form which renders it particularly susceptible to chemical action. At any time there is also a proportion of lead sulphate ($PbSO_4$) on both plates, but the electro-chemical differences are due to the lead dioxide and lead.

During discharge H and SO_4 ions normally migrate to the plates and the following chemical actions there take place. On the positive—

$$PbO_2 + 2H + H_2SO_4 = PbSO_4 + 2H_2O$$

On the negative—

$$Pb + SO_4 = PbSO_4$$

These equations represent the chemical changes in their simplest form. A completely adequate explanation would involve much more detail.

Sooner or later, depending upon the capacity of the cells and their rate of discharge, these active materials are largely converted to lead sulphate, though never completely. The cell is then said to be *discharged.* The reactions of the cell are reversible, and on passing a current in an opposite direction the material upon both plates, viz. lead sulphate, is reconverted to lead dioxide and lead. Thus during charge the following reactions occur—

On the positive—

$$PbSO_4 + SO_4 + 2H_2O = PbO_2 + 2H_2SO_4$$

On the negative—

$$PbSO_4 + 2H = Pb + H_2SO_4$$

There are certain obvious signs of the practical completion of the charging operation. These include high density of the acid, which is produced during charging and absorbed by the plates during discharge, and the rich brown colour of the newly formed lead dioxide. In addition, there is the high voltage required to maintain the correct charging current, and the rapid evolution of gas from both plates. Normal voltage curves for charge and discharge are shown in Fig. 23. It must be remembered that the voltages here referred to are those taken while the cell is being operated at its correct rate, either charging or discharging.

A number of points require careful attention in the use of accumulators. In the first place, when not in use, they should be kept charged. The lead sulphate due to discharge only functions satisfactorily when freshly made and porous.

Standing effects its consolidation, a condition known as *sulphating,* from which it is difficult to recharge the accumulator without special treatment.

The designed rates of charge and discharge should be strictly adhered to. Accumulators require gentle treatment in this and every other respect. The level of the liquid should be maintained by the frequent addition of distilled water, and the accumulators should be housed under conditions which admit of free ventilation when charging, and also to ensure freedom from contamination from other acid fumes which are deleterious and rapidly decrease the capacity.

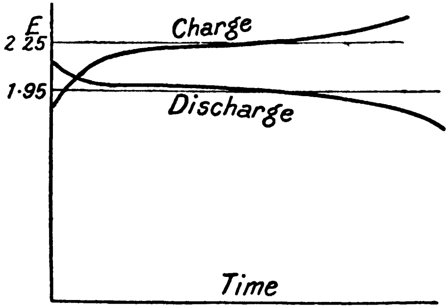

FIG. 23. ACCUMULATOR CURVES

The Dynamo. The general principle of the operation of the dynamo will be appreciated and usually understood. Suitably wound coils of wire rotate rapidly between two or more magnetic poles. If a closed circuit exists a current is set up, and this current is of the alternating type. This a.c. is very suitable for many purposes for which electrical energy is required. It is, however, not the type required for electrodeposition. In alternating current the voltage, and therefore the current, changes its direction very rapidly, usually 25 or 50 times per second. This is called the *frequency* or *periodicity.* For the purposes of electro-deposition the current is required all in the same direction, or, as it is termed, *unidirectional.* This change is effected by means of a commutator built up of a number of insulated copper segments upon which play brushes so arranged that at the moment the polarity is reversing the segment moves away from the brushes and others come into contact with them, always delivering current to the brushes in the same direction. By arranging the rotating coils in parallel and series, it is possible to vary the voltage and current, these also being influenced by the strength of the field magnets and the speed of rotation.

The dynamo comprises a number of essential parts. These include the field magnets, which are excited by current passing through coils wound upon them. These magnets terminate in poles. In earlier types there were two poles. Four is now a much more common number. It is between these poles that the magnetic field is developed. Their coils are the field windings. The current they carry is the exciting current. The armature is an iron drum or ring upon which the rotating coils are mounted. The magnetic field is concentrated through these armature coils, and rotation develops the voltage. The armature coils terminate in the commutator segments, from which the brushes pick up the current when an external circuit is provided. The position of the brushes is important, and requires careful setting and maintaining, otherwise considerable sparking occurs. To allow for this setting they are mounted on a rocker and may require some slight changes in position with variations of the load.

Methods of Excitation. There are several methods of exciting the field coils. They are of considerable importance. This excitation may be effected by means of current developed in the machine or from an external source. When an external source is used the method is that of *separate excitation* (Fig. 24). With current developed in the machine, excitation may be effected in three different ways which are illustrated in the accompanying diagrams. For example, Fig. 25 shows what is called the series system of excitation, in which the whole of the current produced in the machine passes round the field coils. Fig. 26 shows the system known as shunt winding, in which only a part of the developed current passes round the exciting coils, while Fig. 27 shows a further method of excitation (compounding) in which of the whole of the current developed in the machine, that used externally passes round the field magnets by means of a few coils, while a portion of the current passes as a shunt round the field circuit by more numerous coils. The differences in the methods of excitation are best noted by the variations of the voltage produced with variations of load on the machine. With separate excitation there is wide control of the exciting current, and it is therefore easy to maintain a constant voltage with variations of load. This is obviously very desirable, although it may sometimes not be possible to supply current from a separate source. Nowadays, where electric supply of the direct current type is common, separate excitation, with its great advantages, can be easily

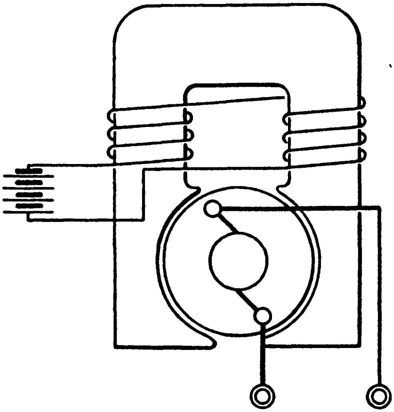
FIG. 24. SEPARATE EXCITATION

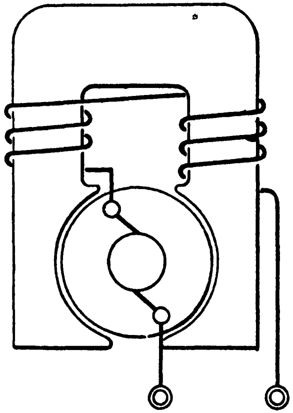
FIG. 25. SERIES WINDING

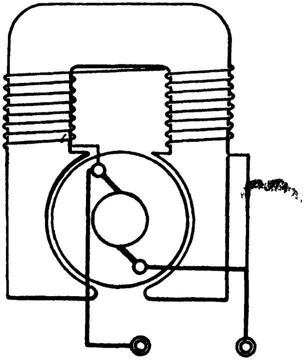
FIG. 26. SHUNT WINDING

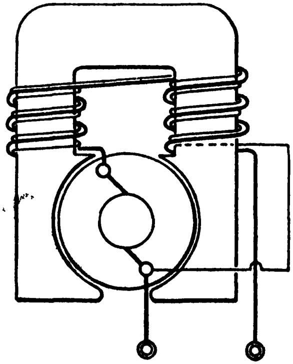
FIG. 27. COMPOUND WINDING

applied. In the case of an a.c. supply a separate d.c. exciting dynamo can be mounted on the same base.

In some earlier types of machine the whole of the developed current was sent round the field magnets. As the current which was first generated by the residual magnetism of the field magnets developed, the P.D. increased. This is shown in Fig. 28, curve *B*, where curve *A* shows what can be done with separate excitation. These curves are called ***characteristic curves***. This series winding, where the excitation coils are in series with the main circuit, served the purpose of a number of lighting dynamos where the current was not very large. The system is altogether unsuited to plating purposes. For this, shunt windings have long been used. In this system only a small proportion of the total current developed is passed round the field coils, and this portion is capable of regulation by means of a rheostat. When additional current is used in the main circuit less is available for the field windings. The P.D. therefore falls slightly. This is shown in Fig. 28, curve *C*. This falling off, however, is readily corrected by taking out some of the shunt resistance, and thus a practically constant P.D. can be maintained. This type of excitation has been much used.

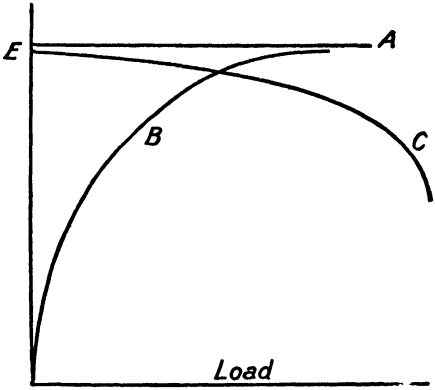

FIG. 28. CHARACTERISTIC CURVES

An advantage—and an important one, too—attaching to shunt wound machines is that if by chance there should be some reversal of the current in the main circuit—and this might happen if the machine is slowed down with a polarized vat still in circuit—the polarization current might suffice with a series winding to reverse the polarity of the field magnets with a reversal of the current when the machine is restarted. This might be disastrous; in any case it is undesirable. Shunt windings and separate excitation eliminate this possibility. Again, variations of the current in the main circuit can be made by quite slight variations of the shunt winding current, thus considerably reducing, if not in some cases completely eliminating, the need for large resistance coils in the main circuit.

It will be observed that while with series windings the P.D. rapidly increases with increase of load, it slightly falls in the case of the shunt wound machine. This would suggest a combination of the two systems of field windings, to affect a practically constant P.D. for varying loads. Such a combined system is known as compound winding, and is one largely used for electro-plating machines. In fact the combination of the two systems can be so effected that a slight increase in P.D. results from increased load, this being desirable in electro-deposition on a large scale. This system is one of over-compounding.

With the larger type of machines required to-day several points are noticeable. Usually these are not belt driven as formerly. More commonly an electric motor is directly coupled to the dynamo, the combination constituting a motor generator. The arrangement is compact and very extensively used.

Again, modern plating conditions demand very much larger currents than formerly. This has been occasioned by the much more rapid methods of deposition and the larger scale on which these operations are carried out. Large currents are particularly required for the deposition of chromium. Motor generators having outputs of 1000, 1500, and 2000 amperes, and even larger currents are now quite common, and provide a striking contrast with the much smaller belt-driven dynamos formerly used. These large currents are difficult of commutation with a single commutator. The machine is, therefore, constructed with two commutators, thus conveniently diminishing the dimensions and adding considerably to the facility for picking up the current with the brushes. Again, in these larger machines, separate excitation is almost invariably used and foolproof devices added to preclude the possibility of damage to the machine.

The Motor Generator. A machine of this type is shown in Fig. 29. Its capacity on the output side is 10 volts, 4000 amperes, and provides an example of the type in common use for chromium plating.

A number of important features of this type of machine will at once be obvious. Not only in construction, but also in erection, these machines are the product of the expert electrical engineer. Too often is it assumed that the installation of such a machine is merely one of bolting down to some sort of foundation. Rather should the responsibility be handed over to the electrical engineer with his superior knowledge and experience of this important matter. For easy and noiseless running, several conditions are essential. The two machines should be mounted on a common base, which then requires an ample foundation of concrete. This metal base is of cast iron, which, without being unduly massive, provides that rigidity which is necessary for perfect alignment of the two components. As an additional precaution for noiseless running the machines are then bolted down on to a lead sheet or felt layer.

In setting up such machines, the perfect levelling, or alignment, is of extreme importance to prevent the possibility of undesirable vibration when running, and of springing of the frame, leading to unduly warmed bearings. It will be appreciated that this is by no means an unskilled task. It is one which should be undertaken by the engineer with his expert knowledge, experience, and appreciation of its importance. With these massive machines, lubrication assumes considerable importance, and the design of the bearings should be such as to meet this need adequately. For the same reason, also, it is not desirable to tighten the machines on to the bed frame until, after some running, they have settled down in their bearings.

Another important feature of the machine is the double commutator, and, with it, the robust type of brush gear. Too much care cannot be taken of this part of the machine, otherwise losses occur through sparking, with the undue wearing of the commutator. Copper-graphite brushes are in

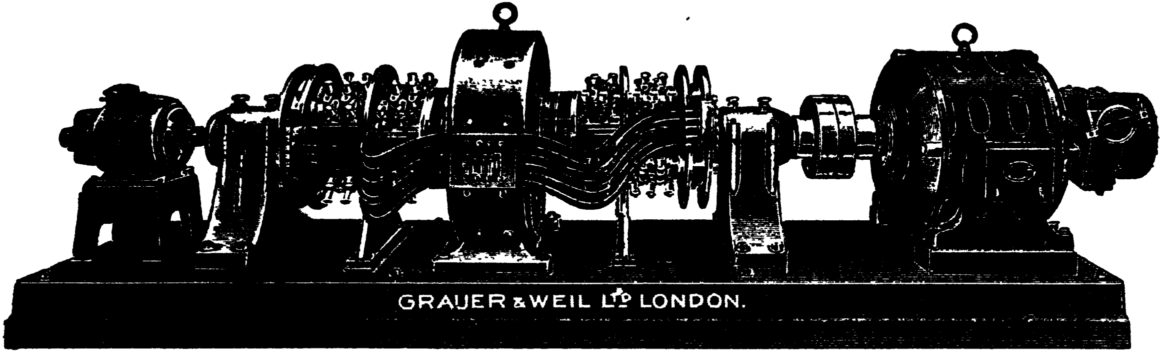

FIG. 29. MOTOR GENERATOR, 10 VOLTS, 4000 AMPERES

common use. Further, the mounting of the brush gear on the rocker necessitates careful insulation. Ample brush area must be provided to pick up the current without sparking. Further, the speed of the machine should be as low as possible. High speed machines are cheaper in construction, but are much less efficient in operation.

The cast-iron bedplate is machined to ensure accurate laying down on the concrete foundation, and also to receive the two or three machines.

Machines for electro-plating should be capable of giving an overload of at least 25 per cent for a reasonable time without overheating, and the motor should be of such capacity as will allow for this. The machines are usually coupled with a degree of flexibility to permit of slight variation of alignment.

In operation, these machines should be carefully protected from fumes and dust, and, while generally boxed in for this purpose, should nevertheless be ventilated with fresh air.

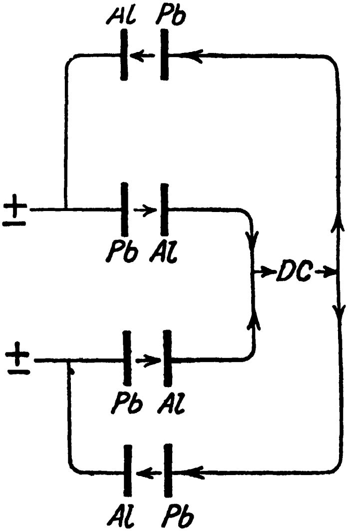

FIG. 30. ARRANGEMENT OF ELECTRODES IN LEAD ALUMINIUM RECTIFIER

A.C. Rectifiers. It will be appreciated that a.c. has no direct application in the processes of electrodeposition. This type of current, however, is more usually distributed from the power stations. Its conversion from the usual high voltage of distribution to d.c. at suitable voltage for plating is usually accomplished by the use of motor generators previously described. On the still larger electro-metallurgical scale, these two machines are combined in one and called a *rotary convertor*. Where small currents are required from a.c. the motor generator hardly meets the case. A smaller and simpler appliance is obviously required.

This small scale conversion has been effected in several ways, and the methods have been extended to plants of large capacity. They will be briefly described.

The Lead-Aluminium Rectifier. In many electrolytes, aluminium as an anode becomes coated with a layer of oxide with high insulating properties. Some applications of this in the production of protective deposits are referred to in Chapter XXIII. When certain phosphate solutions are used the oxide film has sufficient insulating power to prevent current leaving the plate as an anode but yet allowing it to receive current as a cathode. This principle can therefore be used in the rectification of a.c.

In Fig. 30 a suitable arrangement of lead and aluminium electrodes is shown admitting of the conversion of a.c. to d.c., which can then be used for plating purposes or for charging accumulators. The directions of the several currents are shown, and also the way in which they are collected together to produce unidirectional current. The films of aluminium oxide produced will withstand up to 100 volts or more, and so can be applied to such a source of a.c.

Their efficiency, however, is poor, and the arrangement is not much applied. It does, however, simply and clearly illustrate one method of rectification

The Westinghouse Metal Rectifier. In this example no solutions are used, the whole of the materials being dry. The operation is similar to that of the receiving crystal of the wireless set. In the latter there is usually the crystal and in contact with it the cat's-whisker, the crystal having the property of allowing current to pass in one direction to a very much greater extent than in the other. This effects the selection of those portions of the waves which are in one direction and with other effects brings them to such a type as can be used in the telephone.

Fundamentally the Westinghouse Rectifier consists of a plate of copper upon which is formed a layer of cuprous oxide by a special heat treatment. Rectification takes place at the junction of the pure metal and oxide layer, which is some thousandths of an inch thick. The resistance measured in the copper-copper oxide direction is of the order of 1000 times that in the opposite direction. Thus a rectifier rated at 1000 amperes will have a leakage current of about 1 ampere corresponding to a no load loss of 0·1 per cent.

An electrical connection to the copper is made by mechanically removing the oxide over a small surface, while the oxide is sprayed with zinc to distribute the current evenly over the whole of the surface. A number of rectifiers are connected together to form a bridge connection giving full wave rectification on single- and three-phase supplies.

. The chief advantage of the Westinghouse rectifier is its permanence. Its life appears to be unlimited from theoretical considerations of its operation. Practical experience is limited to about twelve years' continuous service at full load, after which no changes in characteristics have been noticed.

The efficiency is peculiar in remaining practically constant from full load down to a quarter load, the value being from 75 to 80 per cent over this range. The unity power factor of the rectifier is important, especially as in some tariff schemes the consumer is penalized for a bad power factor.

The high efficiency maintained down to a low load together with the absolute freedom from breakdown, without the necessity for any maintenance or replacements, make the Westinghouse rectifier worthy of consideration for all sizes. A further advantage lies in the fact that no special foundation is necessary. In fact, the rectifier may be mounted on a wall.

Recent improvements in the construction and design of these rectifiers have suited them to much larger outputs than hitherto, and rectifiers of this type are being used for plating where outputs of 2000 amperes or more are required.

The rectifier necessitates the use of a transformer to reduce the voltage to a figure to suit the required output.

Moreover, where it is desired to run various plating processes at the same time, each with varying voltages and currents, this may be economically achieved by the use of a single transformer with a number of tappings on the secondary winding, and dividing the rectifier into a number of sections each rated at, say, 100 amperes. If a low current at a low voltage is required, one rectifier may be energized from the lowest voltage available from the transformer, while a higher current at a higher voltage may be taken at the same time from the same transformer utilizing a higher voltage tapping and several rectifier sections joined in parallel. The scheme has the great advantage of flexibility, while the efficiency is high, no losses in resistances being introduced.

A metal rectifier can be damaged only by overheating, although it should not be kept in too close proximity to the plating baths. If the heat, produced by the losses, can be dissipated by forced cooling, the output may be increased. The air for this purpose should be free from dust, and should therefore be drawn through a fine mesh gauze screen which should be periodically inspected and cleaned.

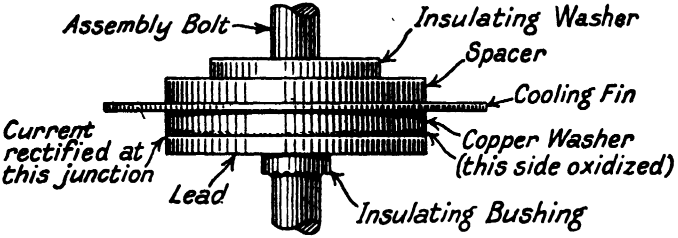

FIG. 31. WESTINGHOUSE METAL RECTIFIER, SINGLE UNIT

Fan cooling is economical on outputs of 1000 amperes and over, the saving in cost of the rectifier generally not justifying the expense of a fan for smaller outputs. A ball-bearing squirrel cage motor, driving a fan, will run continuously for 12 months without attention, while the plant may be automatically shut down if the fan stops, if desired.

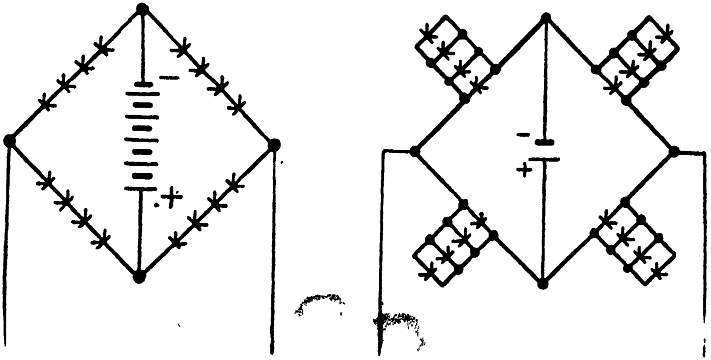

FIG. 32. METAL RECTIFIER. UNITS IN SERIES AND PARALLEL

The construction of a single unit is shown in Fig. 31, while Fig. 32 shows the arrangements of these units in series and parallel, Fig. 33 showing the form of the input and output currents.

Recent developments in the metal rectifier include the change from the copper-oxide element to that of selenium-iron. Another and even more important development is the introduction of oil immersed rectifiers which replace the fan-cooled type described in earlier editions. The "Westalite" selenium compound type rectifiers are used in all oil-cooled models instead of the copper-oxide type which has previously been used in fan-cooled sets, but the important feature from the practical point of view is the development of the use of oil as a cooling medium for electro-plating rectifiers. The main advantages are that the rectifier elements, being oil immersed, are immune from the highly corrosive atmosphere of the plating shop and rectifier tanks may be placed adjacent

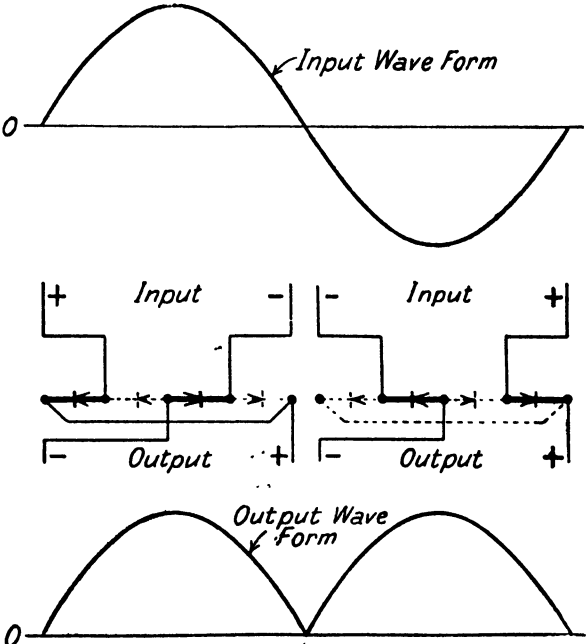

FIG. 33. METAL RECT[illegible], INPUT AND OUTPUT CURVES

to the vats which they supply, thus limiting the amount of bus-bar necessary and minimizing the voltage drop in the bars.

The efficiency of these modern rectifiers is slightly higher than that of those previously in use, and there appears to be justification in stating a general figure of 80–85 per cent which also remains practically constant down to a quarter of full load.

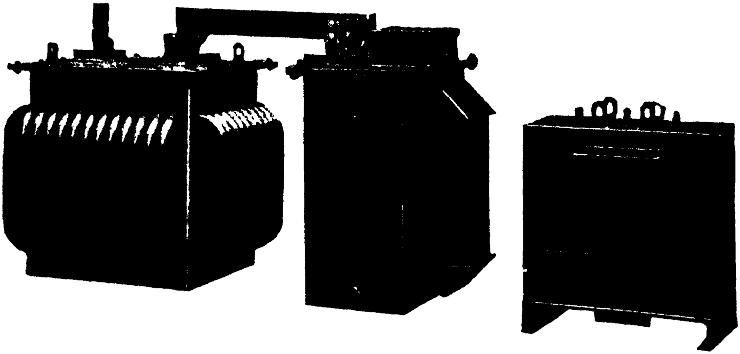

FIG. 34. WESTALITE RECTIFIER SET

Concerning the sizes of these modern sets, those for 5000 amperes output are frequently built, while the major demand is for sets of 1000 to 3000 amperes. Equipments are still built in sections and the larger single oil-filled rectifier tank will handle 2000 amperes at 8 volts. For higher currents tanks are joined in parallel.

Fig. 34 shows an equipment comprising three sections, viz. rectifier, main transformer and regulator.

CHAPTER VII

PROPERTIES OF ELECTRO-DEPOSITING SOLUTIONS

Essential requirements of electro-plating solutions—Metal content—Conducting salts—Density of solutions—The specific gravity bottle—Hydrometers—Effect of drag-out—Acidity—pH value—pH of plating solutions—Making the pH test—The capillator—The Hellige comparator—The B.D.H. Lovibond comparator—pH test papers—Addition agents—Colloids—Throwing power—Factors influencing throwing power—Quantitative expression—Throwing efficiency—British Standards Institution Scale

Essential Requirements of Plating Solutions. Obviously, depositing solutions are required to exhibit a number of properties, and while all those desirable may not be found in any single solution as many as possible should be aimed at.

1. They should contain a large proportion of metal. 2. Good conductance is necessary to reduce the energy absorbed in the process. 3. They must be stable not only to the metal to be plated but also to the air, though this qualification is not met by the cyanides which are continuously being decomposed with the evolution of hydrocyanic acid and the accumulation of carbonates in many solutions. 4. They should effect good anode solution, thereby maintaining the metal content of the solution. 5. They should produce regular and adherent deposits. 6. They should "throw" well. 7. If possible, they should combine all these properties in a solution of comparatively simple composition capable of simple analyses.

Upon working, however, a solution of quite simple original composition may easily become more complex owing to the production of new compounds as the reactions proceed. In some cases it is difficult to trace exactly these new substances, and to add them to the original solution. It is generally agreed that after some use a solution works better than an entirely new one. This is called *ageing*.

Metal Content. While at first it might be thought an all-important matter to have a high metal content, experience proves that this is by no means an infallible guide. Metal content is one thing, but metal ion concentration around the cathode is even more important. A usual copper sulphate solution containing 200 gm. of the blue salt per litre has only one-quarter of this blue salt in the ionized form. Instead, therefore, of a metal content of 50 gm. per litre, we are more concerned with the 12 gm. of copper in the ionic form. The introduction of sulphuric acid lowers this copper ion concentration and this is found to enhance the value of the solution in spite of the reduced copper ion concentration. A reduced metal ion concentration increases the power of the solution to deposit in recesses. This is later referred to under the term "throwing power." Generally, however, a higher metal concentration admits of a higher ion concentration. A value of the metal content is a better expression of the strength of a solution than the varying amounts of the different salts used to supply this metal.

Conducting Salts. Metallic compounds, however, are not usually good conductors, and the addition of other salts which, freely dissociating, contribute to conductance, is essential to many solutions. A very wide choice is available, and many sulphates and chlorides have been applied to this purpose. Other properties also determine the choice. Where possible, the mineral acids are employed in that they provide hydrogen ions which migrate rapidly and thus make an important contribution to the conducting power. Where these stronger acids are not permissible to any extent, as, for example, in the "acid" baths for nickel, iron, cobalt, and zinc, neutral salts must be employed. Of the sulphates, those of sodium, potassium, ammonium, and even magnesium have been used. Chlorides, as those of sodium and ammonium, are frequent additions. These salts offer other advantages upon which their selection must finally rest. When required, they should be added in known quantities, and kept under control.

Each constituent of a solution should have some definite purpose to serve, and it should be present and maintained in the best proportion to serve that purpose.

Other salts are frequently added. "Free cyanide" in all cyanide solutions is essential. Periodical tests should be made to ascertain whether the amount present is adequate or not. Failing a regular test, the condition of the anodes is likely to reveal deficiencies in free cyanide. If the matter can be corrected by test before this deficiency occurs, it is all to the good.

Still other salts form during the process. All cyanides, for example, are subject to decomposition by the action of the acid in the air, and also even by that of carbonic acid gas. The latter reaction is more prevalent. Carbonates result thus—

$$2NaCN + H_2O + CO_2 = Na_2CO_3 + 2HCN$$

These in controlled quantities are beneficial rather than detrimental. They contribute to conductance, and for this reason are frequently added. As they invariably form in cyanide solutions, their original addition need only be in small amounts. Sooner or later, however, as they are not automatically removed, they may accumulate to an undesirable extent. Masses of carbonate crystals may then appear on the sides and at the bottom of the tank. The greater solubility of potassium carbonate may be regarded as a point in favour of potassium cyanide in preference to the sodium compound, the carbonate of which is very much less soluble.

Density of Solutions. Rather too much emphasis has formerly been laid on the density of plating solutions. This information is of the greatest value where there is one main constituent. This happens in the chromium bath and in some nickel solutions. Then density, which may readily be determined by one or other form of hydrometer, constitutes some guide as to the metal content of the solution. Where, however, other salts are added, density determinations lose much of their former significance. The density of any one of the usual cyanide solutions, for example, provides no indication as to its metal content owing to the presence of other salts in large quantities.

In the acid copper bath it is usually reckoned that the copper compound and the acid equally contribute to density, so that the density provides an approximate estimate of the combined bluestone and acid. The determination of the latter, which to the chemist is a very simple matter, admits of the computation of the copper sulphate, and, therefore, of the copper in the solution.

Specific Gravity Bottle. The use of a small bottle of the type shown in Fig. 35 provides an accurate method of determining the density of a liquid. The bottle is first carefully dried outside and inside and weighed. The drying of the inside can best be effected by warming the bottle after rinsing with distilled cathode is even more important. A usual copper sulphate solution containing 200 gm. of the blue salt per litre has only one-quarter of this blue salt in the ionized form. Instead, therefore, of a metal content of 50 gm. per litre, we are more concerned with the 12 gm. of copper in the ionic form. The introduction of sulphuric acid lowers this copper ion concentration and this is found to enhance the value of the solution in spite of the reduced copper ion concentration. A reduced metal ion concentration increases the power of the solution to deposit in recesses. This is later referred to under the term "throwing power." Generally, however, a higher metal concentration admits of a higher ion concentration. A value of the metal content is a better expression of the strength of a solution than the varying amounts of the different salts used to supply this metal.

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Specific Gravity Bottle. The use of a small bottle of the type shown in Fig. 35 provides an accurate method of determining the density of a liquid. The bottle is first carefully dried outside and inside and weighed. The drying of the inside can best be effected by warming the bottle after rinsing with distilled water and then blowing a current of air through it, thereby displacing the water vapour formed. The dried bottle is then weighed. It is filled with distilled water and as the stopper is inserted excess water is expelled, the last traces passing through the fine orifice in the stopper. The outside is then carefully dried and the bottle again weighed. Assume for the moment that one gramme of distilled water occupies one cubic centimetre (which, strictly speaking, it only does at a temperature of 4° C.) this indicates the volume of the bottle in cubic centimetres. The water is run out and the inside of the bottle washed several times with small quantities of the liquid to be tested and finally filled with this liquid and weighed again. We thus get the weights of equal volumes of water and the liquid from which the density of the latter is found by dividing its weight by that of the water. This method is well worth resorting to on a number of occasions. Obviously when once the weight of the contained water has been determined it applies to all future tests. Further the bottle can be counterpoised by a carefully adjusted lead weight.

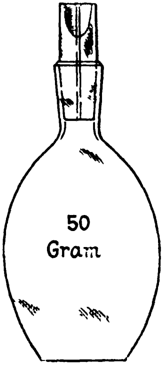

FIG. 35. SPECIFIC GRAVITY BOTTLE

FIG. 36 HYDROMETER

It is suggested that the accuracy of doubtful hydrometers can be reliably checked by the use of the bottle, this being easy of manipulation and accurate in handling.

Hydrometers. For workshop purposes the density is usually taken by means of hydrometers (Fig. 36), of which several types are in common use, differing mainly in the value of their scale readings.

The Twaddell instrument is usually put up in sets of six with the following ranges—

No.	Scale Reading	Density Range
1	0–24	1·00–1·12
2	24–48	1·12–1·24
3	48–74	1·24–1·37
4	74–102	1·37–1·51
5	102–138	1·51–1·69
6	138–170	1·69–1·85

This scheme allows of opening out what would be on a single instrument a very cramped scale.

Scale readings are converted to density by the following formula or any of its simple variations—

$$D = \frac{(N \times 5) + 1000}{1000}$$

or

$$D = 1{\cdot}000 + \frac{N}{200}$$

where N is the reading on the scale.

The Beaumè instrument has a different relation between scale reading and density. It is made for liquids both heavier and lighter than water, the relevant formulae being—

For liquids heavier than water

$$D = \frac{144}{144 - N}$$

For liquids lighter than water

$$D = \frac{144}{134 + N}$$

where, again, N represents the scale reading.

In other types the density is read directly, the graduations varying from 1000 (representing unity) upwards so that the density is one-thousandth of the observed reading.

Other instruments are also made, with various names, on which, in some cases, some of these well recognized scales are used without reference to the densities which they represent For them there should be no use in the workshop of to-day.

Details of these hydrometer scales and their relevant densities will be found in Tables XXXIV and XXXV.

TABLE XXXIV

TWADDELL HYDROMETER

Degrees	Sp. Gr.
0	1·000
2	1·010
4	1·020
6	1·030
8	1·040
10	1·050
12	1·060
14	1·070
16	1·080
18	1·090
20	1·100
25	1·125
30	1·150
35	1·175
40	1·200
50	1·250
60	1·300
70	1·350
80	1·400
90	1·450
100	1·500
120	1·600
140	1·700
160	1·800
170	1·850

TABLE XXXV

BEAUME HYDROMETER

Degrees	Sp. Gr.	
	Heavier than Water	Lighter than Water
0	1·000	
2	1·014	
4	1·029	
6	1·043	
8	1·059	
10	1·075	1·000
12	1·091	0·986
14	1·108	0·973
16	1·126	0·960
18	1·143	0·948
20	1·161	0·935
22	1·180	0·922
24	1·200	0·911
26	1·220	0·900
28	1·242	0·889
30	1·263	0·878
40	1·385	0·828
50	1·532	0·783
60	1·714	0·742
70	1·946	0·706
7[illegible]	2·087	0·689

Effect of "Drag-Out." In continuous use there must be a considerable loss of solution due to that adhering to the surface of withdrawn work. In the case of the more precious metals there is some care in utilizing a first wash water from which the precious metals may be recovered. This practice does not obtain in the case of the more common metals. The losses cannot, however, be ignored. They can be estimated with tolerable accuracy. By an analysis of a solution after a definite interval, the loss of any single constituent might be taken as some measure of this drag-out. This, however, could only apply in cases in which it was certain that the anode and cathode efficiencies balanced. With both the acid copper and nickel baths this might reasonably be assumed. For example, the following are the results of the analysis of a nickel solution after a period of six months—

Single nickel salts .	from	283 to 252	gm. per litre
Sodium chloride. .	from	6·82 to 6·1	gm. per litre

There is a marked depreciation in both of these figures. Moreover, they are of the same order. This can be seen by taking the ratio of the nickel salts to the sodium chloride. At the commencement of the period this value is 283 ÷ 6·82 = 41·6 while at the end of the period it is 252 ÷ 6·1 = 41·3. The practically constant ratio is indicative that both compounds have been lost in the same proportion. Any marked variation of this ratio might be taken to indicate variations in the anode and cathode efficiencies, but with modern anodes and methods of operating the solution, these do not frequently arise. The proportional loss of nickel salts over the period in question is therefore—

$$\frac{283 - 252}{283} = \cdot 11$$

representing an annual loss of 22 per cent. This may be regarded as somewhat excessive, but in this particular bath, a large amount of tubular work was being done without corking up the open ends. Only careful draining of individual parts would succeed in reducing the loss.

Another interesting case can be referred to. In one example of deposition, an alloy of nickel and cobalt was being deposited, the cobalt content in the alloy being of the order of 15 per cent. Nickel anodes were used, additions of cobalt sulphate being made from time to time. According to theory there should be a steady increase in the nickel content of the solution equivalent to the amount of cobalt added. This, in fact, was observed by analysis in an experimental tank which was worked intensively (that is, a large number of ampere hours in proportion to the volume of solution) and in which all the work was washed with distilled water so that the washings fell back into the tank thereby making good the loss of water occasioned by the elevated temperature at which the solution was used. On a commercial tank, however, this anticipated increase in nickel content did not mature, the nickel remaining practically constant. The anticipated increase in nickel content was exactly balanced by the drag-out loss which was thus measurable in terms of the ampere-hours put through.

The whole matter of drag-out suggests that more care might be taken in draining and rinsing work leaving the vat, not only from the point of view of economy, but also that of keeping the solution more nearly to its original and presumably required composition.

Acidity. The acidity of many plating solutions is of vital importance. In the case of the copper sulphate bath it is high and very variable. In nickel, zinc, and iron solutions the amount of acid admissible is very much smaller, and needs to be under careful control. Many defects in nickel-plating arise from too great acidity. Yet sulphuric acid is being formed at the anode if this electrode is not functioning properly. This is evidenced by the appearance of gas (oxygen) at the anode and later by gas (hydrogen) at the cathode. The whole matter deserves some consideration with a view to an intelligent appreciation of the methods of control.

When an acid is added to a solution the whole of it does not function in the reactions. Only that portion which is ionized is of any account. What we are concerned with is not so much the total amount of the acid added as that portion which has dissociated, or the proportion of hydrogen ions produced. The term *acidity* means the concentration of these ions, as these are wholly responsible for the properties which characterize the acids. *Hydrogen ion concentration* is a term of considerable importance to the electro-plater. It calls for exact definition.

Now the usual methods of adding acid and estimating it in a solution offer no guide to acidity, which refers to the concentration of the hydrogen ions without any variation of this value which would be occasioned by the addition of neutralizing substances. In the following expression

$$H_2SO_4 \rightleftarrows 2H^{\cdot} + SO_4^{--}$$

we have represented the fact that the total acid is in two forms. First, there is that which is molecular and non-conducting.

It is only indirectly of any importance in the solution. Secondly, there is the portion which, having dissociated, has produced the essential hydrogen ions. If by any means these hydrogen ions are removed, more are formed by the further dissociaton of the molecular acid. The concentration of these hydrogen ions is the critical matter.

pH Value. A scale of hydrogen ion concentration which has come into universal use is called the *pH scale.* Its basis will be seen from the following table.

TABLE XXXVI

THE pH SCALE

Litres containing one gram H ions		pH
1	10^0	0
10	10^1	1
100	10^2	2
1000	10^3	3
10000	10^4	4
100000	10^5	5
1000000	10^6	6

Thus if we have 1 gm. of hydrogen ions in 100 litres of solution, the pH value is 2. As the acidity increases the pH value decreases. This is a scale which will soon become familiar, and has been applied in many departments of scientific and industrial work.

In pure water there is a very small proportion of hydrogen ions due to a little dissociation of the water. Ordinarily these are balanced by the OH ions also present. They can, nevertheless, be detected and measured, and thus water, which is ordinarily neutral, has a pH value which is of the order of 7 or more, meaning that in pure water we have 1 gm. of hydrogen ions in more than 10,000,000 litres of the liquid. Even alkalis contain some hydrogen ions, but these are more than balanced by the preponderance of OH ions which characterize alkalis. The hydrogen ion concentration in the strongest alkali solutions is represented by a pH value of 14, meaning that we have 1 gm. of hydrogen ions in 100,000,000,000,000 litres of the alkali.

pH Values of Plating Solutions. Now it has come to be recognized in recent years that this pH value is of considerable importance in many plating solutions, and a simple method for its determination is essential. There are several methods, but the one which is best adapted to the workshop is carried out by means of a series of indicators which gradually change their colours with varying pH values. They differ from the ordinary indicators used by the chemist such as litmus, methyl orange, and phenolphthalein. These have varying degrees of sensitivity, as shown in Table XXXVII.

TABLE XXXVII

COMMON INDICATORS

Indicator	Colour		pH Range
	Acid	Alkali	
Litmus	red	blue	5–8
Methyl Orange	pink	yellow	2·9–4·0
Congo Red	blue	red	3–5
Phenolphthalein	colourless	violet	8·3–10

Now a number of these indicators are chemical compounds of the type of very weak acids which may be denoted by the simple but general formula HX where X is the acidic radical. In water they ionize thus—

$$HX \rightleftarrows H^{\cdot} + X^{-}$$

In the case of methyl orange, HX is a pink compound. Hydrogen ions are colourless while the acidic radical X is yellow. In water the solution is orange, intermediate between the pink compound and the yellow X radical. The addition of alkali removes the hydrogen ions with the accumulation of X radicals, while the addition of acid, or what amounts to the same, hydrogen ions, suppresses the dissociation with the elimination of the yellow X radical and the production of the pink compound. Other indicators including litmus and phenolphthalein behave in a similar manner.

It will be seen that litmus is far more sensitive than methyl orange, while phenolphthalein is also very sensitive. Usually it served if the nickel bath was sufficiently acid to affect litmus but not methyl orange or congo red. This meant a pH value of the solution between 4 and 6. More exact determinations are now agreed to be necessary. For this purpose there are some indicators which change their colours appreciably with small changes of pH. Some of these are given in the following table—

TABLE XXXVIII

pH INDICATORS

Indicator	Colour Change	pH Range
Thymol blue	Red to yellow	1·2–2·8
Brom-phenol blue	Yellow to blue	3·0–4·6
Methyl red	Red to yellow	4·4–6·0
Brom-cresol purple	Yellow to purple	5·3–6·8
Brom-thymol blue	Yellow to blue	6·0–7·6

It will be seen that these indicators cover a very wide range of acidity, though each has a somewhat limited range.

There are, however, a few indicators which give decided colour changes over practically the whole of this scale. These are commonly called *universal indicators*. By their use it is possible to determine at once the approximate pH value, and then, by the application of one or other of those mentioned above, to obtain its more exact value.

These indicators are of great value in the electro-plating room. Ordinarily for nickel-plating the pH value should be from 5·2 to 5·8. The figure varies somewhat for the different types of plating. The indicator most commonly used, therefore, is brom-cresol purple.

Making the pH Test. The preparation of the standard colours for this testing is a task which must be considered outside the range of the electro-plater. He will, therefore, usually purchase his testing set. The standard colours are set up in very convenient forms, to four of which brief reference will be made.

1. **The Capillator** (Fig. 37). The set includes one or more of these series of colours with a supply of capillary tubes, which, fitted with small rubber bulbs, serve as pipettes. Standard indicators are also included in the set as required. By means of these pipettes equal volumes of the solution and

indicator are mixed and the mixture drawn back into the pipette and compared with the series of standards. There is little difficulty in effecting a comparison, and the pH value is thus readily determined. While, at first, the idea of pH testing seemed remote from workshop practice, the operation has been reduced to one of extreme simplicity, and is regularly practised in many workshops. A little oral instruction will prove of immense value rather than a written detailed description.

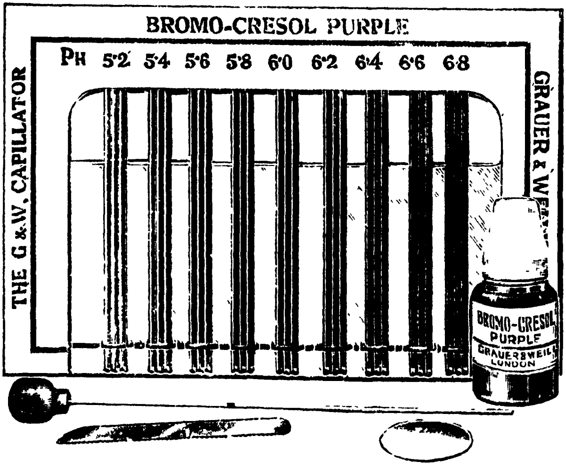

FIG. 37. THE CAPILLATOR

2. **The Hellige Comparator.** The permanence of the standard colours in the solution form may be open to doubt. Their substitution by permanent colours is at least desirable. This is realized in the Hellige comparator. In a convenient form adapted to the plating shop this set, which is shown in Fig. 38, comprises a disc, containing the graded standard coloured glasses, which is movable in a box so that the colours may be brought side by side with a sample of the plating solution, to which a definite volume of standard colour solution has been added. From a comparison of colours by transmitted light the pH value is readily read off.

A special disc is required for nickel solutions in which compensation is made for the green colour of the nickel solution. A suitable range of pH values in a disc for nickel solutions is from 5·2 to 6·8 with brom-cresol purple or from 4·4 to 6·0 with methyl red.

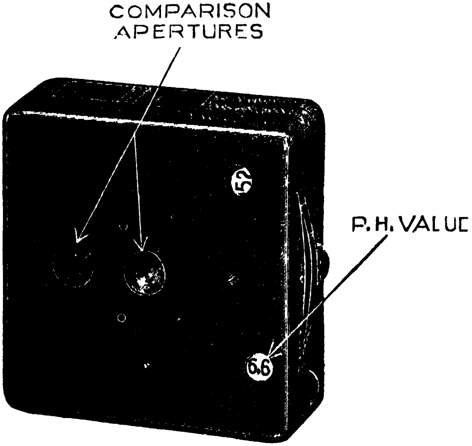

FIG. 38. HELLIGE COMPARATOR

Again it may be said that a little practice following the instructions supplied with the set is of much more value than a lengthy written description.

The same principle of pH determination is applied in many other departments of industrial analysis.

3. **The B.D.H. Lovibond Comparator.** The usual type of Lovibond comparator has been modified by the B.D.H. to adapt it to the more accurate determination of the pH of strong nickel solutions (Fig. 39). For this purpose two colour discs are used, one for solutions containing 120 gm. of crystalline nickel sulphate per litre and the other for solutions containing 200 to 250 gm. per litre. These discs are adapted to the use of the usual indicator, viz. bromo-cresol purple. While this correction gives a very reliable figure it is nevertheless pointed out that all colour indicator figures for pH differ somewhat from those obtained by the electrometric method.

This latter method ranks as the most accurate, but involves the use of apparatus which must be regarded as outside the range of workshop practice. Moreover, the corrections which need to be made are not so simple that they can be expressed in any single figure. They have therefore been determined on a number of solutions typical of those used in the practice of nickel-plating, and the determined corrections are given in the following table (XXXIX) these corrections constituting deductions to be made from the apparent pH value as determined by the colour comparison method.

FIG. 39. B.D.H. LOVIBOND COMPARATOR

4. **pH Test Papers.** Recently pH test papers have been introduced giving a pH reading by the mere immersion of the test paper into the solution. These papers, in the form of strips, carry a number of narrow bands the centre one of which comprises the test indicator material (A) on either side of which

are coloured stripes corresponding to the changes of colour which are developed with solutions of slightly varying pH. In making the test the paper is immersed in the nickel solution and the pH is obtained by a comparison of the colour produced by the indicator strip with the standard colours on either side.

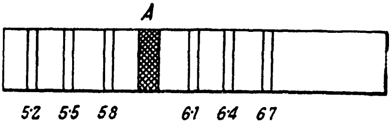

FIG. 40. pH TEST PAPER

The paper is obviously limited to a somewhat narrow range of pH, but this may easily cover the usual range for the ordinary compositions of the nickel bath. The diagram (Fig. 40) is sufficient to indicate the type of test paper.

TABLE XXXIX

TABLE SHOWING CONCENTRATION IN GRAMS PER LITRE OF VARIOUS SOLUTIONS AND THE FIGURE TO BE DEDUCTED FROM THE APPARENT pH VALUE TO ALLOW FOR SALT ERROR

Nickel sulphate crystallized .	240	240	240	210	120
Nickel chloride crystallized .	—	30	—	—	—
Boric acid	30	30	30	30	—
Potassium chloride . . .	19	—	—	—	8
Potassium sulphate . . .	—	—	22	—	—
Ammonium sulphate . .	—	—	—	—	22
Correction in pH divisions .	0·5	0·55	0·55	0·5	0·2

Addition Agents. It is well-known that even trifling quantities of certain substances added to a depositing solution markedly influence the physical nature and the mechanical properties of the resulting deposit. Sometimes these changes are detrimental and the substance requires removal. With other substances the addition effects a vast improvement in the character of the deposit. Such substances are, therefore, desirable additions, and the best quantities require determination and maintenance. Carbon disulphide in the silver solution giving a bright deposit, sugars in the zinc solution, and peptone in lead perchlorate are illustrations of this phenomenon. Many others will be referred to in the subsequent chapters dealing with the deposition of the several metals. Sometimes these results are so profoundly beneficial that their addition proves the salvation of the process. In any case, they have attained very wide use in the modern processes of electrodeposition.

Addition agents are, perhaps, well defined as "substances which, while not necessary ingredients, are intentionally added to metal depositing solutions in small quantities to produce a beneficial change in the character of the deposit."

FEATURES OF ADDITION AGENTS. A number of special features mark the use of these materials. In the first place it is often surprising how small an amount will effect the desired change. Moreover, there is quite a small range of concentration of the material. With an excess the result may be far worse than that with no addition at all. Control of the quantity is all-important.

Further, there appears to be some consumption of the addition agent, this being absorbed to a limited extent in the deposit, and therefore requiring further addition to the solution. Control is essential. Testing the amount present by chemical analysis is often far too difficult a proposition to be of practical value. Control must, therefore, be effected by a careful study of the character of the deposit. It may in some cases be possible to ascertain the actual consumption of the material and make additions in accordance with it, but in no case should these additions be made without a record being kept. The information thus obtained is of immense value in tracking down the usefulness of the substance, and the data thus available contribute to the further study of what can at first only be regarded as a mysterious subject.

Mystery certainly attaches to the fact that no single addition agent is equally applicable to two solutions. Each solution requires its specific "drug," if this term can be allowed. Thus it has been shown by Mathers & Guest* that while glycerine is useful in the acid zinc solution—and then only at low current densities—it serves no useful purpose in copper or nickel solutions.

There seems to be no fundamental principle underlying the

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* *Trans. Amer. Electrochem. Soc.*, 1941.

use of these materials. It may, however, be that, when we know more about the manner in which they act, we may be able to anticipate the possible results of certain additions, and wait for the experiment only to confirm the anticipation. Up to recently, however, the main success has been achieved simply by repeated trials of numerous substances.

It has sometimes happened that the results obtained have been due not particularly to the substance added, but to a small trace of impurity in it. Such an observation then led to the examination of the impurities, and so tracking down the actual material responsible for the change. Even the change of wood lining in a vat has produced a wonderful change in the character of the deposit obtained from the contained solution, the result disappearing as the material worked out of the wood and into the deposit. A watchful eye on all such phenomena is of immense value.

Colloids. Addition agents are usually colloidal, and this term requires some explanation, being of frequent use. Colloids are not any particular kind of substances. They may perhaps be well defined as "Ultramicroscopic particles between the dimensional range of solutes and suspensions which, carrying electrical charges, are amenable to migration (to electrodes) under the influence of an applied P.D." Suspensions are substances reduced to a fine state of division, which, if they are insoluble, enable them to remain suspended for a long time in water or other liquid, but which are large enough to be separated by filtration. They have no special electrical properties, and are usually big enough to be seen with the ordinary microscope. Very, very much smaller than these particles, are the molecules which, with soluble substances, so intimately mix with the solvent as to constitute a molecularly homogeneous mixture. The molecules are too small to be seen individually with the most powerful microscope, and are not electrically charged. Now the suspensions are roughly about 100 times as large as the molecules, and between the two dimensions we can easily imagine that it should be possible to get at least some material too fine to be filtered out and too coarse to be regarded as molecules. Materials in this range of dimensions are said to be colloidal. The colloid particles are, however, electrified, and mainly owe their unique properties to the electrical charges they carry. Some migrate to the anode and others to the cathode. One or two features of this colloid motion are of interest in this connection.

Many of the metals can be produced in the colloidal form. For example, it is possible to get such metals as platinum, gold, and silver, metals which are ordinarily regarded as quite insoluble in water, into such intimate contact with water as to appear to be soluble, and to impart a characteristic colour to the water. Curiously enough, these colloidal metals carry a negative charge, and therefore migrate to the anode. Other colloids, and gelatine is one of them, change their charge with change of concentration of the acid in a solution.

Now, for the colloids to influence deposits they must, in the first place, migrate to the cathode, and they are usually traceable in the deposit. Several explanations of their beneficial influence have been offered. By absorption in the deposit they may cause the metal to collect as very small crystals, and this would conduce to smooth deposits. This is quite likely. Alternatively, the following view has been advanced. A cathode may have a number of small points at which some irregularity has occurred. This may have been due to some irregularity on the surface when put into the solution. It may have been occasioned by the collection of dirt from the solution, the metal growing over the dirt particle giving a roughness which ordinarily becomes accentuated. These rough points then pick up more than their share of the current because they are somewhat nearer the anode. They grow rapidly. This is common experience. This excessive current brings the particles of the colloid, when such is present, to these conspicuous points, and as they are by no means completely absorbed they constitute a layer of non-conducting material round the points at which they have become largely collected. It is well-known that such colloids markedly increase the resistance of the bath forming insulating layers of high resistance materials on the electrodes. The congestion of colloids at the rough points diverts the current from them for a time, until the general level of the metal builds up to them, thus producing a smoother deposit.

Neither of these explanations may wholly account for the observed facts. They do, however, provide a simple explanation and this is more satisfactory than no explanation at all. A wider appreciation of the properties of these colloids might profitably be sought and provide a more complete explanation of the smoothness which they occasion in electro-deposits.

Many examples of these addition agents will come to notice in dealing with the separate solutions for the deposition of metals.

Throwing Power. Throwing power in an electro-depositing solution may be defined as the ability of the solution to produce even deposits on irregular surfaces. It is certainly one of the most important properties.

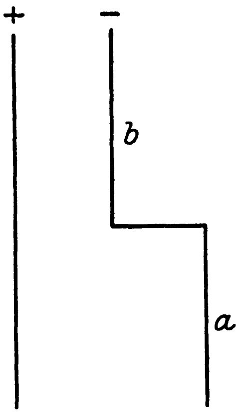

FIG. 41. THROWING POWER

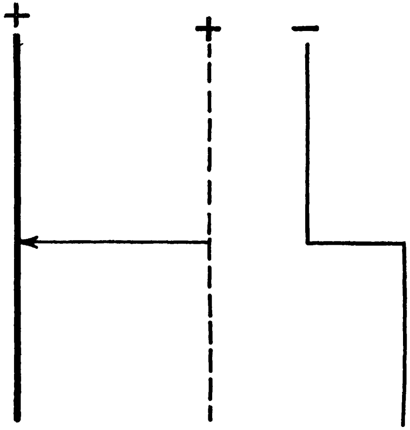

FIG. 42. THROWING POWER

Consider the conditions illustrated in Fig. 41. Assume that the whole of the resistance of the bath is that of the solution. This being so, and there being a constant P.D. between the electrodes, the portion of the cathode marked (*a*) being twice the distance from the anode of another portion marked (*b*) will receive, per unit area, only one-half of the current, and therefore one-half of the deposit of that produced at (*b*). This in general is not the result required. A more uniform deposit would, in most cases, be considered more desirable.

By increasing the distance between the anode and work the relative distances between of (*a*) and (*b*) from the anode are more nearly alike. (See Fig. 42.) This should mean a more uniform current, and, therefore, more even deposit over the whole surface. This is known and commonly practised, although increasing the resistance of the bath, and, therefore, the P.D. necessary to maintain the required current density.

While the subject will not be treated in a full, quantitative manner, at least some weighings of deposits can easily be made to explore the problem in a simple manner. In Fig. 43 a single anode, *A*, supplies the metal for three cathodes of equal area and arranged as shown. The cathodes are in parallel, and therefore represent different parts of the same piece of work. After a current has been passing for some time these cathodes are weighed separately. These increases are recorded in Table XL as percentages of the whole deposit.

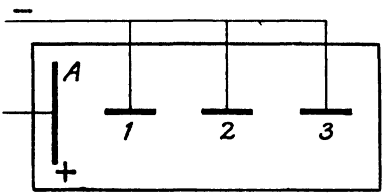

FIG. 43. THROWING POWER
(Arrangement of electrodes for simple test)

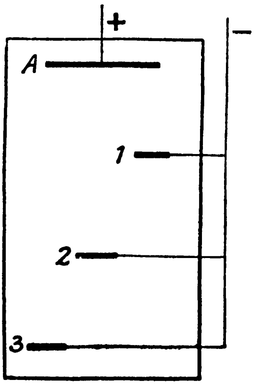

FIG. 44. THROWING POWER
(An alternative arrangement of electrodes)

TABLE XL

Throwing Power

Solution	Percentage Deposit on Cathodes		
	1	2	3
Acid copper . . .	65·7 66	19·5 21	14·8 13
Cyanide copper . .	37	31·5	31·5
Zinc sulphate . .	70 74	17·1 18·5	12·9 7·5
Zinc cyanide . .	43·1	32·8	24·1
Alkaline zinc cyanide .	38·3 40·4	31·6 33·7	30·1 25·9

An alternative arrangement of the cathodes is shown in Fig. 44. A similar experiment gave the similar percentages recorded in Table XLI.

TABLE XLI

Throwing Power

Solution	Percentage Deposit on Cathodes		
	1	2	3
Acid copper . .	58·3	30	11·7
Zinc sulphate . .	62·5	34·7	2·8
Alkaline zinc cyanide .	43·4	31·9	24·7

These figures were obtained in actual experiments. The two sets are of the same type. From them we at once learn that with copper and zinc sulphate solutions, both used in practical deposition, there is little tendency to "throw." In the cyanide solutions, however, the deposits on the three cathodes are much more nearly alike. The cyanide solutions are said to throw well, the deposits from them being more regular in weight, and, therefore, in thickness on all parts, whether near to, or distant from the anode. Moreover, the figures for zinc cyanide are improved by the addition of alkali. We could at once draw the conclusion that, while zinc sulphate may be satisfactory for plain work like galvanizing sheets, for the deposition of zinc on irregular parts, especially with depressions which must be satisfactorily plated, the cyanide solution is preferable. Another method of roughly testing this throwing power is that of plating short tubes placed endwise between the anodes. By sawing the specimens open, the degree of penetration can be noted.

Factors Influencing Throwing Power. There are three factors which, taken together, determine the throwing power of a solution. The first is the inter-electrode distance. This has already been referred to. Secondly, there are the current efficiencies of the different current densities on the several parts of the irregular surface. A higher current density may mean either a smaller or even a larger current efficiency, and this affects the weight of metal deposited. Thirdly, and possibly the most important of all, is what the electro-chemist calls *cathode potential.* By this is meant, in simple language, the difficulty of extracting the metal from the electrolyte at the cathode. It will be appreciated that it is more difficult to extract copper from the cyanide solution than from the acid solution. The simple immersion of iron is sufficient to prove this. This may be regarded as a type of chemical resistance, and would at once account for the better throwing power of the cyanide solution over that of the sulphate. Moreover, it is harder to extract zinc from a solution containing alkali than from one without alkali. Usually in the comparison of sulphate and cyanide solutions, this chemical resistance outweighs solution or ohmic resistance, and the throwing power is correspondingly good. Further, the addition of acid to a neutral copper sulphate solution increases the throwing power because it lowers the concentration of the copper ions, and therefore adds to the difficulty of extracting copper from the solution.

Quantitative Expression. It has for some time been deemed advisable to express throwing power quantitatively. As a first step in this direction, Blum and Haring* devised a throwing power box, rectangular in section, 10 cm. × 10 cm. and 60 cm. long internally. Two plates at opposite ends constituted the halves of the cathode, a gauze anode being placed

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* *Trans. Amer. Electrochem Soc.*, 1923, 44, 313.

intermediately so that one half-cathode was five times as far away from the anode as the other. These two half-cathodes represent differently situated parts of the same piece of work. The arrangement is shown in Fig. 45. Experiments were conducted so that the deposits on the half-cathodes could be weighed and related. The ratio of the cathode distances from the anode was called the *primary current distribution ratio* (P.C.D.R.)—in this case 5. The ratio of the weights on the near to that on the distant half-cathode was then called the *metal distribution ratio* (M.D.R.). The difference of potential between the anode and the two half-cathodes is of course the same, and if this were wholly absorbed in overcoming the ohmic resistance of the solution, then the M.D.R. would be practically the same as the P.C.D.R. Any deviation of the M.D.R. from the P.C.D.R. indicated throwing power either positive or negative. Thus with a M.D.R. of 4, throwing power was expressed as

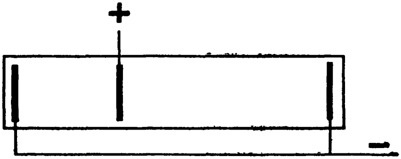

FIG. 45. DISPOSITION OF ELECTRODES IN THROWING POWER BOX

$$\frac{5-4}{5} \times 100 = 20 \text{ per cent}$$

According to this expression, throwing power is quantitatively defined as the deviation (in per cent) of the metal distribution ratio from the primary current distribution ratio. A number of results will be given later. According to this scheme, however, ideal throwing power, that is when the metal distribution ratio is unity, is only 80 per cent. Negative throwing powers are those in which the metal distribution ratio exceeds that of the primary current distribution ratio. Sometimes these negative values are of a high order running into hundreds or even thousands, figures not easily comprehensible. The scheme cannot be regarded as free from objection.

Throwing Efficiency. To bring the figures within more reasonable dimensions, Heatley* suggested putting the throwing power as a percentage of the maximum possible with the distance ratio adopted. In the above case, for example, a throwing power of 20 per cent represents 25 per cent of the maximum of 80 per cent possible. This new figure was termed *throwing efficiency,* which was then defined as "the amount of the actual improvement of metal distribution ratio over the primary current distribution ratio in comparison with the ideal improvement based on perfectly uniform deposition over all parts of the cathode." On this basis ideal deposition becomes 100 per cent, but there still remains the difficulty that negative values are of the incomprehensible type. This is illustrated in the tables XLII to XLIV which follow.

British Standards Institution Scale. Later, the matter was exhaustively explored by a committee set up by the British Standards Institution.† It was agreed that several conditions must be met in any reasonable throwing power expression. These include—

1. The adoption of the terms *linear ratio* and *metal ratio* in place of the previous terms primary current distribution ratio and metal distribution ratio, respectively.
2. The maximum (ideal) throwing power of 100 per cent.
3. A throwing power of zero when the metal ratio is equal to the linear ratio.
4. The absence of deposit on the distant cathode should be expressed as – 100 per cent, thus eliminating larger values of the incomprehensible hundreds and thousands.
5. Intermediate values should be evenly distributed between these extreme values.
6. The elimination as far as possible of the influence of the linear ratio, thus leaving throwing power as a property of the solution.
7. The expression of the throwing power to the nearest whole number as meeting all the requirements of practical needs, especially in view of the difficulty of reproducing values in successive experiments with great accuracy.

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* *Trans. Amer. Electrochem Soc.*, 1923, 44, 283.

† *J. Electrodepos. Tech. Soc.*, 1934, ix, 144.

TABLE XLII

Comparison of Throwing Power Scales

Linear Ratio 5: 1

Metal Ratio	Throwing Power		
	Old Scale	Throwing Efficiency	New Scale
1	80	100	100
1·5	70	87·5	77·7
2·0	60	75	60
2·5	50	62·5	45·5
3·0	40	50	33·3
3·5	30	37·5	23
4·0	20	25	12·5
4·5	10	12·5	6·6
5·0	0	0	0
6·0	- 20	- 25	- 11·1
8·0	- 60	- 75	- 27·3
10	- 100	- 125	- 38·5
20	- 300	- 375	- 65·2
100	- 1900	- 2375	- 92
∞ (no deposit)			- 100

TABLE XLIII

Throwing Power of a Cadmium Solution

Linear Ratio	Metal Ratio	Throwing Power		
		Old Scale	Throwing Efficiency	New Scale
2: 1	1·845	8·7	17·5	8·4
3: 1	2·6	13·3	20	11·0
4: 1	3·33	16·7	22·3	12·5
7: 1	5·42	22·5	26·4	15·2
10: 1	7·455	25·5	28·3	16·4

The following recommendation was therefore made to meet these requirements—

"The standard method recommended for determining the value of the throwing power is by the use of a rectangular trough constructed of, or lined with, insulating material, of

10 cm. internal width, filled with the solution to a depth of 10 cm. and having two half-cathodes 60 cm. apart, electrically connected together so as to be at the same potential, and an intermediately disposed and parallel gauze or perforated anode, the exposed area of the electrodes being equal to the cross-sectional area of the solution. The temperature must be maintained constant and uniform in all parts of the cell during the experiment. Then

TABLE XLIV

THROWING POWER OF AN ALKALINE ZINC SOLUTION

L.R.	M.R.	Throwing Power		
		Old Scale	Throwing Efficiency	New Scale
2 : 1	1·75	12·5	25	14·2
3 : 1	2·38	14	21	11·7
4 : 1	3·33	16·7	22·3	12·4
6 : 1	4·80	20	24	13·6
9 : 1	6·98	22·4	25·2	14·4

$$\text{Throwing power} = \frac{L - M\,(100)}{L + M - 2}$$

where

L (Linear ratio) is the ratio of the distances from the anode of the remote and the near half-cathodes respectively, and

M (Metal ratio) is the ratio of the weights of the metal deposited on the near and remote half-cathodes respectively.

Temperature, current density, and linear ratio should be stated when expressing the results."

A comparison of the three systems is made in Table XLII over a wide range of metal ratio with a linear ratio of 5 : 1, while Tables XLIII and XLIV give a number of results obtained with different solutions and expressed by the three methods to which reference has been made. The advantages of the system proposed by the British Standards Institution will, we think, be apparent.

Further, Table XLV gives the approximate values of the

TABLE XLV

THROWING POWER OF VARIOUS SOLUTIONS

Deposited Metal	Solution	Temp. °C.	CD amp./ft² average	Other Conditions	L	M	Throwing Power			Source of Measurement
							Old Scale per cent	Throwing efficiency per cent	New Scale	
Nickel	Nickel sulphate 140	21	6	pH 5 7	5	4·18	16	20	11	Haring
	Boric acid 15	21	13	pH 5·7	5	5·00	0	0	0	,,
	NH_4Cl 13	21	6	Air agitation	5	10 21	- 104	- 130	- 39	,,
	gm./litre	21	6	H_2O_2 added	5	22 1	- 342	- 428	- 48	,,
	Do.	25	6	pH 5·6	4·19	4·18	0	0	0	Flowers and Warner
		25	32	pH 5·6	4 19	4·59	- 9	- 12	- 6	
		25	6	pH 1·9	4 19	17·45	- 316	- 415	- 67	
		25	32	pH 1 9	4 19	5 99	- 43	- 56	- 22	
Copper	$CuSO_4$	Room	26	—	5	4 53	9	12	6	Haring and Blum
	H_2SO_4	Room	26	Dextrose added	5	4·72	6	7	4	
Copper	cyanide	21	6	—	5	3·20	36	45	29	Haring and Blum
		45	6	—	5	2·75	45	56	39	

throwing power on several scales for a number of practical plating solutions and these figures are, we think, immediately intelligible and indicate the practical value of throwing powers of the solutions referred to. At the same time it must be recognized that any one metal, like nickel or chromium, is not deposited with the same facility on cathodes of different metals. A throwing power experiment may thus give a different value with a cathode of copper from one on which the metal under investigation has already been deposited. The term *covering power* might perhaps be appropriately applied to this initial stage of deposition. The problem is one which merits investigation.

CHAPTER VIII

ELECTRO-PLATING PLANT

SELECTION of workshop—Erection of plating tanks—Capacity of tanks—Applications of rubber in electro-plating plant—Generators—Arrangement of accumulators—Arrangements of vats—Conductors—Connections—Rheostats—Instruments—Filtration of solutions—Heating of solutions—Combined agitation and filtration—Handling small parts—Plating barrels—Automatic plating

THE installation of electro-plating equipment and the lay-out of the plating and polishing shops are matters requiring careful thought if work is to be carried out efficiently, expeditiously, and with the minimum of discomfort to the workers. It will, however, only be possible here to touch upon some of the chief points.

Selection of Workshop. When the plater has the choice of several shops, determining factors in reaching a decision are height, light, ventilation, drainage, and the disposition of electric power, gas, and water supplies.

Good lighting, preferably natural, is essential for inspection of work to ensure cleanliness, and for the detection of faulty plating or badly polished work.

In view of the unpleasant atmosphere of both plating and polishing shops, the importance of ventilation can hardly be over-emphasized. This is especially the case when dipping and chromium plating are to be carried out, in addition to the use of a number of warm cyanide solutions.

The draining off of liquids spilt in the plating shop is equally important, and no shop is complete without a gully or runaway for water, disposed centrally in the shop. A slight slope from either side enables such liquids to be readily washed away, the gulley comprising a half channel covered with a grating. A fall of one inch in ten feet is usual.

If the plating shop floor cannot be surfaced with some acid-resisting material such as asphalt, a smooth surface of Portland cement should be applied. This, or an asphalt surfacing, should be continued up the walls for some distance. Such a floor should then be covered with duckboards or wood gratings constructed in sections to permit of their being easily taken up to recover lost work.

Both the polishing and plating shops should be as near as possible to the department producing the articles to be plated. They should, moreover, be near to one another, the enamelling and lacquering plant being of easy access in order to make for unified control.

Erection of Plating Tanks. The preparation of a preliminary plan is advantageous to prevent haphazard lay-out. All tanks for similar operations should be grouped together, thus enabling pickling and swilling to be carried out so that the work has only to be transported short distances, prior to entering the plating tanks.

As cleaning is the most important part of plating, a good light is necessary to enable the work to be inspected. Every effort should be made to avoid congestion in the plating shop, due to operators engaged in different operations having continually to pass one another, and the vats should therefore be preferably arranged to promote a continual flow of work from cleaning—swill tanks—pickling—swilling—to plating tanks, rinses, etc.

These several considerations will also have reference to the position of drains, windows, supply of gas, electricity, and other services. Tanks requiring spray exhaust equipment may with advantage be grouped together, enabling one main exhaust duct to be erected, this being so situated as to have easy access to a roof or window for exhaust purposes. Tanks requiring heavy current, should be placed near to generators, to avoid undue cost of installation of heavy bus-bars.

Plating tanks should be mounted on wooden joists or brick piers to give access of air beneath. This prevents rotting of the bottom of the tanks, and is an aid to cleanliness as the whole of the shop floor can be rinsed down from time to time.

As tanks will be of many different depths, they should be surrounded by platforms at a reasonable working distance from the top of the tanks, say 3 ft. or 3 ft. 6 in., thought being had towards the ease of the workers reaching across wide tanks. Alternatively, deep tanks can be sunk into the ground with a lining of impervious material.

The usual types of vats are well known to the plater, but it may be desirable to point out that great savings can be effected by the choice of the best types for each particular purpose. In the case of lead-lined wood tanks, a lead of 4 lb. per sq. ft. may suffice for the nickel and similar baths, while a sulphate copper bath would better be constructed with 6–8 lb. lead, while for tanks holding comparatively strong acids 8–10 lb. lead would be still more serviceable.

Again, where iron tanks are in use, ⅛-in. plate will suffice for most purposes, but for the chromium solution, or for very large cyanide baths, it is advisable to employ tanks made from ¼ in. plate.

If such tanks are to be heated, it is advantageous to fit the burners with a small inverted Vee-shaped baffle plate, in order to prevent the flame from impinging on to the bottom of the tank. When mounted, these baffle plates will be within about ½ in. of the bottom of the tank. This method has advantages over that of fixing the baffle plate direct to the bottom of the tank, as owing to expansion and contraction, this method tends to promote a breakdown at this point.

For chrome tanks, it is advantageous to install the chrome-plating tank in an outer tank filled with water, thereby providing a jacket for same. The heat supplied by this method, is very uniform, and moreover, the necessity of putting heating coils into the corrosive chromium solution is thereby avoided.

The ordinary household or Potterton Boiler can be usefully employed for supplying the heat to the water in the outer jacket, and this again can be controlled by a thermostat, thereby effecting considerable saving in consumption of gas.

Again, for lead-lined wooden tanks 1½-in. to 3-in. timber is used bolted together with pins and plates. Subsequently the lead lining is further lined with matchboarding to prevent short circuiting.

The choice of wood for this purpose, however, calls for some attention. It should be free from resin, especially where warm solutions are to be used, and there is a trend to-day to the substitution of glass in place of wood as a protective to the lead lining of tanks.

Enamelled iron tanks are extensively employed for hot solutions especially in the case of the precious metals.

For the sawdust tank galvanized iron of 12 gauge usually suffices. The pan may be 1 ft. 4 in. deep including a 4-in. false bottom containing the water for heating and a filler in the corner.

Wrought iron or mild steel tanks, formerly riveted, are now more usually welded, especially in the case of those used for chromium-plating. Added strength is imparted by the use of angle iron running round the top of the tank.

For heating such tanks, the older form of iron stand and heating ring is now abandoned. In its place the tank is mounted upon piers of brickwork with gas jets below. It is preferable to carry this brickwork up the sides of the tank, protecting it from draughts and effecting economy of gas required for maintaining the temperature once this has been attained. Systems of heating are, however, referred to later.

Where solutions are being used warm, it is preferable, though not necessarily followed in practice, that these should be under hoods, up which is provided satisfactory ventilation. The atmosphere of the plating shop is not likely to be very healthy even at the best of times, and everything possible should be done to eliminate unnecessary fumes. In the case of the chromium tank, special arrangements are necessary, and these are referred to under that section.

A useful appliance for exploring the depth of a solution consists of a small electric lamp of say 2 or 4 volts mounted in a sealed tube so that the tube can be inserted in the solution, the wires touching across the terminals of the bath. The condition of the electrodes, the disposition of fallen work, and other information can thus be easily acquired.

Capacity of Tanks. Every plater should have some good idea of the capacity of the tanks in his plant. This is readily obtained from the dimensions. Thus for a rectangular tank—

$$\underset{\text{(cub. ft.)}}{\text{Volume}} = \underset{\text{(ft.)}}{\text{length}} \times \underset{\text{(ft.)}}{\text{breadth}} \times \underset{\text{(ft.)}}{\text{depth}}$$

Further, as 1 gal. of water weighs 10 lb., and 1 cub. ft. of water weighs 62·5 lb.,

$$1 \text{ cub. ft.} = 6{\cdot}25 \text{ gal.}$$

No tank is used to maximum capacity. Hence the volume of the solution is more important This will be—

$$\text{Gallons} = \underset{\text{(ft.)}}{\text{Length}} \times \underset{\text{(ft.)}}{\text{breadth}} \times \underset{\text{(ft.)}}{\text{depth}} \times 6{\cdot}25$$

and it is convenient to know for each size of tank the volume (preferably in gallons) contained per foot depth. A number of examples are given in Table XLVI.

TABLE XLVI

CAPACITY OF TANKS

Shape	Dimensions	Gallons per Foot Depth
Square	1′	6·25
	1½′	14
	2′	25
	2½′	39
	3′	56
Rectangular	2′ × 1′	12·5
	2′ 6″ × 1′	15·6
	3′ × 1′	18·8
	3′ × 1½′	28·1
	4′ × 1½′	37·5
	4′ × 2′	50
	5′ × 2′	62·5
	5′ × 2½′	78·1
	6′ × 2½′	93·8
	6′ × 3′	112·5
Cylindrical (flat bottom)	Diam.	
	1′	4·9
	1½′	12·25
	2′	19·6
	2½′	30·6
	3′	44·2
	3½′	60
	4′	78·4

Where cylindrical tanks are in use the calculation is almost as simple for—

$$\underset{\text{(cub. ft.)}}{\text{Volume}} = \underset{\pi r^2 \text{ (sq. ft.)}}{\text{area of circular base}} \times \underset{\text{(ft.)}}{\text{depth}}$$

where r is the radius in feet, while the volume of the solution per foot depth will be—

$$\text{Gallons} = \underset{\text{(sq. ft.)}}{\text{area of base}} \times 6{\cdot}25$$

As an example, a cylindrical tank with a flat bottom is 2 ft. across; the volume per foot depth of solution will be—

$$\text{Gallons} = \pi r^2 \text{ (sq. ft.)} \times 6{\cdot}25$$
$$= \frac{22}{7} \times 6{\cdot}25 \doteqdot 19{\cdot}6$$

Similar figures are also shown in Table XLVI. The volumes of solution in any regularly shaped tank can therefore be readily computed.

Of considerable importance is the need for some mark on the inside of the tank to show the level at which the solution should be maintained. While this is important from the point of view of keeping the solution at its proper strength, it is even more necessary when solutions are to be periodically analysed. Thus an inch error in the depth of the solution which should normally be 24 in., represents an error of more than 4 per cent. It is of little use to apply accurate chemical analysis on solutions sampled so carelessly. Before a sample is taken for analysis the solution should be made up to its correct bulk and then well stirred to ensure homogeneity.

Applications of Rubber in Electro-plating Plant. The use of rubber lined tanks is now established practice but the present very successful application of this material has not been without the recognition and overcoming of many unforeseen difficulties. Rubber is a material capable of taking up quite large proportions of other finely divided materials with a view to enhancing its properties for special requirements. Both the soft and hard varieties of rubber have been pressed into service. Early rubber linings for tanks were of the softer type. They however soon showed signs of a limited life. One failure was that of blisters which developed behind linings, the collected water having apparently filtered through the lining in a practically pure form leaving behind the dissolved salts with added acidity. Rubber-to-metal adhesives have, however, improved so that this trouble is now much less frequent. Again the harder rubber linings showed marked signs of cracking due to unequal expansion, but this difficulty has been got over by introducing between the steel and hard rubber lining an intermediate layer of the softer variety.

Another trouble was that of contamination of the solution from one or more of the various chemical substances used in the particular type of rubber including also the accelerators used in the vulcanizing process. These effects are not altogether amenable to forecasting, but trials of the available types of rubber compounds can be and are made as the best indication of the probable success of the lining.

So successfully have some of the problems been solved that at the present time rubber finds increasing use in the field of electro-plating plant. Tanks for plating, rinsing and pickling are now in extensive use. In other directions, too, pumps, hoods and ducts together with the smaller items of plant such as plating barrels, baskets and trays are providing rubber with an increasing field of usefulness in electro-plating, but the exact phase of application should at least be known to the rubber manufacturer in order to avoid pitfalls which occasioned earlier troubles.

Generators. Full reference has already been made to the essential points in the erection of these machines. It only needs to be emphasized here that the largest measure of isolation should be provided consonant with proximity to the use of the current. Too often these generators are housed in locations in which they are in immediate contact with many types of deleterious fumes, such as might well shock the electrical engineer, who usually takes such care in maintaining his machines free from fumes and dust.

Arrangement of Accumulators. A set of accumulators in either the laboratory or works offers not only the advantage of continuous work over long periods, including night periods when a generator may not be running, but also that of a variation of voltage for the different types of deposition and the further advantage of separate circuits independent of each other.

Thus in Fig. 46 is shown diagrammatically a set of six accumulators arranged to four bus-bars giving at least three independent and separate voltages on separate circuits, while no fewer than six variations of voltage are possible without, however, entire independence. On discharge the possible voltages are—

Between	*A*	and	*B*	2	volts
,,	*B*	,,	*C*	6	,,
,,	*C*	,,	*D*	4	,,
,,	*A*	,,	*C*	8	,,
,,	*B*	,,	*D*	10	,,
,,	*A*	,,	*D*	12	,,

Other arrangements with three bus-bars and a different number of accumulators can easily be worked out. On charge the voltages will be approximately increased by 25 per cent, while from the outer bars the full voltage of the generator may be taken even without the cells being on charge. Such an arrangement is especially useful for laboratory and research work and seems to have advantages for workshop practice which have not been fully exploited.

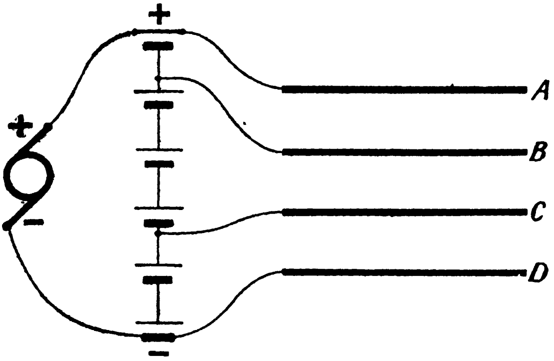

FIG. 46. ARRANGEMENT OF ACCUMULATORS

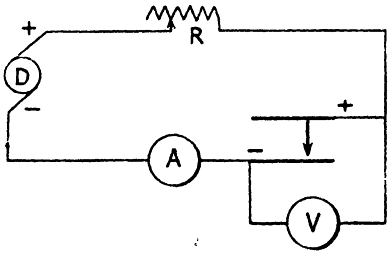

FIG. 47. SIMPLE ARRANGEMENT OF APPARATUS

An alteration of the connections to the bars will effect variations of the voltage on each consecutive pair, but in use there should be some attempt at equalizing the discharge of the whole of the cells for the maintenance of their efficiency.

Arrangement of Vats. The most simple arrangement of the essential apparatus of electro-deposition is shown in Fig. 47

in which the vat, rheostat, and ammeter are put in series, with the voltmeter as a shunt across the vat. The order of the several parts of the circuit is immaterial so long as the positive pole of the generator is connected either directly or indirectly to the anode, and similarly, the cathode is connected either directly or indirectly to the negative pole of the generator. Fig. 48 shows an alternative and equally efficient arrangement.

Where two or more vats are concerned, these must be connected to the generator in parallel through bus-bars. This parallel arrangement has the following advantages—

1. The E.M.F. of the generator need be only that required for the solution requiring the highest E.M.F.;

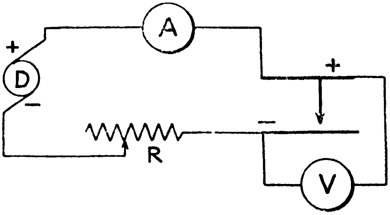

FIG. 48. ALTERNATIVE ARRANGEMENT

2. Each vat can be used quite independently of the others so that,

3. Each vat is under separate control and can take vastly different currents.

These are obviously the requirements attaching to a workshop in which different classes of electro-deposition are undertaken.

Only in very special cases is the series system of connecting vats required. These are usually the cases in which a large number of vats of the same type are doing the same work over long periods. In series—

1. The current must be the same in each vat unless, either by accident or design, some of the current is definitely shunted around any single or number of vats.

2. If one vat is put out of use the current stops in the whole of the circuit unless the defective vat is short-circuited.

3. The E.M.F. of the generator would need to be equal to the sum of the E.M.F.'s required in the individual vats.

Fig. 49 shows the arrangement of four vat circuits to conducting bars arranged as in Fig. 46 so that each vat can be connected to a different and most useful voltage, thereby reducing the need for the introduction of rheostats into the circuit and minimizing the E.M.F. loss in a high resistance rheostat.

Conductors. The conveyance of the power from the generators to the vats again calls for some element of design. Too often cables or rods are employed which are altogether inadequate to the nature of the work they are required to perform. For small currents, say up to a few hundred amperes, round copper rods are convenient, these being mounted upon insulators, especially in view of the fact that all woodwork is so liable to become saturated with conducting liquids and give rise, therefore, to undue leakage of current. When the current to be carried comes up to the region of 1000 amperes, flat copper strip is to be preferred. Usually the sectional allowance is 1 sq. in. for 1000 amperes.

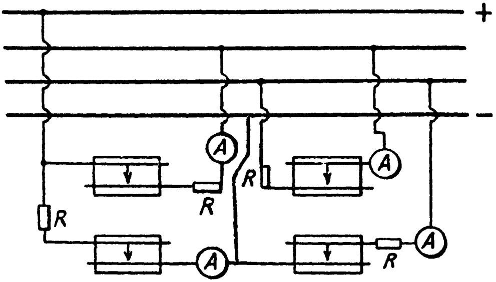

FIG. 49. SHOWING FOUR INDEPENDENT VAT CIRCUITS

In selecting the type of conductor allowance has to be made for the difference in the surfaces of circular, square and rectangular conductors having the same sectional area. Of the three types it will be appreciated that circular rods present the least surface and therefore the least cooling effect, while the rectangular bars present the greatest surface and therefore have the greatest cooling effect. This allows of the use of higher current densities in rectangular bars than circular rods, the square section occupying an intermediate position.

These allowances are made in the data included in Table

XLVII, which gives approximate current carrying capacities of conductors of different sections, it being remembered that in the electrodeposition industry we are concerned with relatively short conductors with only a small potential drop and are more concerned with the prevention of undue temperature rise.

TABLE XLVII

DIMENSIONS AND CARRYING CAPACITIES OF CONDUCTORS

Section	Dimensions	Area	Surface Area for 1 Inch of Length	Permissible Current for Copper on Basis of 1000 Amp. per Sq. In. for Circular Sections
	Diam.	Sq. In.	Sq. In.	
Circular	$\frac{1}{8}''$	0·0123	·393	13
	$\frac{1}{4}''$	0·0491	·785	49
	$\frac{3}{8}''$	0·1105	1·18	111
	$\frac{1}{2}''$	0·1963	1·57	197
	$\frac{5}{8}''$	0·3068	1·96	307
	$\frac{3}{4}''$	0·4418	2·36	442
	$\frac{7}{8}''$	0·6013	2·75	602
	$1''$	0·7854	3·14	786
	Square			
Square	$\frac{1}{8}''$	0·015	·5	19
	$\frac{1}{4}''$	0·0625	1·0	79·5
	$\frac{1}{2}''$	0·25	2·0	318
	$\frac{3}{4}''$	0·562	3·0	715
	$1''$	1·000	4·0	1270
Rectangular	$\frac{1}{2}'' \times \frac{1}{8}''$	0·062	1·25	88
	$\frac{1}{2}'' \times \frac{1}{4}''$	0·125	1·5	150
	$1'' \times \frac{1}{8}''$	0·125	2·25	225
	$1'' \times \frac{1}{4}''$	0·25	2·5	355

These dimensions are even more striking when registered in terms of the weight, and therefore the cost, of the copper required to carry the various currents. Relevant figures are shown in the accompanying Table (XLVIII).

TABLE XLVIII

WEIGHT COPPER CONDUCTORS PER 1000 AMPERES

Section	Dimensions	Permissible Current on Basis of 1000 amp. per Sq. In. Circular Section	Lbs. Copper per Foot Run
	Diameter		
Circular	1/8"	13	3·7
	1/4"	49	3·9
	1/2"	197	3·87
	1"	786	3·9
	Square		
Square	1/8"	19	3·2
	1/4"	79·5	3·1
	1/2"	318	3·1
	1"	1270	3·06
Rectangular	1/2" × 1/8"	88	2·77
	1/2" × 1/4"	150	3·25
	1" × 1/8"	225	2·17
	1" × 1/4"	355	2·74

Frequently a number of copper strips are used instead of a single strip.

The system admits of more cooling, and, therefore, higher current densities. Further, the spacing of the strips is effected at joints and corners, and, if necessary, additional spacing pieces can be inserted and the whole bolted together. This system is invariably used where heavy currents are employed. For most vats, connections can then be made with 1 in. copper strip of the required thickness.

In the use of wires for slinging work in the vat much higher current densities are permissible. The accompanying table (XLIX) shows the usual current-carrying capacities of copper wires of different gauges, and a simple calculation will show that in the case of the 8 G. wire carrying 80 amperes, the current density is of the order of 4000 amperes per sq. in., while that of the 16 G. wire carrying 24 amperes is more nearly 8000 amperes per sq. in. section.

Connections. The connections to the electrode rods require

TABLE XLIX

Approximate Carrying Capacity of Bare Copper Wires, with Low Voltage

Gauge	Diam.	Approx. Ohms per 1000 ft.	Amperes
24	·022″	21·1	5
22	·028″	13·0	7
20	·036″	7·9	10
18	·048″	4·4	15
16	·064″	2·5	24
14	·080″	1·6	30
12	·104″	1·0	42
10	·128″	·625	60
8	·160″	·4	80

more care than was once accorded to them. The old connection with cable and binding screw is quite unsatisfactory and out of date. The ends of these electrode rods should be flattened, tapped, and the leading-in strip attached by nuts preferably of the wing nut variety. Where brass tubes are used these can be filled at the ends and a flat end soldered on. The ease of making and breaking these connections for cleaning is all-important.

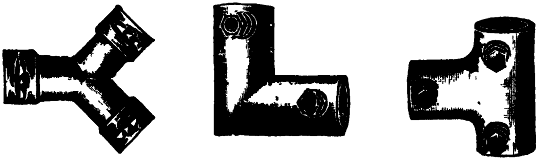

Fig. 50. Connections

Three of these connections are shown in Fig. 50.

In the choice of bars for carrying anodes and cathodes, while circular sections are in common use, the advantages of square sections should not be overlooked. Suspension from a circular rod may, with a loose connection, result in only one point of contact. With a square rod, more points of contact seem assured.

Rheostats. Whatever variation of current has been provided for on the generator, it will be desirable that finer adjustments can be made on the individual tanks. Rheostats are required for this purpose. A feature of them is that they must be substantial enough to carry the whole of the current required in the vat. They are, as is well-known, usually composed of coils of wire. On the very small scale nickel-silver offered some attraction on account of its high resistance. In comparison with iron, however, this metal is costly, and iron is therefore nearly always used. These coils are mounted on iron or slate frames with suitable switches. Reference to the older type of catalogue and textbook will invariably show that these coils were mounted in series one with another. A disadvantage attaching to the series system is that a single coil is usually called upon to carry the maximum current, the other coils being for the time idle. This also necessitates an unduly thick wire for this end coil. The system has now given place to rheostats of the parallel type, in which all the coils are mounted in parallel. The switch, of the plate type, first engages with a single coil which carries the whole of the small current. For increasing the current the switch is moved to take up the next coil or coils in parallel with the first coil thus decreasing the resistance and increasing the current, and, with it, the carrying capacity of the coils. By this system the maximum current is shared by the whole of the coils in parallel, thus keeping down the diameter of the wires, and preventing some of the coils standing idle when there is a call for the maximum current to be carried.

The principle of the parallel rheostat is that with conductors in parallel the total conductance is the sum of those of the individual conductors so connected, that is, the sum of the reciprocals of their resistances. Thus imagine three conductors put in parallel with separate resistances of a, b, and c ohms respectively. Their conductances are therefore represented by the values, $\frac{1}{a}$, $\frac{1}{b}$, and $\frac{1}{c}$ respectively. These, added together, give—

$$\frac{1}{a} + \frac{1}{b} + \frac{1}{c} = \frac{bc + ac + ab}{abc}$$

and their combined resistance is therefore—

$$\frac{abc}{bc + ac + ab}$$

In place of *a*, *b*, and *c* put the figures 2, 5, and 10 ohms, and the resistance of the three conductors in parallel is therefore—

$$\frac{2 \times 5 \times 10}{50 + 20 + 10} = \frac{100}{80} = 1{\cdot}25 \text{ ohms.}$$

The maximum resistance is obtained with the single thinnest coil, while the minimum resistance is produced by the whole of the coils in parallel.

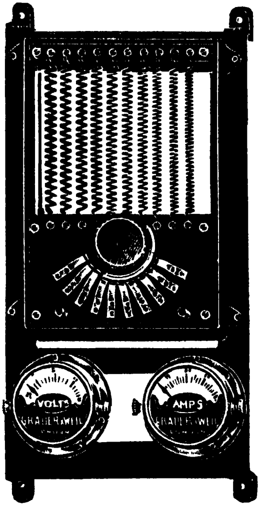

FIG. 51. PARALLEL RHEOSTAT

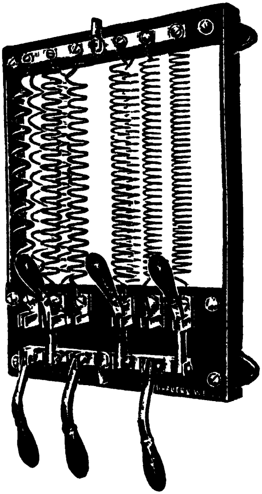

FIG. 52. SWITCH TYPE RHEOSTAT

Two types of these parallel rheostats are shown in Figs. 51 and 52, the smaller one being for currents of a few hundred amperes, while Fig. 53 shows the type available for heavy currents of 1000 amperes and over. These give ease of control with minimum loss of power and are altogether to be preferred to the older series type.

Fig. 52 shows a type of switch rheostat of simple design.

In the number of coils of wire comprising the resistance no two are alike. There is progressive variation in both length and thickness of the wires. A little consideration will show that with five such coils of wire no fewer than thirty

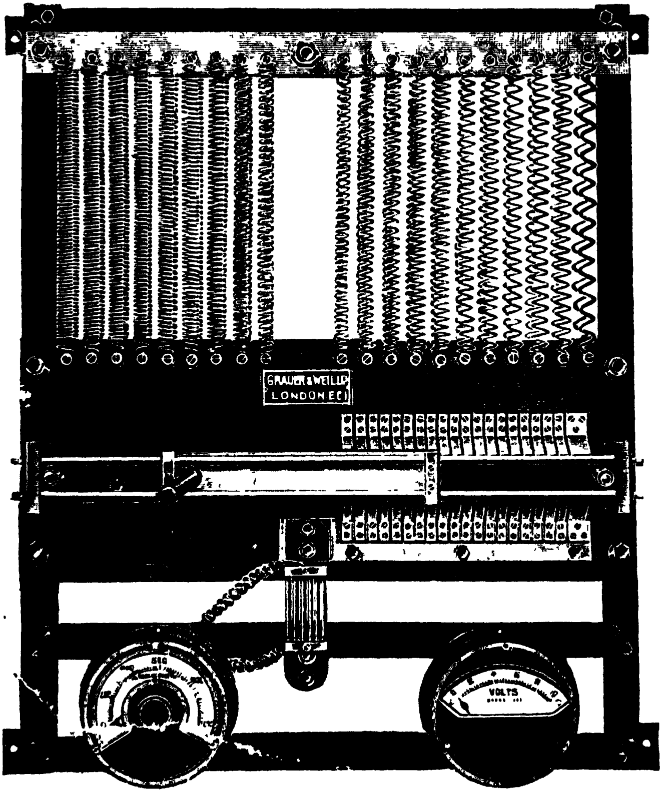

FIG. 53. LARGE PARALLEL RHEOSTATS FOR HEAVY CURRENTS

different resistances may be made up by the use of switches in each of the coils.

Instruments. Ammeters and voltmeters must be freely used in the plating shop. Nothing of a definite character can be done without them. Their use, either separately or conjointly, has been discussed in an earlier chapter. Here we are more concerned with their form.

To-day very much heavier currents are required to be measured than formerly, and the developments in the electrical industry are such as also demand accurate instruments for large currents. Meters of excellent types are therefore available. These differ markedly from former ones used in the plating shops. These earlier instruments were, for the most part, of the gravity type, in which two similar pieces of iron are surrounded by a coil through which the current passes, magnetizing both alike and causing repulsion. One piece is fixed, while the other is attached to the pivoted needle causing its deflection. When the current ceases the needle reverts to its original position by the action of gravity or by a spring. Such instruments had at least one advantage, in that they read equally accurately or inaccurately currents both direct and alternating so far as the latter were required. The modern type of instrument comprises a moving coil which is more dead beat in its action, but only reads direct current in one direction. These are readily obtained of ample range and accuracy.

Both ammeters and voltmeters are essentially of the same construction and operate on the same principle. In the ammeter the coils are few in number and of relatively large section to carry the current. The resistance is therefore low and the instrument is in series in the circuit.

The voltmeter, on the other hand, has many coil windings of fine wire. This means high resistance, the instrument being used as a shunt and operating by a very small current withdrawn from the main current. In both cases—

Number of coils × current—are of the same order.

Two features may be briefly referred to. For the larger currents, ammeters are provided with suitable shunts by means of which the main share of the current does not pass through the instrument, but only a very definitely predetermined fraction of it. This enables the dimensions of the instrument to be kept down. It is essential, however, that the shunts should be secure and free from attack by the corrosive atmosphere of the plating shop. Any slightly increased resistance here through poor contact throws the readings widely out.

Secondly, these instruments should have a very open scale. Former types of instruments, with scales of only a few inches, are quite out of date, the modern scale comprising more than a semi-circle of the dial and running to as much as 18 in. in all. They, moreover, give more uniform readings over this extended scale. Such an instrument is shown in Fig. 54.

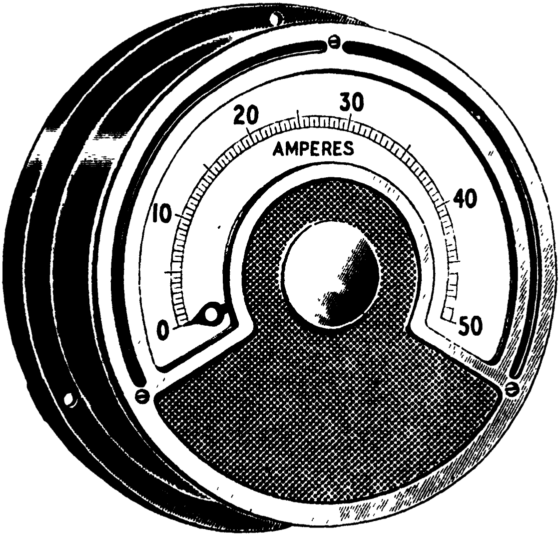

FIG. 54. AMMETER

Filtration of Solutions. One essential point is that solutions must be kept free from suspended matter. This is all-important where thick deposits are being grown. So necessary has it come to be recognized, that the modern plating equipment includes plant for the continuous filtration of the electrolyte with its heating and circulation through the tank. Suspended matter is apt to be deposited on the cathode and, becoming covered by the deposit, produces a roughness which, once started, accentuates with undesirable results. In other cases the particles may be insulating enough to prevent deposition, leading to porosity.

Like many other advances the full importance of this filtration was not at first realized. In the first instance it was thought that filtration necessitated the removal of only relatively coarse particles, and for this purpose single layers of felt were generally, and it was thought, satisfactorily, used. Later observation, however, seemed to show that such coarse material could be thrown back into the solution without impairing its deposition properties, and that the really essential filtration involved the removal of the finest particles. There was also the accompanying need for doing this on large volumes of solution necessitating a rapid rate of filtration. These appreciated needs called for a considerable tightening up of the filtration process involving the use of entirely (as far as electro-plating goes) new methods.

A comprehensive survey of the subject has been given by Wernick and Silman* who first state that while initial porosity may disappear with increasing thickness of deposit, yet there are few applications of electrodeposition (in which porosity is important) in which such requisite thickness of say ·002 in. can be economically applied. Hence the greater need for the elimination of the sources of porosity.

These authors classify modern filters under five headings—

(*a*) The filter cone,
(*b*) The filter press,
(*c*) The filter candle unit,
(*d*) The pre-coated unit and
(*e*) The centrifugal filter.

A few words may with advantage be added about each of these types of filter, but for more detail the paper by these authors should be consulted.

(*a*) The filter cone which was first in use has at least the disadvantages that it is not applicable to the scale of modern electrodeposition and, moreover, while capable of taking out coarse particles only, may indeed even introduce organic impurities from the filtering medium deleterious to good deposition.

(*b*) The filter press. These have long been in use in the filtration of large volumes of liquids handled in the chemical and hydro-metallurgical industries. They consist of a number of wooden frames over which are stretched layers of filtering

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* *J. Electrodep. Tech. Soc.*, 1940, xvi, 79–114.

medium so clamped together that they act in parallel and thus introduce a large area for filtration. More recently, rubber coated steel frames have replaced wood thereby eliminating contamination from that somewhat uncertain material. Such filters are eminently satisfactory in many cases in the absence of alkalis (in which glass wool fabric can be substituted), but fail to give the desired degree of purification where rapid or bright nickel plating solutions are concerned, for visible clarity may not be adequate to the highest degree of plating.

(*c*) The candle unit comprises a number of cylindrical porous candles made of compressed fired kieselguhr about 10 in. long and 2 in. in diameter. These again are placed as it were in parallel, the solution being forced under pressure from the outside so that the collected residues can readily be removed. These candles have an exceedingly fine structure such that material of the order of ·1 micron (1 micron = ·001 mm. or 39 millionths of an inch) may be removed. However, this fine precision of filtration is offset by (1) a very low rate of filtration, (2) the high pressure required to force the liquid through the very fine interstices of the medium, (3) the rapid rate at which the filter becomes clogged up and (4) the cost of repeated cleaning and reassembling the unit.

These disadvantages have now to some extent been overcome by the substitution of stoneware for kieselguhr. There is some loss in the degree of filtration, but the stoneware will stand up to much rougher treatment in use and in the mechanical process of brushing away the slime during cleaning.

Another improvement, this time to prevent the clogging up of the candle material which is difficult to thoroughly clean, is that of starting a new unit by adding a quantity of kieselguhr to the first solution to be filtered. Kieselguhr is a relatively light substance and produces a uniform mixture with the solution, and is thus deposited uniformly on the new candle. This first deposit readily traps the suspended matter of the solution and makes an effective filtering medium. Moreover when the time comes for cleaning, the deposit is readily washed off and a new charge of kieselguhr added to the next volume of solution to be filtered. The life of the candle is thereby considerably lengthened. Further, the enamelled pots in which these units were first set up have since been replaced by rubber-coated steel with advantages which are obvious.

(*d*) The pre-coated unit. This involves dispensing with the filter candle and substituting a suitable base upon which to deposit the filtering layer. Such materials include pure nickel or monel metal for nickel solutions, stainless steel for cyanide solutions with rubber-lined steel, vitreous enamel or nickel-clad steel as a material for the container. Upon this principle two systems used in America and in this country have been followed, and for this purpose, and others also, special types of pumps have been designed. The choice of material for this purpose has not been an easy problem. Even for the very slightly acid nickel plating solution, relatively free from coarse material, it has been found that pumps constructed from bronze or nickel suffer a considerable amount of erosion due to the setting up of stray currents. Other materials pressed into service have been Bakelite and even Pyrex glass, this latter evidencing remarkable progress in glass technique.

(*e*) The centrifugal filter, in which high rates of filtration are possible with high outputs. Plants now in operation on this principle and driven by turbines employ speeds up to 50,000 revolutions per minute and develop settling forces as high as 62,000 times gravity, while others, motor-driven, speed up to 22,000 revs. per min. with a settling force up to 15,500 times gravity. These machines, however, call for the greatest accuracy in construction and setting up in order to secure smooth running. Hence the larger adoption of power speeds of 1400 revs. per min. for the filter bag.

Finally, reference may be made to the increasing use of anode bags to prevent the anode particles from finding their way into the solution. These, however, are liable to fracture in addition to the risk of introducing organic impurities into the solution. Anode bags of the woven glass fabric type have, therefore, found some use in America.

Among filtering media may be mentioned kieselguhr, which is a fine diatomaceous earth with remarkable absorbent properties. More recently activated carbon has been successfully pressed into service. It has been used more in America where complex organic addition agents are in greater use than in this country in the composition of bright nickel solutions. It has already been considerably used in the chemical industries and may be made by a variety of methods. The charcoal from coco-nut hulls provides one example, while from coke and other forms of carbonization carbon good activated carbons are made by treating the carbon, with steam. This process seems to open up a markedly porous surface which is essential for filtering and other absorbent processes.

Heating Solutions. Plating solutions follow the usual rule of increased conductance of solutions with increase of temperature. They are, therefore, often heated. This can be effected in many ways, a number of which will not require even suggestion. For example, a current of hot water from any convenient type of stove can be circulated through pipes of a suitable metal immersed in the plating solution.

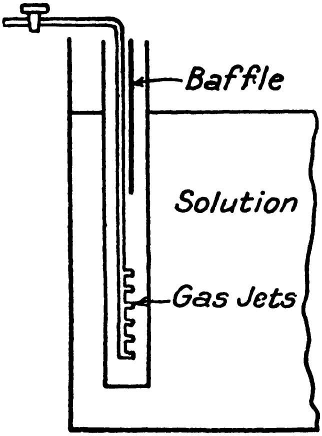

FIG. 55. INTERNAL GAS HEATING

Fig. 55 shows a wide lead pipe closed at the bottom. A small gas flame is introduced so that the hot air rises on one side of the tube and the cold air for the flame descends on the other side. A dividing plate assists this circulation of the air. This is serviceable where only moderate temperatures are required.

A large volume of solution having attained the required temperature will maintain it with a little care and protection, especially if covered during the night.

Combined Agitation and Filtration. Modern workshop practice has thoroughly demonstrated the need for agitated solutions, with continuous filtration to ensure the complete freedom from dust which otherwise so prominently encourages rough deposits. Systems, some simple and others more elaborate, now cater for this dual function. An example is shown in Fig. 56, which comprises a motor driven rotary air compressor, air reservoir with air filter, and the necessary lead filter coil and perforated agitating coils.

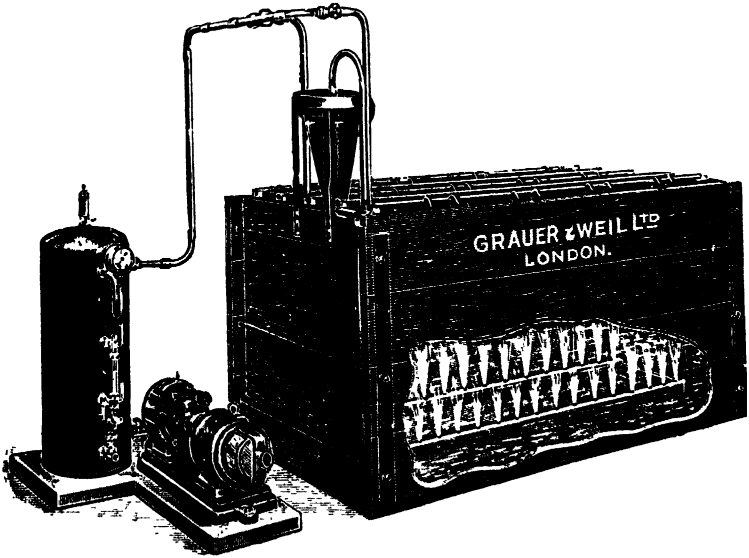

FIG. 56. PLATING BATH FITTED WITH FILTER AND AIR AGITATION

The solution is drawn from the far end of the plating tank and passes through the filter funnel containing a felt filter bag which is readily changed when necessary, and then returned to the opposite end of the tank.

The air reservoir contains some water through which the compressed air must pass, thus eliminating dust and oil before the air enters the solution. Regulating valves on the air supply provide control for both the filtration and agitation.

Acceleration of deposition with increased current density can also be obtained by applying a reciprocating motion to the cathode bars, or alternatively and better, to both rods. A system of this type is depicted in Fig. 57, in which is shown a bell crank by the use of which it is possible to vary the length of the stroke. The motion may be applied either by belt drive or direct by the use of a suitable motor.

Handling Small Parts. Modern practice calls for the plating of numerous small instrument and machine parts requiring to be handled in considerable numbers. Such small parts are well beyond the range of individual wiring. For the several operations through which they must pass, perforated trays and baskets are largely employed. For the cleaning operations, including dipping, these are usually of stoneware, while in the later plating processes they may be of wire. These wire baskets, however, become heavily plated with the metal. This involves waste, in addition to which the articles are stationary in the tray. They have, therefore, been largely replaced by the use of barrels.

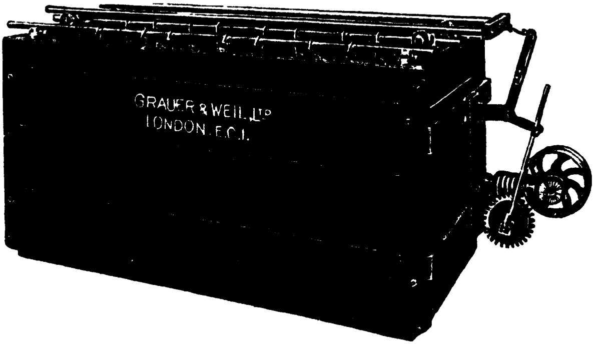

Fig. 57. Rod Motion

Plating Barrels. These are rotated so that the work is kept in motion, and the several parts each given due exposure to either the cleaning material or plating solution. For both cleaning and plating operations they are frequently of hard wood, slightly inclined to the vertical and rotated, after the work and liquids have been introduced (Fig. 58). The mounting is

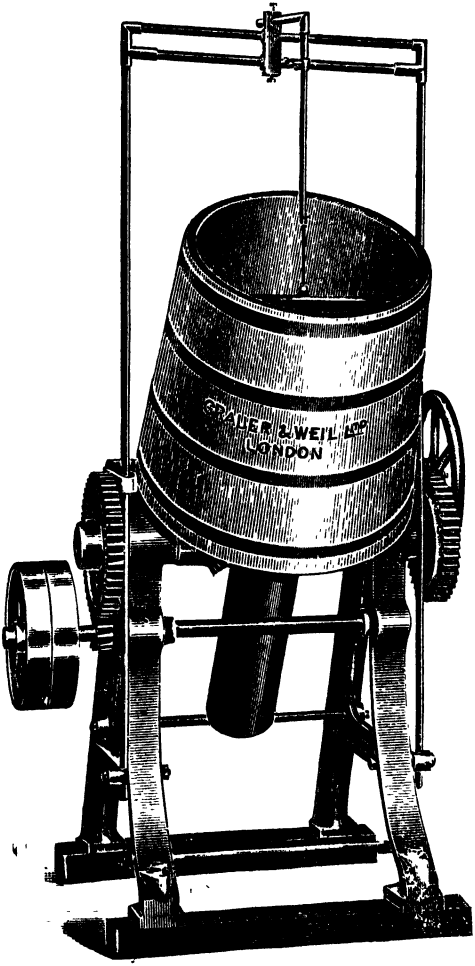

FIG. 58. PLATING BARREL

such that the barrel can be tipped so that the contents are poured out, passing through a sieve, thus separating the work from the solution. Another advantage of the system is the continuous burnishing action of the parts on each other, this taking the place of any individual treatment, which would be quite out of the question.

Formerly plating tank barrels were commonly arranged horizontally. They were of perforated insulating material, such as celluloid suitably stiffened, or ebonite, a cathode contact being made inside them, upon which the small parts made contact during rotation. The barrel, which might also be of xylonite, was non-conducting and did not pick up any metal, leaving, therefore, the whole of the current to the work contained therein.

More recently some of the difficulties attaching to this type have been removed by the introduction of plating barrels more of the type of those used in the cleansing operations. These newer barrels are suitably lined, having regard to the composition of the plating solution. Mounted at an angle from the vertical, they are open at the top, giving access for inspection. An anode is conveniently arranged, allowing for quite a small inter-electrode distance, thus keeping down the resistance, which is further reduced by the abolition of perforated material common to the former horizontal types.

Automatic Plating. The modern applications of electroplating, particularly in the motor trade, have necessitated the handling of many large parts with the minimum of labour, and with increased speed. To ensure the latter, many devices have been employed to keep either or both of the electrode rods in motion. Many rocking devices are in use, and in addition, the solutions are circulated, filtering and heating appliances also being included, or, with less frequent filtering and simple types of internal heating, solutions are kept stirred within the plating tank. Compressed air agitation has proved both simple in application and effective in operation.

A step further in the application of automatic operation involves mounting the work on a moving, endless rack, so that after one or several motions round the tank sufficient metal will have been deposited.

On the largest scale, however, elaborate plants for automatic plating are rendering considerable service where a continuous succession of parts passes through a sequence of operations. Illustrations can be drawn from the plating of many motor parts. From the polishing shop these require to pass through a succession of cleansing solutions, with intermediate rinsing prior to passing through the plating tank.

In the case of nickel plating these successive stages are numerous. In an example described by Maurer* the following thirteen stages were involved: (1) Electrocleaner, (2) rinsing, (3) acid dip, (4) rinsing, (5) coppering, (6) rinsing, (7) a sulphuric acid dip to remove all traces of alkali from the copper plating, (8) rinsing, (9) bright nickel plating, (10) dragout, (11) rinsing, (12) rinsing and (13) drying out. Each of these operations demands definite maxima and minima of time ranging from seconds for rinsing to 15 minutes for nickel plating. Moreover, the work must be transferred from one tank to another without unnecessary delay. The journey of the work through the individual tanks must be adjusted largely by the length of the tank as the work is mounted on a chain drive of uniform speed. Again, three or four stages involve the use of current necessitating the complete insulation of these tanks from each other. In addition, there will be accessories, such for example as a relatively large storage tank for the nickel solution together with filtering equipment, pumps and heating installation. In the plant under consideration the current consumption is of the order of 60,000 to 72,000 ampere-hours per day of 24 hours with a consumption of 113 to 141 lb. of nickel anodes per day. A finer point in the arrangement is the transfer of the work from the main rack to one of higher speed between the successive tanks.

The ingenuity of the engineer has been equal to the task of designing and constructing plant for the mechanical handling of such work through a succession of tanks.

One of the latest types is the "Duplex Carriage Transfer Plant," which effects considerable reduction in costs by eliminating handling between the individual operations and, at the same time, ensuring an improvement in the quality of the work by the essential standardization of the various processes and conditions.

In this plant, a general view of the loading end of which is shown in Fig. 59, two moving carriages are carried on a

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* *Metal Industry*, 19th July, 1940.

Fig. 59. Loading End of Duplex Carriage Transfer Plant

steel structure. From the upper carriage suspended chains pass over pulley wheels attached to the lower carriage. To these chains are attached hooks which engage with baskets or bars carrying the work.

These two carriages may move together or independently. The forward movement of the upper carriage without the lower raises the chain and the basket or bar of work which may be engaged with it. The same movement of the two carriages carries the raised basket in a forward direction.

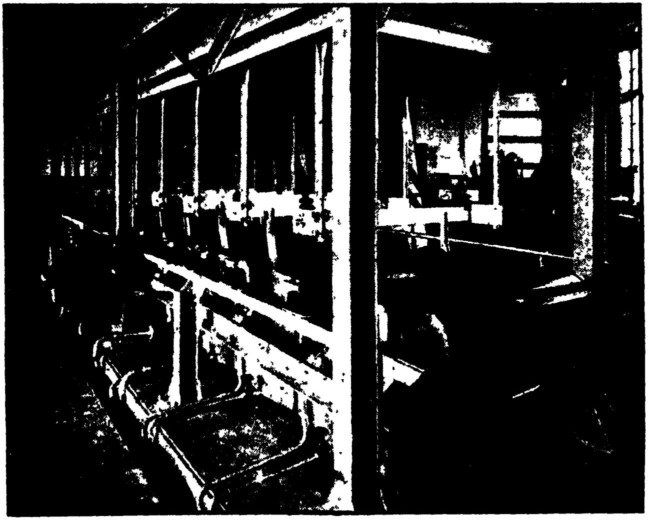

FIG 60. AUTOMATIC BARREL PLATING

Both of these carriages are driven from a single electric motor with suitable worm reduction.

The motions produced by these carriages may be adapted to a sequence of processes in which immersion in successive tanks is required to be of the same duration. This, therefore, applies to such processes as pickling and rinsing, in which the latter process may require several tanks. But in many processes, and those of electro-plating are illustrative, the time of immersion in successive tanks may be very different, for while pickling and rinsing may require only two or three minutes, nickel plating may necessitate immersion in the bath for at least thirty minutes. In this case the lifter hooks are arranged to deposit the work baskets or bars on to a continuous conveyor chain running alongside the vat.

Thus every emergency of condition can be catered for, and the illustration shows a plant for bright nickel and chromium plating in a series of fourteen tanks with an overall length of 150 ft.

The plant may also be adapted for barrel plating, an example of which is shown in Fig. 60.

Other adjustments allow for heating the solutions by one or other of the three alternative methods of gas heating, electric immersion heaters and steam coils.

In this direction, as also in that of the much improved type of solutions now in use, there is the best evidence of the advances which have been made during the past ten or fifteen years in the art of depositing metals by the agency of electricity.

CHAPTER IX

MECHANICAL CLEANING

INTRODUCTION—Mechanical processes—Sandblasting—Barrel cleaning, burnishing, and polishing—Emery bobbing and scurf mopping—Felt bobs—Stitched mops—Finishing chromium and "Staybrite" materials—Theory of polishing—Materials employed—Notes on polishing and finishing

Introduction. Before any of the usual processes of electro-deposition upon metals can be resorted to, it becomes imperative to impart to the surface of the basis metal a uniformity which is essential for the production of a satisfactory finish upon the deposited metal. There is a wide gulf between the rough metal which emanates from the manufacturer and the finely finished product seen in the showroom.

These preparatory processes are roughly, though not exactly, divisible into two groups—

1. Mechanical operations which are usually accomplished with dry materials.
2. Chemical and electrolytic processes.

This grouping is serviceable from the point of view of presenting an outline of the several operations concerned.

Mechanical Processes. A feature of the modern methods is the rapidity, with saving of labour, over the processes practised years ago. The several stages involve sand-blasting, grinding, and emery-bobbing, these being the most important.

Sandblasting. This method of oxide or scale removal is dependent on the friction obtained on the surface of the work by particles of fine sand or steel balls projected upon it by means of a jet of compressed air. The method is of great service in cases in which, owing to the presence of considerable amounts of scale to be removed, the ordinary pickling processes would be too prolonged. The method is particularly effective where there is no considerable amount of grease to interfere with the action of the sand. It is also often used to obtain a fine matt surface on otherwise smooth work.

Owing to the space occupied by the essential plant and its somewhat high cost, the sand-blast method is not favoured where small work has to be dealt with. In the cycle trade, however, it has been found economical to employ a sand-blast chamber for the removal of scale, brazing marks, etc., from cycle frames prior to enamelling, a very smooth surface being the result. Its principal application would appear to be for castings where it is impossible to pickle without leaving in the pores of the metal acid which may subsequently cause trouble during and after the plating operations.

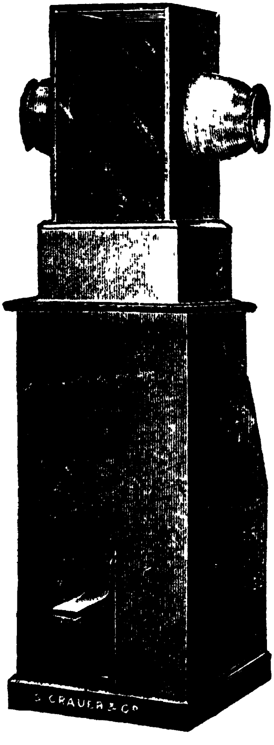

FIG. 61. FOOT SANDBLAST

On the other hand, care must be taken to avoid too great an air pressure, as this leads to the imbedding of the sand particles, and necessitates subsequent pickling with hydrofluoric acid to dissolve out the sand. Figs. 61 and 62 show two types of sand-blast machines in common use, the work being held in the hands over the jet from which the stream of sand issues. With the type involving the larger chamber, the operator uses a helmet with glass peepholes for protection for the eyes. The abrasive effect is due to the angular fragments of sand, and their sudden impact with a relatively hard surface. It is generally recognized that hard surfaces are more easily sandblasted than soft ones. Sooner or later the angular points wear away, the sand grains becoming rounded, and the sand is then much less effective.

Barrel Cleaning, Burnishing, and Polishing. In order to eliminate as far as possible all handling costs, small articles may be cleaned, burnished, or polished in rumbling barrels, thereby enabling the largest quantity to be dealt with in the minimum of time. The outer scale of castings and the sharp edges of stampings, etc., are removed by barrel scouring.

Barrels rotating either vertically or horizontally (Fig 63) may be employed, the former being open at the top for the reception of the articles to be treated. Iron barrels are usually employed for the scouring process, or any process where the abrasive nature of the material is such as to occasion considerable wear of the barrel. Wood barrels are employed for ball burnishing and barrel finishing.

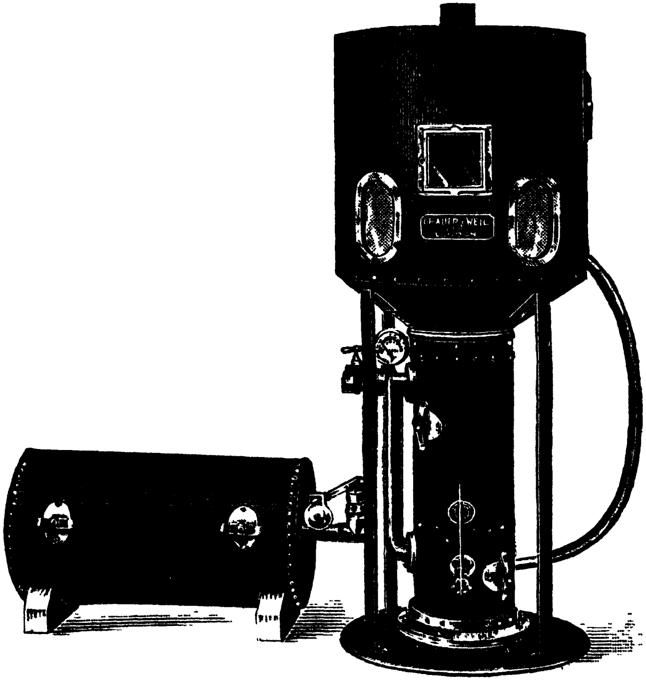

FIG. 62. POWER SANDBLAST

Cast-iron articles are barrelled with emery and oil until the desired surface is obtained, then rinsed in paraffin oil, and finally immersed in a suitable cleaner before passing to a burnishing barrel, where they are rotated with about half their own bulk of small steel balls and soap solution.

If further lustre is desired, they may then be transferred, after drying out in sawdust, into a polishing barrel of suitable shape, and rumbled with leather cuttings, lime, and other polishing materials. Pumice powder, Tripoli powder, and other abrasives may also be used, according to the nature of the material to be scoured or polished, materials having a soft surface requiring the use of the milder abrasives.

When the steel balls are not in use, they must be preserved in soap solution, or smeared in petroleum jelly, to prevent rusting, which renders them useless for the ball burnishing process.

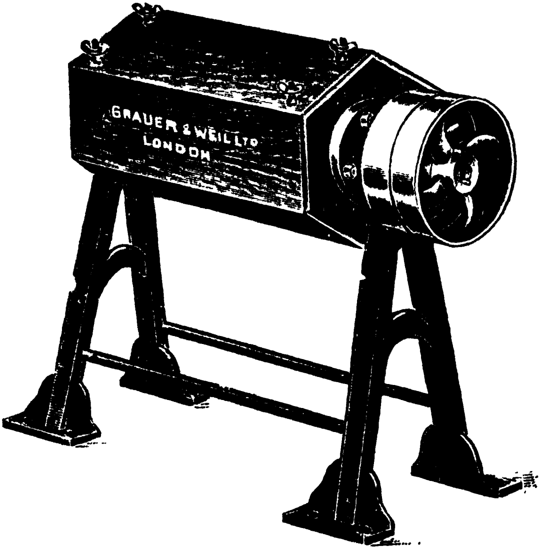

FIG. 63. RUMBLING BARREL

Non-metallic substances may also be scoured and polished in a similar manner, it being merely necessary to adapt the type of abrasive and polishing medium to the nature of the material under treatment.

The speed of rotation and angle of fall should be arranged to suit the shape and surface condition of the article to be polished. An average speed would be from 30–60 r.p.m., care being taken at all times that the speed of rotation is not sufficient to cause the work to be carried around with the barrel, thereby rendering the operation useless.

Emery Bobbing and Scurf Mopping. These operations are carried out with leather-covered wooden wheels, felt bobs and stitched mops dressed with emery, the grade of emery depending upon the surface condition of the work and the amount of scale to be removed or levelling of the surface to be done.

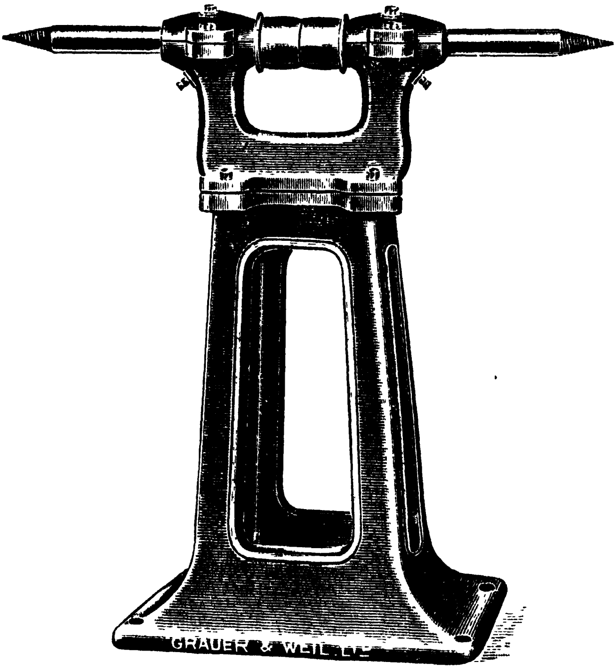

FIG. 64. POLISHING SPINDLE ON STAND

These wheels are revolved to give peripheral speeds of about 6000 ft. per minute on suitable lathes, which may be belt-driven or motor-driven. Examples are seen in Figs. 64, 65, and 66. The spindles terminate in a taper screw upon which the wheels fasten so that the pressure of work tightens them. Numbers of belt-driven heads may conveniently be operated from a common shaft, and where it is desired to reduce the total load to a minimum, the shaft may be run in ball bearings, and the polishing head equipped with ball races. Many advantages, however, accrue to the installation, especially for large work, of individual motor-driven machines.

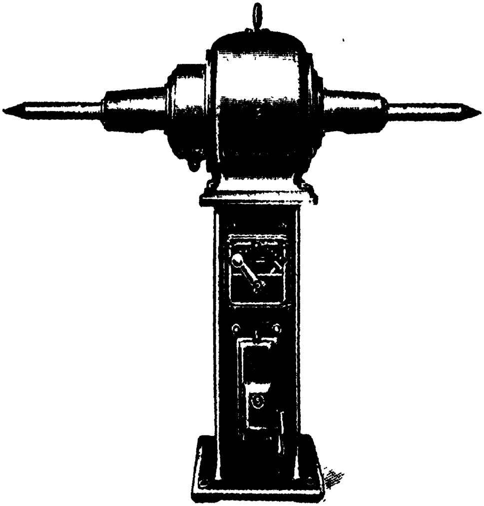

FIG. 65. MOTOR POLISHING LATHE

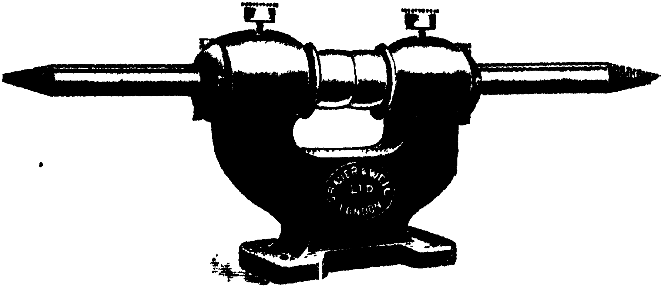

FIG 66. POLISHING SPINDLE WITH BALL BEARINGS

A typical ball-bearing polishing lathe is shown in Fig. 66, and with this type of machine, a much larger number of units can be run from the existing motor supply, without creating an overload. They are fitted with four dust-proof grease-lubricated ball races, and require very little attention.

In the more modern type of machine the spindle is belt-driven from the motor which is situated in the base of the machine. Two advantages at once arise from this separation of the spindle from the motor. In case of failure of the motor it can be quickly replaced while repairs are being made. Further, when changing mops and bobs a trip operated by the foot not only cuts off the motor but disengages it from the spindle on to a loose pulley. A simple and quick movement with the foot, and the spindle, without the usual momentum of the rotor of the machine, can be stopped by hand almost instantaneously.

In either case the machines may be provided with wood tables convenient for holding small work and the polishing materials. In the handling of large work, such tables are conveniently dispensed with to allow the operator more room in which to cope with unduly large and awkwardly-shaped work.

The wooden wheels are made from selected woods, usually composed of two or three layers glued together so that the grain of the layers is at right-angles to that of an adjacent layer, to avoid splitting when the wheel is in use. Strips of seahorse or bullneck leather are then cut and fixed to the periphery of the bob by gluing and pegging (Fig. 67). The surface is then turned, and dressed with glue and emery. For this purpose only the best glue should be used, and the wheel is rolled in a tray or trough containing the right grade of emery, and allowed to dry. For sanding silver work, the same type of bob may be employed, but sand and oil are used in place of emery. Solid leather bobs are also used for sanding, and are made from either bullneck or nickbob leather, it being possible to turn these bobs to various shapes with the aid of a sharp tool, such as a chisel, so as to be able to get into the angles and crevices of variously-shaped work, which would be impossible with the ordinary flat-edged bob.

In course of time, the emery loses its cutting power, and it becomes necessary to dress the bob. This is done by removing the old emery by rotating the wheel and holding to it a hard tool or piece of pumice. This removes the worn surface of the bob, leaving it true to receive a new dressing.

Felt Bobs. These (Fig. 68) are compounded of wool compressed, when wet, under hydraulic pressure to the thickness and hardness desired. Being more resilient than leather bobs, and also cheaper, they are in general use both for polishing metals and vulcanite. During manufacture the moisture is removed by the centrifugal force of rotation, and by drying in ovens.

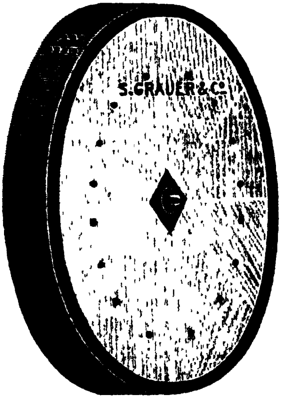

Fig. 67. Leather Covered Bob

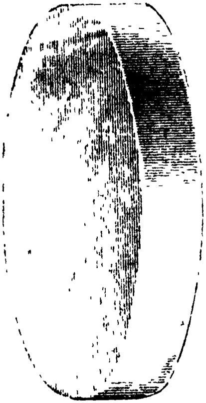

Fig. 68. Felt Bob

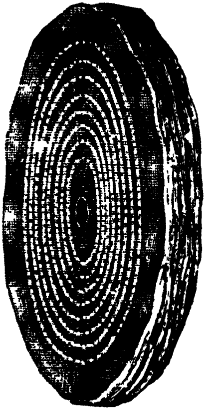

Fig. 69. Stitched Mop

Stitched Mops. These (Fig. 69) are composed of pieces of felt material layered together and then stitched in a circular fashion from the centre to the outside. They are made up in sections approximately $\frac{1}{2}$ in. thick, nailed through the centre and washered, the thickness desired being obtained by nailing several sections together. They can be obtained in almost any diameter from 3 in. up to 18 in., and may either be glued and dressed with emery, or used in conjunction with brushing emery or with emery or other composition. As it is not possible to make these mops perfectly circular, they are usually turned up before use by pressing a sharp tool, or mop-dresser, against the periphery during rotation.

The removal of fine scratch marks and slight imperfections from the surface of the work is usually done by employing large circular fibre brushes in conjunction with flour emery which is used as a composition in bar form. These brushes are obtainable with or without calico layers interspaced between the rows of the fibre. Some workers consider that these layers of calico serve to hold the emery composition, with consequent economy.

The type and quality of abrasive employed depend entirely upon the condition of the surface, and it is common practice to employ several bobs, each dressed with different grades of emery, in order that the work may be ground down in stages, a finer grade of emery being employed in each successive stage.

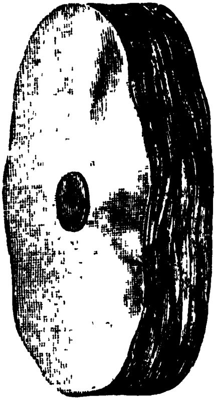
FIG. 70. CALICO MOP

FIG. 71. TRIPOLI COMPO

FIG. 72. FINISHING COMPO

The work, having been ground down by any of the methods suggested above, is ready for buffing to obtain the high polish on which the brightness of the subsequent deposit so much depends. Various grades of polishing mops are obtainable, the choice of which is determined by the nature of the work to be treated. A grey calico mop is most generally preferred for polishing non-ferrous metals prior to nickelling.

This is composed of an American cotton of a fairly robust nature (Fig. 70). These mops are nailed and washered together, 50 laps of the material making a mop 1 in. in thickness. They can be had in any diameter from 3 to 18 in. The abrasive used is Tripoli as a composition (Fig. 71). Where the surface is not to be plated, but finished by polishing, a mirror surface is imparted by the use of a soft type of finishing mop made from the best Egyptian cotton and again obtainable in various diameters, 60 laps constituting 1 in. in thickness.

A special lime finishing compo (Fig. 72) is used with this mop. Where an article is to be plated, this finishing operation is reserved for the deposit. This may be treated by the same sequence of mops and compos, according to the condition of the deposit. In the case of plated iron work, for example, the deposit is apt to be somewhat dull owing to the original surface of the iron. The dullness is accompanied by hardness, requiring a mop of harder texture to effect polishing in a reasonable time. For this purpose mops—erroneously termed white linen mops—are used. These are mops heavily filled, having 90 laps to the inch. When rotating, they present a firm surface to the work, and are generally termed *fast-cutting*. This type of mop rapidly imparts a high polish to the work, which can finally be finished off with a soft mop and a suitable finishing composition.

SILVER AND SILVER PLATED GOODS and other metals of similar soft nature are finished with a soft mop with rouge composition (Fig. 73). They are then given a final mopping with a swansdown mop and a lime composition.

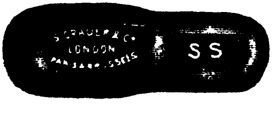

FIG. 73. ROUGE COMPO

Finishing Chromium and "Staybrite" Materials. The advent of deposited chromium, and the use of ferro-chrome alloys of the stainless steel and "Staybrite" type, demand special treatment on account of the extreme hardness of these metals. This involves the use of hard mops with at least 90 laps to the inch and a special hard cutting composition, made from green chromium oxide.

Modern practice and experience produces a chromium-plated deposit of such a bright nature as to require merely finishing with a brown calico mop, and a special No. 5 White Chrome Finish made from alumina or similar abrasive. This latter has completely superseded the use of green chrome oxide composition, which was more costly, and more unpleasant for the worker to use.

The polishing of chromium deposits, with modern methods of deposition, demands very much less severe treatment than was formerly necessary.

The recent introduction of stainless steel and "Staybrite" material has also introduced a finishing problem of some importance.

These metals require grinding in the early stages, on felt bobs dressed with a suitable grade of emery or carborundum, which must be iron-free when used for "Staybrite" material, in order that in the event of any abrasive material becoming embedded in the surface layer of the metal the non-magnetic properties of this type of material (austenitic) shall not be thereby destroyed.

A fine grade emery is then employed on a stitched cotton buff with white bobbing grease, in order to obtain the highest finish possible prior to the polishing operation.

This latter is carried out by means of a soft white or brown calico mop dressed with No. 5 White Chrome Finish, which imparts a final gloss to the material. The peripheral speed of the mops during the finishing operation should be from 8000 ft. to 9000 ft. per minute.

Theory of Polishing. A little reflection will show that the earlier and later stages of producing a highly reflecting surface on a metal are materially different operations. In the earlier stages, using coarse cutting materials such as emery, the successive stages consist in removing a series of coarse scratches by replacing them with a finer set, usually at right angles. This process is carried on until a very even and fine system of scratches covers the surface. The materials used up to this stage are abrasives.

The production of a fine lustre from this evenly scratched surface involves quite a different type of operation. Polishing materials are not scratching materials. Used with a higher speed than in the former stages, they cause the metal to flow from what we will call the tops of the scratches into the valleys, which are thus filled up by the debris from the severe wear of the high speed mop. A uniform lustrous polish thus results by the production of a thin film of surface material which, seen under the microscope, is free from structure, and appears to be a mass of cemented metal powder, hard, durable and lustrous. Thus the metal in the final stages of polishing actually flows slightly as though it were a thick liquid, a condition not altogether impossible considering the pressure applied and temperature usually developed. Some simple ideas like this help the appreciation of the particular purpose of the materials used in the successive stages of the work.

Materials Employed. Reference may now be made to the relatively few materials which are in use in the metal polishing industries.

EMERY. This is a natural product, consisting mainly of aluminium oxide with appreciable quantities of iron oxide which does not add to cutting properties but possibly serves as a binding material. It is found in several important localities, and the natural product has to be crushed, washed, and then screened to give the different grades in common use. These vary from 6 to 200, these figures meaning the number of divisions per linear inch of the screen. A 200 mesh screen therefore has 200 × 200 = 40,000 holes per sq. in., and in the standard screen the wires comprising the screen have an area equal to that of the apertures they produce. This will give some idea of the extraordinary fineness of the material. Beyond this mesh, however, there are the various grades of flour emery, usually numbered 0, 00, 000, and 0000. To obtain these, a process of sedimentation is employed in which the finely crushed material is mixed with water and passed through a series of tanks of increasing capacities. In the first and smallest tank the mixture flows relatively rapidly, and only the coarser particles are deposited, while in the later tanks, which are larger, the flow is proportionately decreased, and finer material settles out. This process of sedimentation is frequently used in the grading of fine powders.

TRIPOLI. This is a siliceous material, consisting of numerous small skeletons of a small plant. The material is mainly a hydrated silica with some impurities, chiefly iron and alumina. It is invariably used bonded with grease as a composition for cutting purposes.

ROUGE. This is an oxide of iron obtained by the distillation of ferrous sulphate. Crocus is obtained in much the same manner, the difference being that rouge is obtained at comparatively low temperatures, while at a higher temperature the grains are larger and the colour totally different. Rouge is the softer material, and is used for obtaining a high lustre. It is commonly applied either bonded with grease as a composition or mixed to a paste with water and applied to the mop.

Chromium Oxide. This is the green oxide obtained by the ignition of the hydroxide, after which it becomes almost insoluble in acids. Its particular application is that of finishing chromium deposits.

Lime. Special varieties for this purpose are Sheffield and Vienna limes, the latter being preferred. This is a mixed oxide of calcium and magnesium obtained by calcining dolomite, which is a natural mixed carbonate. It must be kept dry, as it readily absorbs both moisture and carbonic acid gas. It is particularly serviceable in finishing nickel and also copper and brass work, imparting the highest finish.

Notes on Polishing and Finishing. Many very satisfactory compositions are available for the various stages of polishing. The choice of materials to effect suitable compositions has not been altogether an easy matter, so much depending upon the composition of the grease chosen and its method of application. While the abrasive material is the main thing, much, nevertheless, depends upon other factors, including, most important of all, the adherent properties of the binder. This should suffice to hold the abrasive on the wheel just so long as the abrasive retains its cutting power, after which its ready removal is essential prior to applying further quantities of the composition.

The speed of polishing varies with cutting and finishing, the former being usually done at 6500 ft. per minute while finishing requires the much greater peripheral speed of 10,000 ft. per minute.

The process is mainly one of two stages. The initial cutting stage is effected with emery and tripoli. Final polishing requires rouge, crocus, lime, and green chromium oxide, each with its special application, rouge for the precious metals, lime for nickel, crocus for tin and iron, and green chromium oxide for chromium deposits. In making comparisons of costs, the cost per sq. ft. of surface polished must be made the basis, rather than the cost of the compositions per pound.

CHAPTER X

CHEMICAL CLEANING

INTRODUCTION—Grease removal—Degreasing with trichlorethylene—Mineral greases—Alkali cleaning—Emulsification—Wetting—Use of alkali phosphate solutions—Electrolytic cleaning—Methods of suspending work in cleaners—Maintenance of cleaning solution—Combined cleaning and coppering—Acid pickling and dipping—Copper and its alloys—Iron and steel work—Embrittlement of steel—Zinc, aluminium, and their alloys—Lead tin and their alloys—Scouring — The acid etch — Scratch-brushing — Final rinsing — Drying out

Introduction. The term chemical cleaning of metals applied to electro-plating covers a number of operations, in which mechanical effects cannot be altogether excluded. For the most part, however, we are concerned with the removal, mainly by the processes of chemical action, of all those materials ordinarily present on the surface of metals subsequent to the processes of manufacture and mechanical cleaning. These include many different operations intended for the removal of all greasy compounds, and subsequently those films, which in many cases may have appreciable thickness, of oxides and other compounds definitely attached to the surface of the metal. Further, the surface of the metal must not be unduly roughened in the processes unless this is specially desired.

Grease Removal. First and foremost comes the removal of all greasy materials which would prevent adhesion of deposits and also the uniform attack by the corrosive dips designed to remove scale. Two types of grease materials have to be recognized: (1) Mineral compounds, mainly mineral oils, and (2) Fatty compounds, including oils and fats of vegetable and animal origin. These greasy materials occur in vastly varying quantities on different types of work. They are removed by a number of processes involving (1) the application of solvents either liquid or vapour, (2) the chemical transformation to soluble compounds, usually by means of alkalis, and (3) by the process of emulsification in which they are broken up into sufficiently small globules so that they remain suspended in the cleaning fluid and are thus removed. Each type of treatment has its special application and will be referred to.

Degreasing with Trichlorethylene. There are numerous occasions in industry when de-greasing becomes essential. The use of organic solvents provides a simple process with, however, the serious disadvantage of inflammability and explosiveness. Many otherwise suitable solvents necessitate elaborate fire prevention precautions and high insurance premiums. These dangers are, however, entirely eliminated by the use of solvents of the chlorinated hydrocarbon type, the outstanding example of which is trichlorethylene. The use of this substance has become widespread with the progress of the industry. Trichlorethylene is a non-inflammable liquid, easy to handle and eminently suitable for pre-plating degreasing. Its boiling point is 86·7° C. and freezing point – 73° C. Its specific heat is ·24 requiring therefore only one-quarter of the heat of water to effect the same rise in temperature. Another great advantage is its low latent heat of evaporation—viz. 57 calories per gram—only one-ninth of that of water. A minimum amount of heat is therefore required to produce the vapour from the cold liquid. As the properties and quantity of de-greasing material to be removed vary, so the types of plant and process employing trichlorethylene vary. In some types of plant, the greasy articles are subjected to the solvent action of the liquid formed by condensation on the surface of the articles; in others, the work is immersed in the boiling liquid, and yet again, in others, it is subject to both liquid and vapour treatment.

The plants for this purpose are compact and self-contained, requiring only a source of heat which may be steam, gas, electricity, or even crude oil, a supply of cooling water and connection to a water drain. They operate on well-defined principles each with its definite application. Where grease is to be removed and the subsequent process is not too critical, it may be sufficient to degrease by the "straight vapour" method. This is done in a simple type of plant which consists in effect of a rectangular tank containing the trichlorethylene in the bottom, arranged for a suitable method of heating, and provided with a condensing coil round the sides near the top to maintain this solvent vapour at an approximately constant level. The trichlorethylene is boiled, filling the plant with vapour, and the greasy work, placed in baskets, or suitably suspended, is introduced in the vapour when the vapour solvent condensing on its surface runs off, removing the grease, which is carried to the bottom of the tank where it

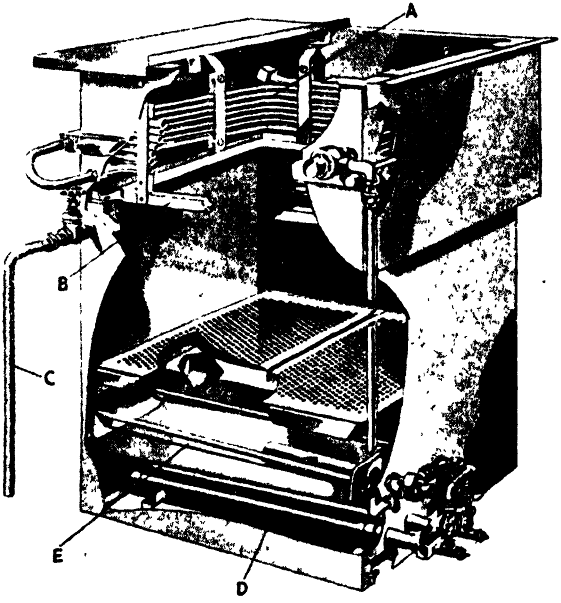

FIG 74. GAS-HEATED STRAIGHT VAPOUR DEGREASING PLANT

A = Cooling coils.
B = Distillate trough
C = Distillate pipe-off.
D = Gas burners.
E = Trichlorethylene sump.

accumulates in the sump liquor, and has to be periodically removed. The work dries as removed from the vapour with a minimum of grease on its surface.

A typical straight vapour plant is shown in Fig. 74.

For the purposes of pre-plating the process must be much more thorough in view of the critical after-operations. The problem, too, is complicated by the presence of polishing solids on the work. It therefore becomes necessary to combine with the vapour method that of washing in the hot liquid solvent.

The usual procedure is a liquor wash followed by vapour treatment (or washing in a series of boiling liquid baths of increasing cleanliness and carried out in a "multi-liquor" plant). By first immersing the work in the liquor, the tripoli powder, for example, is transferred from suspension in solidified grease to suspension in solvent, in which form it is easily dispersed by the boiling liquid.

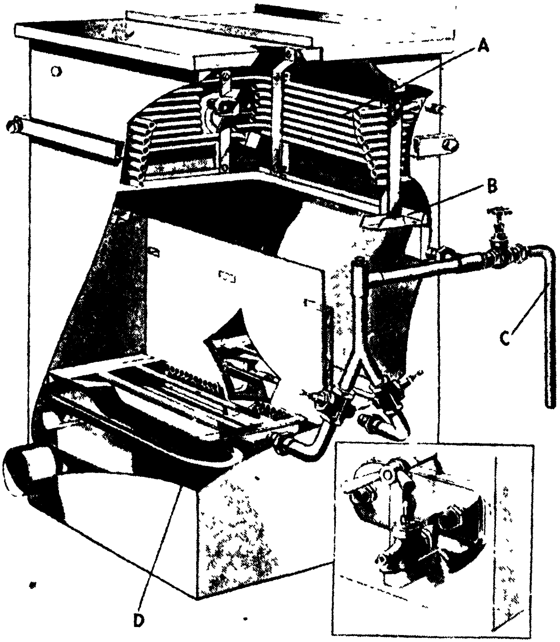

FIG. 75. LIQUOR-VAPOUR PLANT SHOWING THE TWO COMPARTMENTS
Inset shows detail of improved mud-door for cleaning out the plant

A = Cooling coils.
B = Slung distillate trough.
C = Distillate pipe-off for solvent recovery.
D = Steam-heating coil.

With liquor-vapour plants the work may then be transferred to the vapour compartment for the final cleaning and drying, the complete operation taking only about three minutes (Fig. 75).

A two-liquor degreasing plant is very suitable for degreasing zinc base die-castings and all classes of metal work before bright nickel plating, which demands a high standard of cleanliness of the metal surface.

After grease mopping, the work is immersed in the first compartment, in which the rapidly boiling solvent releases and disperses the grease-bound polishing compound. After a few minutes of this treatment, the work is transferred to the second compartment containing clean liquid solvent which swills away any impurities carried over from the first cleaning.

While the solvent is boiling the dissolved grease and suspended dirt are being collected in the concentration compartment at the back of the plant. The clean vapour from this compartment is condensed and fed into the bottom of the clean liquor compartment. In this way all impurities are displaced over a weir in the bottom of the first liquor compartment, the dirty liquor from the bottom of which is, in turn, displaced into the concentrator.

The work is therefore thoroughly degreased and washed in a continuously self-cleaning liquor bath. So treated, it requires only a short period of immersion in the electrolytic alkaline cleaning bath, which is enabled to fulfil its proper wetting-out function.

A multi-liquor plant may contain four compartments, the first three containing the heated solvent, while the fourth is known as the concentrating compartment. These compartments conveniently overflow one into the other. The first compartment is continuously fed with fresh distillate while the last compartment, accumulating the dirty solvent, is operated to distil off the solvent, leaving the grease behind for periodical removal. Should the plant become foul in all compartments owing, for example, to an exceptional run of work, it is only necessary to leave the plant idling for a period—say during the lunch hour—for the self-cleaning action to restore the first and second compartments.

Should water inadvertently gain access to the plant, it may give rise to staining and will cause the solvent vapour to form a fog. By a special device, the bulk of the water may be removed gravitationally, while the last traces are removed by passing the solvent through a filter of soda ash.

Any trichlorethylene adhering to the work after removal may be dried off in a heated oven which is fitted in other types of plant.

Though non-inflammable, care should still be taken in its use. The vapour should not be inhaled. It causes drowsiness and unconsciousness, and in extreme cases, death. As the vapour undergoes chemical change with high temperature producing injurious gases, it should not be exposed to naked lights. Smoking should not be indulged in while in contact with the vapour.

The method gives a clean surface prior to a brief, final chemical or electro-chemical process, and has therefore become an essential part of the plating equipment. The complete removal of grease permits of the more uniform attack of other cleaning baths, the more perfect work leading to less stripping with fewer rejections and hence a reduced cost per piece. By this method all types of grease are removed.

Mineral Greases. These non-saponifiable materials, commonly used in the composition of polishing compounds together with other non-saponifiable products can also be removed by the use of such solvents as carbon tetrachloride, petrol and benzine. Carbon tetrachloride is non-inflammable and therefore has its advantages over the other two inflammable materials, which involve a certain amount of risk. Vapour and liquid degreasing is undoubtedly the more popular and successful treatment followed by further operation of alkaline or electrolytic cleaning to ensure the removal of the last traces of greases left from the previous operations.

Alkali Cleaning. Fatty compounds are composed of basic and acidic parts which are separated by the action of a hot caustic alkali, for example, potash. By this treatment the insoluble fats are converted into soluble compounds by the general reaction—

$$\begin{array}{c}\text{Insoluble}\\\text{fatty compound}\end{array} + \text{Potash} \rightarrow \begin{array}{c}\text{Soluble}\\\text{soap}\end{array} + \text{Glycerine}$$

For example—

$$\underset{\substack{\text{glyceryl stearate}\\\text{(stearin)}}}{C_3H_5\,(C_{17}H_{35}COO)_3} + 3KOH = \underset{\substack{\text{potassium stearate}\\\text{(soft soap)}}}{3C_{17}H_{35}COOK} + C_3H_5(OH)_3$$

Both products are soluble, and the absence of grease is seen by the even flow of water over the surface.

For many years this operation was effected by boiling and scouring the work with a crude potash solution containing ½ lb. American potash per gallon (50 grm. per litre). This, in general, proved effective. In course of time, the alkali loses its property in virtue of its conversion into other materials, and also to some extent by absorption of carbonic acid gas. This process of chemically converting the fat or oil into soluble compounds, the chief of which is soap, is called *saponification*. During the process small amounts of mineral grease are also removed.

3. Emulsification. This removal of small quantities of unsaponifiable material by potash led to the view that the removal of grease might be, to some extent, mechanical as well as chemical. It is now well recognized that much of the grease is removed not by chemical action but by what is called *emulsification*, that is, its extreme subdivision, so that it appears to become dissolved. Many insoluble oils can, by shaking or other processes of agitation, be broken down to such extremely fine particles that they show no signs of separating as insoluble oils. Many medicinal emulsions illustrate this fact. The process of emulsification plays its important part in the cleaning of metals. It is found possible to effect it with much weaker caustic liquors than were formerly used. Mild alkalis such as sodium carbonate are more effective than was once imagined, and to such a solution, materials such as sodium silicate (water glass), sodium phosphate, sodium aluminate and borax are now added. Several of these form fine precipitates, and these, scouring against the greasy surface, effect the fine grinding of the grease, thus bringing about its emulsification and therefore removal. In any case a small proportion of caustic alkali, now commonly caustic soda, is present. This mechanical subdivision of the grease is illustrated when cleaning the hands with a minimum of soap and some fine pumice powder.

It is almost impossible to write down definite recipes for these cleaning mixtures. They are capable of wide variation, partly according to the nature of the metal to be cleaned and the dirt to be removed. A typical formula may be taken as follows—

Soda ash (Na_2CO_3)	6 oz.	40 grm.
Caustic soda ($NaOH$)	2 „	13 „
Tri-sodium phosphate (Na_3PO_4)	2 „	13 „
Sodium cyanide ($NaCN$)	2 „	13 „
Sodium silicate	1 „	6·25 „
Water	1 gal.	1 litre.

The presence of the sodium cyanide prevents the staining of the work and the sodium silicate exerts an abrasive action on the work. It should be observed that while such metals as zinc, aluminium, and tin are much less soluble in such a liquid than in a strong caustic solution, there is nothing to be gained by leaving them longer than absolutely necessary in the cleaning liquids on account of the solvent action of these liquids on such active metals.

Wetting. The problems associated with the cleaning of metal surfaces are of far greater complexity than was once thought to be the case. These take into account a number of properties of both the metal surfaces and the solutions. In the first case the metal surface has to be "wetted," that is, the interfacial stresses between the solid and liquid have to be overcome. Soaps are excellent reagents for this purpose. Soaps further possess the power of emulsification of oils and greases and therefore assist in the removal of the dirt usually associated with them. Again, many of the reagents used in cleaning, especially those of the alkali type, possess a remarkable degree of adhesion to the metal surface, and therefore an adequate and even ample supply of rinsing water must be used. A very dilute acid rinse is the safest precaution, the remaining dilute acid being much more easily removed by rinsing.

These and other aspects of the cleaning processes are referred to in a number of contributions to the literature of electrodeposition by Mitchell[*] and other workers.[†]

Use of Alkali Phosphate Solutions. One advantage of the use of phosphate solutions for cleaning would appear to be the fact that where solution is retained, even in very small amount in porous metals, there is the likelihood that with iron and steel it will form an insoluble phosphate, which is generally regarded as having protective properties. What is known as

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[*] *Mon. Rev. A.E.P.S.*, March, 1935.

[†] *J. Electrodepos. Tech. Soc.*, 1931, vii, 157; *ibid.*, 1934, x, 159.

Coslettizing involves passing the clean iron or steel article through a solution of what is called acid phosphate of zinc, thereby developing on the surface a layer of zinc phosphate. This is insoluble and non-hygroscopic, and is thus protective. The process was largely applied on cycle work prior to enamelling. Similarly, while sodium phosphate has alkalinity, it has the added advantage of producing an insoluble product if left in the pores of the metal. This product is stable, and does not undergo repeated decomposition, with the promotion of corrosion, as is the case with sulphates and chlorides. The use of sodium phosphate is, therefore, recommended in ordinary and electrolytic cleaning solutions.

Quite a number of other suggestions have been made as to the removal of any chemicals which might subsequently promote the corrosion of the metal after drying and lacquering. These generally aim at the removal of substances which form soluble salts with the metals, and their substitution by compounds which, in the event of being left in the pores of the metal, will form insoluble compounds, which stand some chance of inhibiting further action. Passing the work through a weak phosphoric acid solution prior to final rinsing might be relied upon to achieve this. Any phosphoric acid left in the pores of the metal would be absorbed by the formation of insoluble metallic phosphates, thus terminating the corrosive attack, whereas chlorides would, if left in the pores, first form chlorides of the metals and these, decomposed later, set free the hydrochloric acid to repeat continually its corrosive work.

Electrolytic Cleaning. This method has of recent years come into extended use. It is a simple process. In a suitable liquid contained in an iron tank which is made anode, the work is suspended as a cathode and a heavy current put upon it. Large volumes of hydrogen are given off and the grease is quickly removed.

In general the liquid is of the same character as those outlined above, the quantities being varied to suit the metal under treatment. The cleansing action is due to several causes. In the first place the electrolysis of all the substances in the solution leads to the production of caustic soda on the cathode exactly where it is needed. Secondly, there is the scouring action of the gas, much of which is deposited under the grease film and thus lifts it off. In fact, with a large amount of grease the removal is obviously mechanical, and the grease rises to and floats upon the surface of the solution, and may even be ladled from it. Thirdly, there is also the scouring action of the fine solids in the solution where these are present. The process is very effective and largely used. With it there is the fear of insufficient current due to too small conductors. Further, some platers prefer to make the work cathode, and then, towards the end of the process, reverse the current by a special switch, and for a short time make the work anode. One advantage which this reversal might effect is the removal of any layer of adherent hydrogen on the surface of the metal. Otherwise it seems inadvisable to run the risk of oxidation of the work by the active anodic oxygen evolved.

One other point in this connection may be noted. The metals lead, tin, zinc, and aluminium are particularly susceptible to solution in these alkaline liquids. When these metals are being treated some metal is sure to pass into the solution and this, in turn, will be deposited upon the work undergoing treatment. To remove this deposit the work may be made anode for a few seconds only, this being the chief justification for anodic treatment in electrolytic cleaning.

If, however, this reversal is effected in the same tank there is the opportunity for the deposit now made on the tank to re-dissolve when the tank is again made anode. These dissolved metals thus accumulate. This may be avoided by the use of a separate smaller tank for the reversed process.

Lower concentration solutions can be employed than when still solutions are used, on account of caustic soda produced as a product of electrolysis at the cathode, and thus the time of the cleaning operation is reduced considerably with lowering of costs and increase of capacity.

Electro-cleaning prior to chromium-plating is to be avoided on nickel-plated work, as it will cause passivity of the metal surfaces.

The use of an exhaust system for removing steam and spray is recommended, especially in large automatic plants where corrosion of the metal equipment of the conveyer, and electrical connections, may cause trouble. Time, temperature, and current are of extreme importance.

Work must be transferred from cleaner to rinses, without loss of time, to prevent surface from drying, and formation of stain thereby. It is often found that the use of hot soaking solutions made up with either straight soap or soap compounds, prove most efficient for the removal of buffing compositions from metals, as they have the ability to soften and penetrate through a soaking action, making it easier for a subsequent removal of the dirty material in the electro-cleaner.

Electrolytic cleaning practice is undergoing some change. At one time, cathodic cleaning only was employed, because the volume of hydrogen liberated at the cathode is double that of the oxygen liberated at the anode, and it was argued that this factor operated in favour of making the article cathode. Of late, however, less importance has been attached to the scouring action of the evolved gas, and more to the plating off effect of solid particle dirt which has become positively charged in the alkaline bath, and. by the process known as electrophoresis, migrates to the negative pole.

Hydrogen absorptions at the cathode, are also avoided. Any passivity of the metal due to absorptions of oxygen, can be removed by a subsequent dip in weak sulphuric acid. Metals such as aluminium, zinc, or die-casting alloys, must be cleaned cathodically, as they corrode anodically.

NOTES ON CLEANING

Methods of Suspending Work in Cleaner. The greatest care should be taken in suspending work in the cleaner to ensure that all parts of the surface receive equal chemical treatment. For this reason the practice of bunching the work on wires is not to be recommended, as obviously by this method only the outer surface of the article receives full treatment.

It is therefore more advantageous to suspend the work on racks or frames in such a manner that no two articles touch one another.

Maintenance of Cleaning Solution. Attention should be given to maintaining all cleaning solutions at full strength. Replenishing the cleaning bath in a haphazard manner should be avoided. It is of little use to add fresh chemicals to a solution already loaded with dirt and grease, and the surface of the solution should be skimmed daily in order to remove any accumulation of scum.

One useful method is to have the cleaning tank fitted with a partition across one end, leaving a trough about 3 in. wide, fitted with a drain tap, so that when the bath is made up for evaporation losses, the scum can be skimmed off over the partition, and the solution left clean for further use.

Combined Cleaning and Coppering. As so much work requires to be coppered in the cyanide solution there seems to be the possibility of combining the cleaning and coppering into a single operation. This is commonly done. It involves the addition of copper cyanide to the cleaning bath, the two operations proceeding simultaneously. This may be regarded as an equivalent to the striking bath in the case of silvering base metals. A formula for the cleaning and coppering bath may be taken as follows—

Caustic soda	8 oz.	50 gm.
Sodium cyanide	8 ,,	50 ,,
Sodium carbonate	8 ,,	50 ,,
Copper cyanide	4 ,,	25 ,,
Water	1 gal.	1 litre.

When the work is chemically clean the copper will be deposited over the entire surface, and this constitutes a guide to complete cleaning. Copper anodes are used in this process in place of the usual iron anodes.

Such a combined operation, however, is not intended to replace that of the removal of the bulk of the dirt by the ordinary cleaning methods. There is no suggestion of using a modified coppering bath on the surface of which a scum of dirt is continually forming and requiring removal. The combined operation is intended only to simplify the preliminary cleaning operations, while still guaranteeing a subsequent satisfactory deposit of copper.

From a chemical study* of alkaline cyanide degreasing and coppering baths it has been shown that sodium cyanide is lost from the bath mainly by its oxidation to sodium cyanate which accumulates in the solution. Its presence, however, seems not to be altogether disadvantageous in that new baths practically free from this cyanate do not appear to degrease so satisfactorily as those which have been in use for some time.

Acid Pickling and Dipping. Subsequent to the removal of grease there comes the important problem of removing either

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* Chaybany: *Proc. 1st I.E.C., E.T.S.*, March, 1937.

thick scale or thin films of tarnish and chemical compounds which have been acquired mainly during the heat treatment attached to the modern manufacturing processes.

During annealing, for example, all the ordinary metals acquire deposits of oxides, and these are not infrequently well burnt in and not easily removed. The treatment required depends largely upon the metal, and, in general, four groups of metals and alloys may be recognized as requiring somewhat different methods of treatment. These are: (1) Copper and its alloys; (2) iron and steel; (3) zinc and aluminium and their alloys; and (4) the lead-tin alloys. No single method of treatment serves for them all. The acids used depend primarily upon the nature of the metals and their oxides.

Again, chemical analysis reveals the fact that usually far more material is removed from the surface of the metal than is found in the acid solution. What appears to take place is that the porous scales permit the acid to penetrate them and attack the metal beneath, scale being lifted off mechanically in layers by the evolved gas, and falling to the bottom of the tank. There they may subsequently slowly dissolve.

Inhibitors. The removal of these scales of oxides in the case of many metals is a more complicated process than appears at first sight. The oxides formed in the annealing processes through which these metals pass in the several stages of manufacture are usually not of uniform composition. In the case of copper, while the outer layer is doubtless of the black cupric oxide, the inner layer nearer the metal will be of the reddish cuprous oxide. This is an easily observed fact. Similar conditions prevail in the case of iron. The outer layer is likely to be of the more oxidized type of ferric oxide (Fe_2O_3), while that adjacent to the metal will surely be of the ferrous type (FeO). The intermediate layer will probably show the intermediate composition corresponding to Fe_3O_4. These outer layers are none too soluble except in relatively hot and strong acid which will naturally "go" for the unoxidized metal, wherever it may be exposed and particularly through the numerous pores in the scale. This attack has considerable disadvantages. It involves loss of metal, high consumption of acid and, with the liberation of so much hydrogen on the surface of the metal, may induce to embrittlement. Some restraining influence, provided by an inhibitor, will be extremely advantageous. It is not difficult to idealize the essentials of such an inhibitor. Its characteristics will be—

1. Easy and complete solubility in the acid.
2. Stability over a wide range of strengths of acid and operating temperatures.
3. Stability over long periods in storage.
4. Free rinsing in soft and hard water.
5. High efficiency involving therefore minimum consumption, and
6. Preferably in the salt form, facilitating transport and storage.

Many substances have been suggested and used with varying degrees of success for this purpose. They may be divided into two groups—

1. Inorganic type, and
2. Organic type.

These would appear to function in very different ways. Amongst the inorganic type are the compounds of arsenic and antimony (e.g. $SbCl_3$). They are used freely in the stripping of deposits in the determination of thickness (page 426). These metals are electro-positive, that is they are more "noble" than iron. They are deposited on the iron by "simple immersion" and there, by reason of the higher over-voltage to hydrogen, resist the evolution of this gas and thus prevent the solution of the metal which displaces the hydrogen from the acid. Those of the organic class function quite differently. They are compounds of high molecular weight. They behave generally like colloids. In the path of the numerous small currents they migrate to the surface of the metal and, congregating there, form a thin film of high resistance which reduces the current and therefore hinders the solution of the metal which gives rise to the current. Or they may be adsorbed on the surface of the metal with a similar result.

It is suggested* that their efficiency is proportional to their molecular weight. In any case it might be possible to give to these inhibitors some quantitative figure for their efficiency. Thus the reduction of the loss of metal in the presence of the inhibitor might be expressed as a fraction or percentage of the

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* Private communication from Mr. F. Taylor.

loss without the inhibitor. The matter is one of which the importance may justify some quantitative investigation.

It will now be convenient to consider the various metals and alloys in the order above mentioned.

Copper and its Alloys. Prominent copper alloys are shown in Table L.

TABLE L

COPPER ALLOYS

	Copper	Zinc	Tin	Nickel	Description
Brasses	70	30			Cartridge brass. Works well in cold.
	66	34			Ordinary brass, casts and works well.
	60	40			Resists corrosion.
	50	50			Common brass for castings.
Bronzes	90		10		Tough and strong. Gun-metal.
	80		20		Hard, brittle and sonorous. Bell metal.
	66		34		Hard, white and brittle. Takes a high polish. Speculum metal.
	95	1	4		Coinage bronze.
	60	25		15	Nickel silver. Average composition.
	80			20	Cupro-nickel. White, tough, draws well.

These metals usually emanate from the manufacturing processes in a tolerably clean condition, with little more than the grease left from a number of finishing operations. In every case, however, there is a slight coating of oxide which must be removed, and this is usually effected by a mixture of strong acids. On occasion, however, there may be appreciable scales of oxides, and we are, therefore, mainly concerned with these oxides of copper and zinc.

Again, the acids which most effectively remove oxide scales are not calculated to leave the type of bright surface desired as a finish when no further finishing can be undertaken. This, therefore, necessitates the use of a further acid dip designed to impart as bright a surface as possible. These dips are respectively called *scaling* and *bright* dips. While their constituents are the same, their proportions differ sufficiently to effect a marked difference in the finished product. The three acids, sulphuric, nitric, and hydrochloric, are all used. Their mixture is in no haphazard proportion. The action of the acids on both copper and zinc has been carefully studied with a view to producing dips which will give definite results.

Several of these results may be referred to. The sulphuric acid in general prevents rapid attack by the nitric acid, and thus maintains much smoother surfaces than could be achieved with nitric acid alone. Again, the action of these acids is dependent upon their degree of dissociation, this being comparatively small in the proportion which occurs in these formulae. Hydrochloric acid is operative in maintaining the solution of both constituents of brass to the same degree, thereby producing a good yellow colour of the dipped metal. In the absence of hydrochloric acid, nitric acid preferentially attacks copper, and leaves a dull whitish surface. A limited amount of hydrochloric acid corrects this defect, while excess of hydrochloric acid preferentially dissolves the zinc, leaving excess of copper on the surface. Dips are sometimes used warm, and this tends to greater solution of zinc, with redder results on brass.

Two satisfactory dips for brass and copper are as follows—

	Scaling Dip	Bright Dip
Sulphuric acid (Sp.Gr. 1·84) .	380 c.c. 136 fl. oz.	435 c.c. 142 fl. oz.
Nitric acid (Sp.Gr. 1·38) . .	72 c.c. 26 „ „	75 c.c. 23·5 „ „
Hydrochloric acid (Sp.Gr. 1·17)	5 c.c. 2 „ „	2 c.c. ⅔ „ „
Water	444 c.c. 1 gal.	491 c.c. 1 gal.

These dips accumulate copper and zinc in course of use. With either or both of the nitric and hydrochloric acids attacking the metal, the nitrates and chlorides first formed are immediately converted into sulphates, thus leaving the acids free for further attack. There is a marked difference with the two dips, and it must be added that manipulation does much towards correct dipping.

Occasionally an intermediate dipping acid is used. Something depends upon the "taste" and experience of the operator, and it may further be added that there are different departments even in brass dipping, justifying the allocation of different classes of work to different operators according to their individual skill. Acid dipping is far from being an unskilled job.

To these dips addition agents are occasionally added. Many of these have been tried. It may seem almost ludicrous to suggest the addition of a little soot to an acid dip, but it may nevertheless have some inhibitive effect, it being known that soot addition will, to some extent, correct the defects arising from an excess of hydrochloric acid.

Manipulation presupposes that all work to be dipped is free from grease. In the presence of grease the attack of the acids must necessarily be irregular and the results unsatisfactory.

Iron and Steel Work. This class of metals requires pickling to remove fairly adherent scale. This scale is a mixture of iron and iron oxide. It is usually porous. The acid pickle used finds its way through these pores, attacks the metal below, and the gas evolved lifts off large flakes of scale, which either fall off or are readily removed by scouring. For this purpose either sulphuric or hydrochloric acids are used. The latter is more frequently employed, as the ferrous chloride produced is very much more soluble than the sulphate. Different workers have different methods of using the acid. Some prefer to start with almost new acid and continue to use it until it is no longer of service, then throwing it away. Others prefer to keep the acid up to a given strength by scrapping a part of the solution from time to time and adding new acid in like proportion. The addition of soot is sometimes recommended, and this may be beneficial in adding to the liquid a material of a colloidal type which, during removal of the scale, is deposited on the exposed iron, thus protecting it from excessive attack. Patented compounds of this type may be particularly useful where pickling is severe, to remove scale which has, during rolling of the sheet, penetrated the surface of the metal, and is therefore difficult of removal.

The frequently experienced difficulty in cleaning rolled steel is due, it is suggested by Lyon,* to the deposit of

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* *Trans. Electrochem. Soc.*, 80, 1941, 367.

carbon resulting from the decomposition of the lubricants applied in the rolling process and this calls for more intensive methods of treatment.

Embrittlement of Steel. Apart from the chemical changes effected during the pickling of iron and steel, others of a sufficiently serious nature occur. One of the most important is that of the acquisition of brittleness. This occurs when the metals are treated with acids such as sulphuric, hydrochloric, or hydrofluoric, from which hydrogen is necessarily deposited. It occurs to a much lesser extent with nitric acid from which hydrogen evolution barely, if at all, takes place.

This brittleness may be got rid of to a large extent by subsequently heating the metal to a temperature of from 100° C. to 150° C. or even by immersion in boiling water. It is considered to be due to the absorption of hydrogen, similar *occlusion* also taking place during plating processes, and with zinc occurs with equal facility with both the sulphate and cyanide solution. It is an admitted trouble in plating and can be minimized by the use of solutions of high metal concentration, with little or no acid, applying only a small current density and keeping the solution both warm and agitated. The whole problem is one which merits, and is doubtless attracting, close investigation.

Zinc, Aluminium, and their Alloys. Of these the following (Table LI) may be mentioned with the note that their compositions are very variable. More exact information should be obtained from the relevant metallurgical literature.

TABLE LI

ALUMINIUM ZINC ALLOYS

Al	Zn	Cu	Mg	Mn	Description
80–98	1–15	1–15	0–1·5		Alloys for casting. Very variable.
94	0·25	4	0·4	0·6	Duralumin (includes about 0·5 per cent of Fe and Si as impurities in the aluminium).
4–22	78–93	0·3	0·1		Die-casting alloys. Very variable.

These metals are readily attacked and dissolved by strong caustic solutions. They can therefore only be treated in cleaners of the mild alkali type containing sodium carbonate, phosphate, and meta-silicate. Used electrolytically these solutions produce alkali on the cathode work which, combined with the scouring action of the flocculated silica, effects the necessary removal of grease with limited exposure to the alkali solution.

Lead, Tin, and their Alloys. These again are numerous in the various branches of industry. A few only are now given in Table LII.

TABLE LII

LEAD TIN ALLOYS

Pb	S	Sb	Zn	
66	34			Plumbers' solder.
32	68			Tinsmiths' solder.
25	75			Pewter.
6–8	75–94	5–7·5	1–9	Britannia metal.
80		20		Type metal.
60	20	20		Stereotype metal.

These compositions are only approximate. Pewter and Britannia metal are most commonly silver-plated, while stereotype plates are often faced with nickel for added endurance.

These provide a still further group of metals demanding special treatment in pickling. Usually they are not treated with acids. Further, potash attacks them by prolonged treatment. The most serviceable treatment is that of electrolytic cleaning in solutions as free as possible from caustic alkalis, and therefore made up from soda ash with the addition of tri-sodium phosphate. This treatment has proved to be sufficient for many types of castings. Where these metals are to be silver-plated they are removed straight from such an electrolytic cleaner to a striking bath to receive a first coat of silver, which is then scratch-brushed, and, after rinsing, the articles are transferred to the main plating tank.

Scouring. The dirt and scale loosened by the various processes of pickling now require removal by some simple mechanical process. A very common method is that of the application of a wet brush, generally of bristle, with or without the application of an abrasive, usually ordinary sand or fine pumice. A special type of trough, with a sliding shelf and divided into two compartments, is in common use. One side is kept clean with running water while preliminary rinsing is done in the other. During scouring, the work can be plentifully washed with water from a hose attached to the tap, and after this preparation the cleaned work is left suspended in the clean water until a batch is transferred to the plating tank.

In view of the fact that many large plants for nickel-plating operate almost automatically, it is evident that hand scouring must be dispensed with and this without detriment to the process.

The Acid Etch. Where work has to be handled on a very large scale the operation of scouring must necessarily be substituted by an equally efficient operation for the removal of scale. This is now largely achieved by the *acid etch.*

The process involves making the work the anode for a relatively short time in the acid bath, the lead lining usually constituting the cathode.

Sulphuric acid is commonly used. An acid of 60° B. density (from 75 to 80 per cent by weight) is common and this is used at ordinary temperature, say 16° C. This is suited to ferrous work, the time of treatment being only a minute or a little more.

This process, incidentally, eliminates embrittlement,* and is now much used.

Non-ferrous work was formerly, but not so successfully, treated in the same manner, until a new acid etch was proposed by A. W. Hothersall † which makes use of a solution of ammonium citrate (made by neutralizing 50 gm. citric acid with ammonia) with from 10 to 20 gm. free citric acid per litre. A recent description of the process suggested the use of a C.D. of 45 amperes per sq. ft. for 30 seconds. On leaving the solution the work has a greyish-blue coloration, which disappears on rinsing. With a lower C.D. of 5 to 10 amperes per sq. ft., film formation does not occur, and this condition is to be preferred.

Alternatively, a 5 per cent solution of "cyanide" may be used. These processes justify the term *anodic etching.*

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* Sutton: *J. Electrodepos. Tech. Soc.*, 1936, xi.

† *J. Electrodepos. Tech. Soc.*, 1932, vii, 135.

Scratch-Brushing. This alternative operation for removing loosened scale has, by the choice of brushes of suitable wires, the advantage of brightening the surface. For small work the brush revolves on a foot lathe. For larger work the lathe can be operated by power. Brushes suitable for both lathe and hand work are shown in Figs. 76 and 77. The common types are of brass, nickel silver, or steel wire, and each of these metals may be of different degree of hardness. The wires are fixed in a wooden stock, being soldered in to give greater strength. Steel wires are suitable for coarse work while many grades of brass are used for the general run of brass and other similar work. Fine crimped brass wire brushes are serviceable for soft metals such as in gilding and silvering, and also for imparting a fine matt surface. In addition to the usual type of circular brush, others of various shapes for different purposes are stocked, so that all parts of very irregular work can be treated. Brushes of average diameter run at about 600–700 r.p.m., a higher rate being required for smaller diameters.

The operation of scratch-brushing is applied not only in cleaning the work but also during deposition of some metals where a smooth finish is required, the deposit being occasionally scratch-brushed to remove slight roughness, and thus maintain a more uniform deposit. This is essential where thick deposits are required with a fair degree of smoothness.

Final Rinsing. Whatever operation may have been performed with metals, special care must be taken before plating to remove from the surface all traces of chemical substances which have been used in the several operations. These—for example dips—have been employed because of their corrosive attack on the metals in cleaning them. Such chemicals cling to the surface of the metals with a tenacity greater than would ordinarily be appreciated. This slight residue of liquids, especially in the case of porous metals, is responsible for much trouble, which frequently does not become apparent until after the work has been lacquered and even kept in stock for a time. Their complete removal must be ensured by repeated rinsing.

This trouble occurs even with smooth metals. It is far greater with porous metals, and leads to the trouble of *spotting out.* Reference is made to this trouble under the different

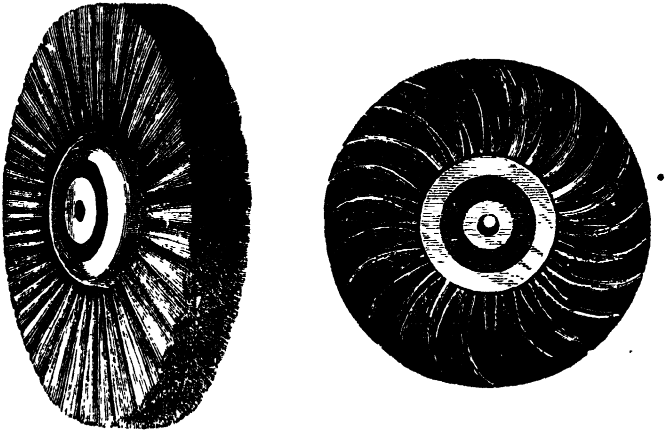

FIG. 76. SCRATCH-BRUSHES FOR EXTERNAL WORK

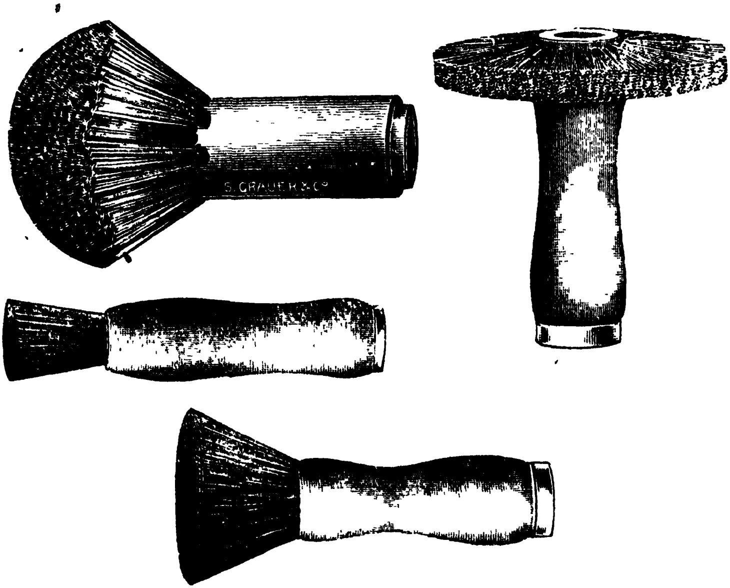

FIG. 77. SCRATCH-BRUSHES FOR INTERIORS

metals treated. In general, however, it may be suggested that more efficient final rinsing would cure many of these ills, the work requiring something more than merely passing through water. Where the metal is likely to be porous, the alternate use of hot and cold rinsing water has the advantage of closing up the pores of the metal with hot rinsing, thereby squeezing out the contained solutions, and drawing in clean water when rinsed in cold water.

This spotting out trouble is an insidious one. At present there is no all-round cure for it. Scientific work and practical experience are agreed as to the causes and also, as far as can be applied, the remedies. Porosity of base metal is the main cause. The depositor has no control over this factor. Within experience, metal is sometimes so porous as to admit the passage of oil, under even a slight pressure, through it sufficiently to lift off a deposit without there being any sign of corrosion, which might attach the blame to the plater.

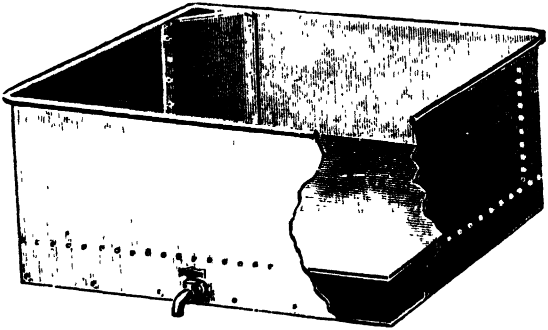

FIG. 78. SAWDUST PAN

As far as possible, though this cannot be regarded as practicable, cyanide liquids should be eliminated from the reagents used in the various processes. Especial care should be taken with the final rinsing, and drying should be as thorough as possible by the use of dry air. Barrelling or burnishing close up pores, and where practicable, are beneficial. Time should be allowed between final drying and lacquering, and only the best lacquers, substantially applied, should be used.

Too much attention cannot be paid to the importance of swilling the work after each operation in clean water, in order to avoid, as far as possible, the carrying over of solutions from tank to tank which, on account of their chemical interaction, may severely interfere with the plating process.

For this reason air agitated swills are to be recommended, and where air agitation and filtration equipment already forms part of the nickel plating plant, the additional cost of carrying the necessary air supply to the swill tanks will be amply repaid.

Chemically cleaned, and also deposited, metals are also prone to tarnishing, and to give these surfaces greater permanence a final rinse through a very weak solution of a soap solution compounded with whale oil soap leaves, even after a final rinse in clean water, a faint trace of soap on the surface of the metal, which has the advantage of a small degree of protection from finger prints in handling prior to lacquering.

Drying Out. Finally the work has to be freed from all traces of moisture. This is usually effected by passing through hot water and drying in warm sawdust. The wood dust should be free from resinous matter. Few woods are thus available, boxwood and maple being the most prominent. Without being too dusty, the sawdust should readily fall away from the dried work, the last traces being removed by the application of a soft brush.

Alternatively, the work may with advantage be dried in a current of warm air. This dries up the moisture left in crevices better than is possible with sawdust, and therefore ensures greater permanency. When used, sawdust is warmed in a pan of the type shown in Fig. 78, the bottom being false, and containing water, so that the flame does not come into contact with the base of the pan holding the sawdust. Centrifuging machines are used in dealing with numerous small parts, though they may not be considered as sufficiently effective.

CHAPTER XI

DEPOSITION OF COPPER

THE ACID BATH

INTRODUCTION—The solution—Theory of the process—Addition agents—Anodes—Current density—Thickness of copper deposits—Vats—Cathode materials—Acid copper troubles—Maintenance of composition—Coppering steel in the acid bath—Examples of thick deposition—Electrolytic copper extraction—Electrolytic refining—Analysis of solutions

Introduction. The deposition of copper has been carried on from the earliest days of commercial electrolysis, the process with copper sulphate being comparatively simple. Difficulties were for a long time encountered with copper-plating iron, and these were not satisfactorily solved till the advent of the cyanide solution. From the sulphate solution, however, thick deposits, such as were required for electro-typing, and, later, electrolytic refining of the metal, were obtained without much difficulty. In recent years copper deposition has found many applications which are not directly related to the production of comparatively thin deposits for protective or decorative purposes, these latter purposes usually covering the aims of the electro-plater. The modern process of nickel-plating calls for a substantial deposit of "acid" copper, so that the solution and process has gained additional interest on this account.

The Solution. The solution is of simple composition with some latitude of concentrations of its two main constituents, and may be as follows—

Copper sulphate (Bluestone) . . .	1½–2 lb.	150–200 gm.
Sulphuric acid (Oil of vitriol) . . .	4–6 oz.	25–37 gm.
Water	1 gal.	1 litre

The function of the copper sulphate is obvious. That of the acid is at least twofold. It largely adds conductance, and, in addition, prevents the formation of rough deposits, giving a finer type of crystal. The solution with some variation is largely used. It is found that in neutral copper sulphate there is the tendency to the formation of basic salts, with the production of spongy and rough deposits. The presence of acid prevents this, and, in addition, adds to the throwing power by the reduction of the number of free copper ions in the solution.

Theory of the Process. The chemistry of the process is relatively simple. Copper sulphate ionizes as follows—

$$CuSO_4 \rightleftarrows Cu^{\cdot\cdot} + SO_4^{--}$$ [illegible] [illegible]

The copper ions migrate to the cathode and, taking up a negative charge (in the form of electrons) from the cathode, become neutral copper atoms, which are deposited. A stream of electrons thus enters the system through the cathode. At the anode the SO_4 ion associates with copper ions formed at the anode, this formation being attended by the evolution of electrons, which pass away from the system via the anode. Ordinarily there are no subsidiary reactions, and as fast as copper is taken from the solution at the cathode an equal amount of the metal becomes converted into ions at the anode, thus maintaining the average strength of the solution fairly constant.

Concurrent with the migration of the copper ions, there is that of the numerous hydrogen ions which contribute largely to the total current.

As these hydrogen ions reach the cathode, they remain in the solution, copper ions being preferentially discharged and the copper deposited.

Addition Agents. Many additions have been made to the "acid copper" bath, as it is generally termed, with a view to improving the character of the deposit. There is no doubt that advantages do accrue from these additions. For this purpose, alum, glue, gelatine, phenol (carbolic acid), and several forms of sugar have been successfully used. Unfortunately, the control of these substances is difficult. Their determination by analysis is by no means easy, and very commonly, therefore, their use is dispensed with, as for the most part very successful deposition can be effected without them.

Additions of phenol (pure carbolic acid C_6H_5OH) are usually of the order of 1 gm. per litre. The quantity required is calculated, weighed out and mixed with approximately twice its volume of strong sulphuric acid. The mixture is warmed to 100° C. for an hour. Phenol sulphonic acid ($C_6H_4(OH)SO_3H$) is formed. The product is added to the bath with ample stirring.

Its beneficial effect is not immediate. Boughay* states that a current of about 400 ampere-hours per gallon of solution is required to bring it into condition. By that time little, if any, of the original phenol remains, and it is therefore highly probable that the essential addition agent is formed by this "ageing" of the solution. The ultimate products include hydro-quinone.

Anodes. These present little difficulty, the efficiency being almost theoretical. In fact, weighings made show rather an excess of metal dissolved over that required by Faraday's law. This is due to the fact that copper, like most metals, is crystalline, and the metal between the crystals is readily dissolved, leaving the crystals free to fall from the plate. A red powder at the bottom of the tank is sufficient evidence of this. This copper may, with other insoluble impurities, float in the solution, become attached to the cathode and cause roughness. Electrolytic copper is often used, and to avoid the trouble of handling the scraps of anodes which must inevitably be left, it has been proposed to deposit copper on perforated lead plates and use these as anodes. The copper can be used down to the last trace.

Current Density. In the solution mentioned above and used stationary a current density of 25 to 30 amperes per sq. ft. can safely be used. Where rapid deposition is required, without the necessity of a smooth surface, the C.D. can be considerably increased, especially with the application of some type of motion of the solution. Figures of C.D. go up to as high as 300 amperes per sq. ft., but these are exceptional. With low acid content, say less than ¼ lb. per gallon, the copper is soft and easily buffed, and this is required of the copper which forms the undercoat for nickel. Harder deposits result from higher acid content and the higher current densities which become possible with agitation.

Thickness of Copper Deposits. As copper is frequently deposited to considerable thickness, the accompanying table (LIII) will be found useful for the rapid calculation

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* *J. Electrodepos. Tech. Soc.*, 1934, ix.

of thickness from the known current density and time of deposition.

TABLE LIII

THICKNESS OF COPPER DEPOSITS FROM ACID BATH

Current efficiency 100%

Current Density Amp./Sq. Ft.	Thickness in Mils in			
	15 min.	30 Min.	60 Min.	120 Min.
10	0·14	0·28	0·565	1·13
20	0·28	0·56	1·13	2·26
30	0·42	0·85	1·70	3·4
40	0·56	1·12	2·24	4·48
50	0·70	1·41	2·82	5·65
60	0·85	1·70	3·4	6·8
70	0·99	1·97	3·95	7·9
80	1·13	2·26	4·52	9·04
90	1·27	2·54	5·08	10·2
100	1·41	2·82	5·65	11·3

Vats. This solution offers the largest choice of materials for vats. Usually wood tanks with linings of 6 lb. lead are employed. Occasionally, for large tanks, slate is substituted, while for small experiments, stoneware and glass are clean and insulating.

New wood linings not infrequently give rise to irregularities in deposition due to certain resins passing from the wood into the solution. These may for a time develop quite bright deposits of copper.

Cathode Materials. Unfortunately, the acid content and also the easy decomposition of the copper sulphate make this solution impossible for many metals usually requiring coppering. Brass and the usual copper alloys are practically the only metals which will stand the action of the solution. All base metals require treatment in an alternative solution Large quantities of copper are deposited from the sulphate solution on materials such as wax and other non-conducting materials after some treatment to render them conductive, these processes being applied in electro-typing. As an example, wood may be coppered by first soaking it in paraffin wax, drying, and black-leading. Other more fragile substances are chemically treated to produce on their surface a thin film of sulphide of silver, this imparting the needful degree of conductance.

Acid Copper Troubles. These are not numerous or difficult to remedy. Dark powdery deposits are due to excessive current for the state of motion of the solution. Anodes will usually work dark, the black residue being an oxide of copper which falls to the bottom of the tank. If the anode works bright this may be regarded as some sign of too great acidity. Throwing power is not expected to a large extent. If unduly low it can be improved by the addition of acid. The separation of crystals indicates the need for more water or, preferably, warming. While it is not usual to work the solution warm, this is sometimes done, the decreased resistance requiring a smaller P.D.

There are, however, other irregularities in acid copper-deposition which cannot directly be traced to the copper and acid content. These are especially noticeable when thick deposits are being made.

Usually a solution of such simple composition might be expected to work without complications over long periods, but this is far from the case with the acid copper bath. Protracted deposition reveals defects which are not apparent with small scale and intermittent work. These defects have been pointed out as the result of wide experience by Ollard.* They relate particularly to the physical character of the deposit. The solution is remarkably sensitive to very small quantities of colloids, one result being that the addition of one part of gelatine per 10,000 parts of solution will markedly modify the structure and hence the properties of the deposit. Such small amounts of substances are usually quite beyond the range of chemical analysis. Copper deposits may be required which are relatively soft. Hard deposits, frequently called for, are often accompanied by considerable internal stresses which give rise to cracking. The aim, therefore, will be to strike the happy medium. Thus a solution may give rise to deposits so soft as to be even with appreciable thickness almost as soft as lead. No simple explanation of this phenomenon is readily forthcoming. It may be that, under ordinary circumstances, unknown colloids are present and lead to the production of

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* *J. Electrodepos. Tech. Soc.*, 1937, xii, p. 35.

deposits which are normally satisfactory. Some new addition may then quite counteract this effect and thus yield a soft metal. Too hard deposits are in the main due to an excess of colloids the removal of which, though it may be effected readily on a small experimental scale, will defy large scale application. Treatment of such solutions with potassium permanganate may remove the colloid while any excess of the permanganate is then removed with hydrogen peroxide, preferably with warming and subsequent filtration. A remedy was found by slowly bubbling sulphur dioxide through the solution while working it with lead anodes, resinous matter rising as a scum which would be skimmed off from time to time.

Too rough deposits are usually the result of either too high a C.D. and also to the presence of suspended matter in the solution. This can be removed by filtration. Sometimes such suspended matter will insulate small areas of the deposit thereby producing pits. These defects are such as can be identified by some experience rather than by chemical analysis, and the watchful trained eye will then best indicate when they are likely to become objectionable, when remedial steps can then be taken.

Maintenance of Composition. With long continued operation there is the tendency for the acid copper bath to increase in copper content with a corresponding depreciation in the percentage of a free acid. This may in part be due to a somewhat higher anode than cathode efficiency and also to the fact that the anodes, especially at the waterline where they are exposed to the combined attack of both the acid and air, are appreciably corroded according to the following equation—

$$Cu + O + H_2SO_4 = CuSO_4 + H_2O$$

Again, copper anodes contain some cuprous oxide, which is not dissolved electrolytically, but chemically, either from the surface of the anode or from the bottom of the tank to which such material naturally falls.

The correction of this by the addition of acid would in course of time unduly load the bath with copper sulphate. A more convenient and practised method is that of running the bath for a time with lead anodes. The copper anodes may be transferred to the cathode bars and so pick up, without waste, the copper deposited during the process.

By this method the following reaction—

$$CuSO_4 + H_2O = Cu + H_2SO_4 + O$$

regenerates acid and the process may be carried on until the desired degree of acidity has been attained. It would appear that there should be no reason why the correction cannot be made by the substitution of lead plates for some of the anodes in the ordinary operation of the bath. It seems, however, to be preferred to make the correction a separate operation rather than combine the correction with the ordinary procedure of the bath.

Coppering Steel in the Acid Bath. So large is the amount of steel work requiring coppering that many attempts have been made to effect this directly in the acid bath. The most notable of these is that of immersing the cleaned steel in a preliminary bath containing 60 gm. of white arsenic (arsenious oxide, As_2O_3) per litre of strong hydrochloric acid (10 oz. per Imp. gallon). A film of arsenic is thus applied by simple immersion and, after rinsing, the work is transferred to the copper bath, where the film of arsenic should prevent the attack of the steel by the acid copper solution while the first copper is being deposited. The process has been applied commercially, but to no great extent.

Examples of Thick Copper Deposition. Reference must now be made, though briefly, to a number of important applications of copper deposition in industry. Some are well known but others have received less publicity.

ELECTROTYPING or *Electroforming*. This process involves the reproduction of surfaces usually required for printing purposes. Engraved copper and steel plates, wood blocks and even set-up type come under this designation. A reproduction in electrolytic copper has many advantages. This is usually made by making an impression of the surface in some plastic material capable of faithful reproduction of all the fine points of the surface. Gutta-percha and various wax compositions meet this requirement. A mixture of beeswax, Venice turpentine, and blacklead finds large application. These moulding compositions, however, do not possess conductance, this property being imparted superficially by the application of a film of the finest blacklead or other conducting material. A deposit of copper in the acid bath now becomes possible and is made from a solution approximating in composition to that given on page 210. After the first film is produced—and this should appear both quickly and smoothly—the deposition can be accelerated by increased current density with agitated solution until a deposit or *shell* of sufficient rigidity is obtained which readily strips from the wax surface. Lack of strength is now made good by the application of a backing of a hard lead alloy composition. The compound plate is then perfectly levelled, trimmed, and usually mounted on a hard wood block to bring it "type high."

Variations of this process allow of the reproduction of surfaces with much greater degrees of "relief" when compositions with more elasticity must be employed. The process finds application in several departments of art metal work.

DEPOSITION OF COPPER TUBES. As far back as 1886 Elmore took out patents for a process for the production of copper tubes by deposition. Such tubes are therefore without seams, while good mechanical properties can be ensured by control of the deposition. Smooth steel tubes or mandrels were first given a film of copper in the cyanide solution, and after rinsing transferred to the sulphate bath. During the depositing process, an agate burnisher was moved along the tube so that each successive film of copper was burnished before it had time to develop any trace of unevenness. Smooth deposits were thus obtained with enhanced mechanical properties and these deposits were readily removed from their steel base and could then be drawn down to smaller dimensions as required.

Copper sheets are produced in a similar manner, deposition taking place on a mandrel of large diameter carrying a longitudinal mark or scratch along which a weakness in the deposit is developed, enabling its removal in the form of a sheet which, as may be required, can then be rolled to smaller gauge. The production of copper ribbon and wire follows along similar lines, a good deal of work in this direction having been done by Cowper-Coles. These processes, moreover, have the advantage that anodes may be made of relatively cheap scrap copper so that the deposition also constitutes a process of refining.

REINFORCED COPPER. A three-ply material with copper facings and a steel interior has been produced by Denny.

What copper may lack in mechanical strength is supplied by the steel. In the production of this material a perforated steel plate is cleaned and then given the necessary thin coating of copper from the cyanide solution. Heavy deposition is then supplied from the sulphate solution until the perforations are completely filled with copper and leave only a slight trace of their presence by depressions in the surface of the deposited copper. The copper deposits on either side are thus riveted together by the numerous deposits in the perforations. The compound plate can now be rolled to appreciably smaller thickness when, by the removal of some of the copper, it can be seen that the originally circular holes are now elliptical, indicating that the steel interior has rolled out with the copper.

This three-ply metal can then be shaped in the ordinary manner, and thus combines all the chemical properties of the copper reinforced by the mechanical properties of the steel interior.

PRINTING ROLLERS. The development of good quality copper by electrodeposition free from porosity and having a close-grained structure has furthered its application to the production of printing rollers for rotary work. This application has also been encouraged by the development of the photogravure process. In the deposition process the rollers are either totally submerged or only partially immersed in the depositing solution. The character of the deposit is, moreover, improved by the application of burnishers, usually of agate, during deposition, and in the resulting product there is freedom from the possibility of the detachment of the copper deposit from the steel mandrel under the pressure of the printing press.

The steel cylinders naturally require a thin film of copper from the cyanide solution prior to being introduced into the acid sulphate solution for the main deposit of copper.

Electrolytic Copper Extraction. Although not within the immediate range of the subject of electroplating, brief reference to the application of the methods of deposition to the extraction of copper from some of its—generally low grade—ores may not be too far out of place. Ores of this type occur in several parts of the world notably at Chili. The extraction of the metal by usual furnace methods is quite impracticable. In Chili, large quantities of ore containing a copper compound composed of both the oxide and sulphate occur. This material is treated with sulphuric acid producing a solution of the sulphate which, after suitable purification, is electrolysed with special insoluble anodes and thin pure copper cathodes. As copper is deposited from the solution, the original acid content increases until a composition of solution is attained in which there is insufficient copper to yield a satisfactory deposit and sufficient acid to be of service in treating further quantities of the ore. The acid liquor is thus used cyclically. With the insoluble anode the bath voltage is of the order of 1·5 volts, and this, with a generally high current efficiency, accounts for the consumption of about 1500 kilowatt hours per ton of copper produced. This and similar extraction processes possibly account for the production of no less than 200,000 tons of the metal per annum, a significant yet not a large proportion of the copper which is in some measure due to the application of the principles of electrolysis.

Electrolytic Refining. In this process large quantities of crude copper obtained by the ordinary metallurgical methods receive their final stage of purification by electro-deposition. It may with safety be said that this was one of the first processes to which current generated by the first dynamos was applied. In the preliminary processes of extraction, rapid and relatively cheap methods are used in order to extract the metal from its ores without any special care as to its composition. It is characteristic of copper ores that they carry notable quantities of gold and silver, which noble metals involve tedious and expensive methods of elimination by the usual metallurgical or chemical processes. Their recovery is, however, readily effected during the refining process by electrodeposition.

Briefly it may be said that, in a solution similar to that used for electrotyping, thick plates of crude copper are made anode to thin cathodes of pure copper. The electrodes are arranged so that there is a minimum internal resistance and consequently as low as 0·3 volt can be used for obtaining the required current density. The anodes decrease in thickness while the cathodes increase. Sooner or later the badly corroded and thin anodes are withdrawn and melted down with fresh crude copper for the further production of anodes, while the cathodes, after rinsing, come on to the market as cathode copper.

The crux of the process, however, lies in the choice of conditions to guarantee the deposition of copper free of the numerous impurities which are ordinarily present in the crude metal. Thus active metals like zinc, iron, and nickel are dissolved from the anode, but there is no risk of their deposition in the relatively strong acid solution. Gold, when present, falls in the insoluble metallic form from the anode into a mud which collects at the bottom of the tank. Silver dissolves from the anode electrolytically, but the presence of small quantities of chlorides in the solution accounts for the precipitation of the silver into the mud as silver chloride. Other impurities as tin, antimony, and bismuth pass into the solution but are largely precipitated as basic compounds, while lead also passes into the mud as the insoluble sulphate. Special care in the control of the process is required to prevent the co-deposition of arsenic and bismuth, as these impurities very seriously affect the properties of the deposited copper. Without going into details, the fact that probably no fewer than 1,500,000 tons of copper are annually refined by this process to produce the "bread" of the electrical industries may be some assurance that these difficulties have been satisfactorily surmounted. With the soluble copper anodes only a low P.D. of about 0·3 volt is required, and this with a current efficiency approaching 100 per cent, accounts for a consumption of electrical energy of the order of 250 to 300 units per ton. The cost of this at, say, a farthing a unit is easily exceeded by the interest on the value of the copper during its stay in the refinery.

ANALYSIS OF SOLUTIONS

The chief constituents required are the free acid and copper sulphate. Other constituents are also required on occasion.

Free Acid. This is quickly determined by titration with semi-normal sodium carbonate.

Dilute the acid bath to one-half its original strength. Take 25 c.c. in a conical flask and run in from a burette the semi-normal Na_2CO_3 until there are the first signs of a permanent turbidity. This represents the precipitation of copper carbonate after the free acid has been neutralized.

$$CuSO_4 + Na_2CO_3 = CuCO_3 + Na_2SO_4$$

If iron is present, the turbidity will have a slightly brown colour. The turbidity can be easily judged by comparison with another sample of the diluted solution to which no carbonate has been added.

Now

$$\underset{106}{Na_2CO_3} + \underset{98}{H_2SO_4} = Na_2SO_4 + CO_2 + H_2O$$

$$\frac{N}{2}\ Na_2CO_3 \text{ contains } 26{\cdot}5 \text{ gm. } Na_2CO_3 \text{ per litre.}$$

Hence $$1 \text{ c.c.} = \frac{26{\cdot}5 \times 98}{1000 \times 106} = 0{\cdot}0245 \text{ gm. } H_2SO_4$$

Let x = c.c. sodium carbonate solution used.

Then $$H_2SO_4 \text{ per litre} = \frac{0{\cdot}0245 \times x \times 1{,}000 \times 2}{25} \text{ gm.}$$

Alternatively, if any difficulty is experienced in correctly judging the first appearance of the turbidity, methyl orange may be used as an indicator when, even in the presence of the copper salt, there will be a sharp change in the colour from purple to green at the point of neutralization.

Further, *if*, instead of semi-normal sodium carbonate, a solution is used containing 10·82 gm. Na_2CO_3 per litre *and* 10 c.c. of the original copper solution is taken for the estimation then—

c.c. of this Na_2CO_3 solution = gm. H_2SO_4 per litre.

ESTIMATION OF COPPER

Density Method. It seldom happens that similar percentages of salts in solution give the same specific gravity. Within the limits of reasonable experimental error, however, this coincidence occurs with copper sulphate and sulphuric acid. In Table LIV the percentage strengths of the two solutions are taken from recognized authorities and from these the grammes per litre have been calculated.

This coincidence was checked by working up a number of correct solutions in the laboratory and determining their densities. These results are shown in Table LV.

TABLE LIV

STRENGTHS OF COPPER SULPHATE AND SULPHURIC ACID SOLUTIONS

Percentage Strength	Copper Sulphate		Sulphuric Acid	
	Sp. Gr.	Grammes per Litre $CuSO_4 . 5H_2O$	Sp. Gr.	Grammes per Litre H_2SO_4
1	1·0063	10·06	1·0061	10·06
2	1·0126	20·25	1·013	20·26
3	1·0190	30·57	1·0198	30·59
5	1·0319	51·60	1·0334	51·67
7	1·0450	73·15	1·0474	73·32
10	1·0649	106·5	1·0687	106·9
12	1·0785	129·5	1·083	130·0
15	1·0993	164·9	1·1048	165·7
20	1·1354	227·1	1·143	228·6
30	1·2146	364·4	1·221	366·3

TABLE LV

SPECIFIC GRAVITIES OF MIXED COPPER SULPHATE AND SULPHURIC ACID SOLUTIONS

Grammes per Litre		Sp. Gr.
$CuSO_4 . 5H_2O$	H_2SO_4	
300	0	1·185
200	100	1·181
150	150	1·183
100	200	1·184
0	300	1·186

Upon this basis, a further table (LVI) has been drawn up for the combined contents of solutions with densities varying from 1·05 to 1·22 and therefore covering the usual range of acid baths. These figures can, if required, be plotted to give intermediate values.

TABLE LVI

SPECIFIC GRAVITIES AND CONTENTS OF MIXED SOLUTIONS

Sp. Gr.	Grammes Mixed Compounds per Litre	Sp. Gr.	Grammes Mixed Compounds per Litre
1·05	77	1·14	223
1·06	93	1·15	239
1·07	109	1·16	256
1·08	125	1·17	274
1·09	142	1·18	292
1·10	158	1·19	310
1·11	175	1·20	328
1·12	191	1·21	346
1·13	207	1·22	364

Now assuming that copper sulphate and acid are the only two constituents, these may be obtained by the determination of one of them, the other being obtained by difference. For example, a mixed solution was taken. Its density with the specific gravity bottle came to 1·094. Its total contents are therefore 148·4 gm. per litre. In the acid titration 10 c.c. took 10·5 c.c. N/2 Na_2CO_3 representing an acid content of 25·7 grm. per litre. The copper sulphate content is therefore 148·4 – 25·7 = 122·7 gm. per litre.

More accurate methods are, however, required and these are carried out by chemical methods.

Estimation of Copper Sulphate. The addition of potassium iodide to copper sulphate produces the following change—

$$2\,CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4$$

Cuprous iodide is a white insoluble compound but in the presence of free iodine looks brown. The iodine is removed by the addition of sodium thiosulphate as follows—

$$2Na_2S_2O_3 + \underset{\text{brown}}{I_2} = \underbrace{2NaI + Na_2S_4O_6}_{\text{colourless compounds}}$$

The standard solution is of sodium thiosulphate $Na_2S_2O_3 5H_2O$ of which 24·8 gm. are required to make a litre of deci-normal solution. A study of the equivalent quantities will show that

$$1\text{c.c. N/10 “thio”} = 0{\cdot}00636 \text{ gm. Cu.}$$

For a number of purposes where the last degree of accuracy is not required, it might suffice to dissolve 25 gm. of the pure crystallized sodium thiosulphate and make it up to one litre. The error involved in this procedure would not be serious in a case in which there is considerable elasticity in the copper sulphate content of the solution. For more accurate work, however, a solution of "thio" would be made up of slightly greater strength and then standardized.

Standardization of "Thio." This may be effected by the use of a carefully prepared standard solution of iodine. Where copper estimations are concerned it would be more usual to standardize with either metallic copper or some pure copper salt. Of these, the sulphate is readily procurable in a pure form.

Weigh out accurately about 4 gm. of copper sulphate, dissolve in water and make up to 250 c.c. Shake. Pipette 25 c.c. of this solution into a conical flask. As a matter of practice of a good habit, add sufficient sodium carbonate solution to produce a turbidity, which is then redissolved in a minimum amount of acetic acid. Add 10 c.c. of a 10 per cent solution of potassium iodide (= 1 gm. KI). This precipitates cuprous iodide and sets iodine free. Titrate with the approximate "thio" solution from a burette until the iodine colour, which is accentuated towards the end of the reaction by the addition of a little starch solution giving a blue colour, just disappears, leaving the white precipitate of cuprous iodide.

In a typical example—

Weight of copper sulphate = 4·025 gm.

Dissolved and made up to 250 c.c.

25 c.c. of this solution required on an average of three titrations 16·7 c.c. "thio."

Hence

$$1 \text{ c.c. "thio"} = \frac{63{\cdot}6}{249{\cdot}6} \times \frac{4{\cdot}025}{1} \times \frac{25}{250} \times \frac{1}{16{\cdot}7}$$

$$= 0{\cdot}0064 \text{ gm. Cu.}$$

The Estimation of Copper. This follows exactly the same procedure as the standardization. Take 5 c.c. of the copper solution. Dilute and add solid sodium carbonate to produce the permanent turbidity. (When using KI there must not be present any free mineral acid. Sodium carbonate effects the neutralization of this free mineral acid.) Just clear the turbidity with acetic acid. Add 10 c.c. of the KI solution. Titrate with the same " thio " solution using starch as the indicator towards the end of the process. Assume that as an average of three titrations 25·5 c.c. of " thio " are required. Then—

$$\text{Grammes copper per litre} = \frac{25{\cdot}5 \times 0{\cdot}0064 \times 1{,}000}{5}$$

$$= 32{\cdot}6$$

and this is equivalent to practically four times its weight of the crystallized salt which is therefore present to the extent of 32·6 × 4 = 130 gm. per litre.

An Alternative Standard "Thio" Solution. Now a "thio" solution containing exactly 24·8 gm. of the crystals per litre has a copper value of 0·00636 gm. A simple calculation shows that a stronger "thio" solution containing 39 gm. per litre will have a copper value of 0·01 gm. per c.c. Each c.c. of this solution required to give the reaction with 10 c.c. of the copper bath represents 0·01 gm. Cu per 10 c.c. of the bath and this is equivalent to 1 gm. per litre.

Hence—

c.c. " thio " per 10 c.c. bath = gm. Cu per litre.

By the choice of these solutions the grammes of copper per litre of solution are read directly from the burette.

Comparison with Density Determination. A common discrepancy in this method of estimation is illustrated in the following example—

Sp. Gr. of copper solution = 1·063.

Combined content of acid and copper sulphate is therefore 98·8 gm.

Acid determination gave 12·5 gm. per litre.

Copper sulphate determined by titration = 81 gm. per litre, giving a total of 93·5 gm. as against 98·8 by density.

This discrepancy is invariably due to the presence of iron salts in the solution, probably originally in the copper salts but also from other incidental causes. The iron compound is most probably ferrous sulphate $FeSO_4.7H_2O$ Its estimation is easily carried out gravimetrically.

Estimation of Iron. Take 10 c.c. of the solution. Warm and add a few drops of str. HNO_3 to oxidize ferrous to ferric compounds. Dilute and add an excess of ammonia solution. This precipitates and redissolves the copper and precipitates the iron as brown ferric hydroxide $Fe(OH)_3$. Filter the deep blue solution and wash the ppt. with hot water. After washing it will be observed that the ppt. instead of being of a clean brown colour is greenish-brown, due to the presence of some copper compound. This is a common experience when attempting to separate a small constituent from a large one. The difficulty is overcome by redissolving the ppt. in warm dilute HCl poured on to the filter, subsequently washing the filter well with hot water. From the solution the iron is again precipitated with ammonia, filtered and thoroughly washed. The filter is then dried, folded up (ppt. inside) and put into a weighed porcelain crucible and heated to redness. The paper is burnt away with the exception of the ash and the iron compound reduced to Fe_2O_3.

In the case under consideration—

10 c.c. of solution gave 0·015 gm. Fe_2O_3.
Now $\underset{160}{Fe_2O_3}$ comes from $\underset{2 \times 278}{2FeSO_4 . 7H_2O}$

Hence 1 litre of copper solution contains—

$$0{\cdot}015 \times \frac{278 \times 2}{160} \times \frac{1{,}000}{10} = 5{\cdot}2 \text{ gm. } FeSO_4 . 7H_2O$$

giving reasonable agreement with the deficiency noted above. The example is taken from actual experience and it may be added that this small amount of iron sulphate produces no difference in the working of the copper solution. In fact, in similar solutions used for the electrolytic refining of copper. ferrous sulphate accumulates to a considerable extent before its removal becomes necessary.

Alternative Method for Iron. Take 10 c.c. of the solution. Dilute, warm, and saturate with H_2S. This precipitates the whole of the copper in an easily filterable form. Filter and wash the ppt. adding together the filtrate and washings and neglecting the ppt. Boil the solution till free from H_2S, this being determined by the use of lead acetate paper. Add a little strong nitric acid to oxidize ferrous to ferric compounds. Cool and add excess of ammonia solution. This precipitates the iron as ferric hydroxide ($Fe(OH)_3$), which is filtered off, washed, dried, and ignited to Fe_2O_3, the calculation being the same as in the previous method. This method of separating the large excess of copper is quicker and cleaner than that involving the excess of ammonia.

Estimation of Phenol or its Sulphonic Acid. While not of very general need, this may be of some advantage to those using this addition agent. The estimation is based on the fact that phenol (C_6H_5OH) or its sulphonic acid ($C_6H_4.SO_3H.OH$) combine with bromine to form tri-bromphenol ($C_6H_2 . Br_3 . OH$). The use of phenol, however, leads to the formation of both hydroquinone ($C_6H_4(OH)_2$) and quinone ($C_6H_4O_2$), both of which also react with bromine, so that the result can only be approximate and is best expressed as the "equivalent phenol."

Prepare a standard bromine solution (alternatively this may be purchased from a supply house) of N/10 strength. This will contain—

Potassium bromate	208 gm.
Potassium bromide	12 ,,
Bromine	8 ,,
Water	to 1 litre

Take 10 c.c. of the copper sulphate solution and dilute to 50 c.c. Add 2 gm. of 20 mesh granulated zinc to precipitate the copper which is filtered off, the filtrate being collected in a 200 c.c. flask. To the solution add 10 c.c. of the standard bromine solution and 50 c.c. conc. HCl. Close the flask with a rubber stopper and warm in a water bath to 50° C. for half an hour. During this time the phenol compound is taking up its equivalent of bromine to form the tribromide compound and an excess of bromine will remain free. Cool. Add 10 c.c. of 10 per cent KI from which the free bromine liberates iodine—

$$Br_2 + 2KI = 2KBr + I_2$$

The free iodine is now titrated with N/10 "thio." Then as—

$$3Br \equiv 3 \cdot 1$$

$$3 \times 80 \equiv 3 \times 127$$

$$1 \text{ c.c. ``thio''} = \frac{80 \times \cdot 0127}{127} = \cdot 008 \text{ gm. Br.}$$

Assume 7 c.c. "thio" used = 7 × ·008 = ·056 gm. Br.

Now 10 c.c. N/10 Br. soln. contain	·08 gm Br.	
and Br. found by "thio" titration	= ·056	,,
Hence Br absorbed by phenol	= ·024	,,

Further—

$$\begin{array}{cc} C_6H_5OH & = 3\,Br \\ 94 & 3 \times 80 = 240 \end{array}$$

Hence soln. contains—

$$\frac{94 \times \cdot 024 \times 1000}{240 \times 10} = \text{Equiv. } \cdot 94 \text{ gm. phenol per litre.}$$

CHAPTER XII

DEPOSITION OF COPPER

Alkaline Baths

Introduction—Solutions—The Rochelle salt solution—Brighteners—Chevreul's solution—Control of solutions—Operating conditions—Effect of carbonates—Defects in working—Concentrated copper cyanide baths—Solution for coppering zinc-base die castings—Stripping copper deposits—Theory of process—Non-cyanide solutions for coppering iron and steel—Ethanolamine solution—Thiosulphate solution—Analysis of cyanide copper solutions

Introduction. There are, as has been stated, requirements in copper deposition which are not met by the acid copper sulphate bath. These are supplied by the use of what is called the *alkaline* or *cyanide* solution. In this solution the copper compound is more stable than the sulphate. This is shown when iron, dipped in the cyanide solution, does not become coated with copper by simple immersion. The essential compound of this solution is either copper potassium cyanide (CuCN.2KCN) or copper sodium cyanide (CuCN.2NaCN). These salts can be purchased, but it is more usual to prepare them from other materials.

A further constituent of the solution is an alkaline cyanide which is free, or uncombined with copper. Its function is to keep the anodes free from the insoluble single copper cyanide which is anodically formed there. Occasionally also, conducting salts are added.

Solutions. The strength of these solutions can best be expressed in terms of the metal content. This may vary from 15 to 30 gm. per litre. Adopting 25 gm. as the metal content, this is equivalent to 1 lb. of copper sulphate per gallon. Two solutions may be given. They are—

(1)	Sodium cyanide (130%) . .	4½ oz.	28 gm.
	Copper cyanide (65%) . .	4 ,,	25 ,,
	Sodium bisulphite . . .	½ ,,	3 ,,
	Sodium carbonate . . .	1 ,,	6 ,,
	Water	1 gal.	1 litre

The sodium cyanide is dissolved in the water and, after warming, which, however, is not vitally necessary though desirable, the single copper cyanide is added, followed by the other two constituents. There should be no difficulty in dissolving the salts.

From the following expressions—

$$\underset{89\cdot6}{CuCN} + \underset{98}{2NaCN} \rightarrow Na_2Cu(CN)_3$$

it can easily be seen that the solution of 1 lb. of pure CuCN requires 1·093 lb. NaCN (130%).

(2)	Sodium cyanide	9·6 oz.	60 gm.
	Copper carbonate (58% Cu)	6·7 „	42 „
	Sodium bisulphite	3·0 „	19 „
	Water	1 gal.	1 litre

The sodium cyanide is dissolved in the warmed water and the copper carbonate added a little at a time with stirring. It should be completely dissolved without difficulty. The remaining constituents are then added.

Alternatively the copper carbonate can be dissolved in a solution made from the sodium cyanide dissolved in three-quarters of the water, the other ingredients being separately dissolved in the remaining quarter of the water and the two solutions mixed. Such alternative methods will be obvious to the intelligent plater, though with lack of chemical knowledge it is easy to go wrong at first.

A slight knowledge of chemistry will further show that the two formulae given are very similar. The actual materials mixed in making the solution are not so important as those which are formed by their interaction.

The Rochelle Salt Solution. This solution which contains a large proportion of Rochelle salt ($NaKC_4H_4O_6 . 4H_2O$) has of late years come into extended use. More recently it has been exhaustively studied by Graham and Read,* who suggest the following as the most appropriate composition and desirable limits for each of the constituents—

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	Normal Compn.	*Limits*
Copper cyanide	4·2 oz.	3·6 – 7·2
Sodium cyanide (total)	5·5 „	4·8 – 5·6
Sodium cyanide (free)	·9 „	·6 – 1·2
Rochelle salt	9·6 „	7·2 – 9·6
Sodium carbonate	4·8 „	2·4 – 9·6
pH	12·6 „	12·2 - 12·8
Water	1 gal.	

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* *Met. Ind.* (*N.Y.*) *Nov.*, 1937.

The pH is adjusted by the addition of caustic soda if it is low, and when high by the addition of sulphuric acid, this latter addition being made with ample ventilation to take off the HCN fumes.

It is recommended that the solution be worked at a temperature of from 120° to 190° F., though the higher temperature gives rise to the more rapid decomposition of the cyanides with the resultant accumulation of carbonates. Current densities up to 90 amperes per sq. ft. are permissible, a usual figure being of the order of 40 amperes per sq. ft. The current efficiency varies with C.D. With 20 amperes per sq. ft. it is 60 per cent at 130° F. and 73 per cent at 160° F., while at 60 amperes per sq. ft. it is 30 per cent at 130° F. and 43 per cent at 160° F.

Anode area should be about twice that of the cathode with a small proportion of anode in the insoluble form such, for example, as iron. Generally speaking the deposits are brighter than those of the acid bath. Comparing the weights of the deposit it will be noted that the copper is in the cuprous form, and that a current efficiency of 50 per cent will give a deposit equal to that of the acid bath with its current efficiency of nearly 100 per cent. Hence with a C.D. of 40 amperes per sq. ft. the rate of deposition will give a thickness of 0·0003 in. in eight minutes.

Of the constituents the free cyanide needs to be kept closely within the limits laid down. Rochelle salt loss is wholly by drag out and can readily be made good by additions after chemical analysis, at least until some good idea of this drag-out loss has been ascertained over a lengthy period of operations.

Brighteners. A number of materials are frequently added to the cyanide copper bath to improve the quality of the deposit. These are commonly called *brighteners*, and they include small amounts of arsenic (applied as a solution of arsenious acid (As_2O_3) dissolved in sodium or potassium cyanide). Other compounds include sodium thiosulphate ($Na_2S_2O_3.5H_2O$) or "hypo" as it is frequently termed.

Chevreul's Solution. This solution, named after the French chemist who proposed it, yields very satisfactory deposits. Its chief constituent is a sulphite of copper having the formula $CuSO_3.Cu_2SO_3.2H_2O$. It is a cupric cuprous sulphite readily made by adding a hot strong solution of sodium sulphite to one of copper sulphate. This preparation is not recommended to the plater. The substance is conveniently obtained from the supply houses as a red powder containing approximately 49·3 per cent copper.

A composition of the solution is as follows—

Sodium cyanide	5½ oz.	34 gm.
Chevreul's salt	4½ „	28 „
Water	1 gal.	1 litre

An equivalent weight of potassium cyanide may be used, if preferred. The cyanide is dissolved in the warmed water, and the red compound added a little at a time with stirring. It readily dissolves, and the solution is at once available for working. It will, however, be found that a new solution does not give the best results at once. Some small amount of working seems necessary to allow the constituents of solutions to become stabilized.

Copper cyanide solutions are usually worked warm. If required to be used cold, they should contain a larger proportion of free cyanide, this being necessary to keep the anodes sufficiently clean and free from the insoluble single cyanide which is not so readily dissolved by the cold cyanide. A usual temperature is about 50° C. (122° F.). There is some latitude about this figure. Again a little experience will be worth a lot of written detail.

The solutions are usually contained in iron or steel tanks, the solution being heated when required either by gas jets below the tanks or preferably by some type of heating and circulating coil.

Control of Solution. A simple method for exercising some control in the composition of these solutions has been described by Pinner and Baker* who used a bent cathode for this purpose. Strips of steel 1 in. wide are bent at right angles 1 in. from the end and used as cathodes, the throwing power of the solution then being shown qualitatively by the extent to which deposition takes place in the recessed bend which is presented to the anode. It is claimed that the ratio of free cyanide to the copper compound can easily be kept to a desirable figure by this test, together with some good idea of the requisite proportions of other constituents, such as

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* *Trans. Amer. Electrochem. Soc.*, lvii, 89 (1930).

carbonates and sodium thiosulphate, and also current density and temperature conditions.

Operating Conditions. There are some plating solutions about which it is difficult to give precise conditions of operation. In this case it is not usual to give exact figures either for the current density or the P.D. to be employed. With the solutions given above, a P.D. of 2 to 3 volts should suffice when the solution is warm, a cold solution requiring a somewhat higher P.D. Again the C.D. is of no great importance, the quality of the deposit being gauged rather by its appearance. In very few cases is the solution used for purposes other than obtaining light deposits upon metals which cannot be treated in the acid bath. Evolution of gas usually accompanies deposition of the metal, and this militates against specifying a definite C.D.

The usual procedure is that of producing a perfect though light deposit on such metals as iron and steel, Britannia metal, zinc, etc., a thicker deposit of copper, if required, being then produced in the acid bath. Occasionally a thin, bright deposit will be applied to brass articles, on which a finish is required such as the acid bath does not give. Only very occasionally will a serviceably thick deposit be given in the cyanide solution, and this only in works which might have no use for the sulphate solution to justify keeping such a solution in stock.

It will be recalled that 1 ampere deposits twice as much metal from this solution as from the acid bath when the conditions of the solution are right for quantitative work. More frequently, however, the actual weight of the deposit will be less than that from the acid bath. This is of no great concern when quality counts rather than quantity.

Effect of Carbonates. The frequent addition of cyanides ultimately leads to the accumulation of carbonates in the solution as, by decomposition, the cyanides are converted into carbonates. Here the use of potassium cyanide shows to advantage, as potassium carbonate is far more soluble than the corresponding sodium compound. For removing large quantities of carbonates the solution may be evaporated somewhat and cooled, when some of the carbonate will crystallize out, leaving a smaller and more desirable quantity in the solution. A more extended reference to the choice of cyanides is made in Chapter XIII dealing with silver plating.

Defects in Working. A number of common troubles in working this solution are easily rectified. The most common is that due to the lack of free cyanide. There appears on the anode a slime, which may be green and even the solution may turn green. The green slime is a basic single copper cyanide. This slime may detach itself from the anode, float in the solution, and even become attached to the cathode, giving rise to rough deposits and a tendency to stripping, even when the work has been properly cleaned. Cyanide must, therefore, be added, first to decolorize the solution and then to allow the anodes to work clean. Excessive cyanide causes gassing, with a reduction in the amount of metal deposited. Trials on a two gallon sample are preferable, the bath then being corrected when the proper proportions have been determined.

Dark deposits with roughness are obviously due to too high a C.D., while roughness may further be due to material floating in the solution. These faults are easily corrected.

Excessive free cyanide, evidenced by undue gassing with little deposit, is corrected by the addition of copper carbonate to the warm solution with stirring. The carbonate will dissolve in the cold solution, but much better when the solution is warm. The addition of carbonate should not be sufficient to cause a green solution. If this should happen a further addition of free cyanide can then be made. Excess free cyanide may also be removed by the addition of the copper sulphite (red ppt) referred to previously.

Both excessive free cyanide and also floating material may give rise to blistery deposits, which, when scratch-brushed or polished, are removed, but similar non-adhesive deposits may arise when both the solution and operating conditions are right but the work imperfectly cleaned, scale or oxide not having been completely removed. This, however, is a fault which, with a plater of some experience, is not likely to arise often, a little experience proving the best tutor.

Especially with cast work, troubles arise with cyanide solutions, and to a lesser extent with all others owing to the porous nature of the metal. There are likely to be microscopic pores in the metal which are not visible to the naked eye. However small they may be, they retain solution which is not removed by rapid rinsing. These minute drops of retained solution soon give rise to chemical reactions with the formation of "spots." "Spotting out" is a common platers' trouble. An appreciation of the cause will soon suggest to the intelligent plater with some experience methods for its elimination. After rinsing the work in cold water it will be advisable to pass the work through a weak acid, either sulphuric, phosphoric, or acetic, not exceeding 2 per cent. The acids decompose the cyanide salts, and produce compounds which are more rapidly washed out. Again rinse in cold water, not too sparingly. A further step towards eliminating the trouble is that of passing the work alternately through hot and cold water. Hot water expands the metal, closing the pores and squeezing out the solution, while cold water following, contracts the metal, opens the pores, and draws in clean water. A final rinse in hot water and hot drying completes the process.

When cyanide coppering some metals as lead and iron a smaller amount of free cyanide in the solution is desirable.

Concentrated Cyanide Copper Baths. While the cyanide copper solution has for so long been used to give only a relatively thin deposit which is subsequently thickened in the acid bath, the solution possesses a number of properties which seem to indicate its probable application for thick deposits, thereby cutting out the need for the additional sulphate solution, and thus saving an operation. Two of these advantages are, (1) the high chemical equivalent of the cuprous ion (which in ordinary solutions is offset by the low cathode efficiency), and (2) the much greater throwing power than that of the acid bath.

It is not surprising therefore that the possibilities of the solution for thick deposits have attracted the attention of some workers with a view to extending its range of application in this direction.

Dr. L. C. Pan* has investigated the problem and as a result of extensive experimental work suggests the following solution—

Copper cyanide (CuCN)	90	gm. per litre
Sodium cyanide (NaCN)	106	,,
Free cyanide (NaCN)	8	,,
Sodium carbonate (Na_2CO_3)	78	,,

This solution is worked at a temperature of about 20° C.

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* *Trans. Amer, Electrochem. Soc.*, lxviii, 471, 1935.

with a current density of 18 to 20 amperes per sq. ft. A smooth matte deposit is obtained with a current efficiency of 95 per cent. The anode assumes a blue coloration, which disappears in the electrolyte.

The advantage of this method of operation will be apparent. The acid bath works with a current efficiency of, say, 97 per cent with a chemical equivalent of only half that of the cyanide bath. Per ampere hour, therefore, we get practically double the amount of copper from the cyanide solution. The current density, too, is now within the range of that of the acid bath at, say, 20 ampere per sq. ft. so that the speed of plating in the new cyanide solution is twice that of the ordinary acid bath.

The acid bath is notoriously poor in throwing power, while that of the cyanide solution ranks among the highest of all plating solutions. Further, the solution being applicable to iron and steel, there would seem to be little further need for the installation of the acid bath in many examples of the coppering of iron and steel and other base metals. This is another case in which long established custom is giving way before modern research.

Solution for Plating Zinc-base Die Castings. The very active character of zinc calls for some special composition of solution in which this metal should be plated. It is well known that there is some difficulty in handling this metal even in cyanide solutions. Blistering of the deposit is a common experience, and the solubility of the metal in relatively strong cyanide solutions is another cause of trouble. In fact, copper can be replaced by zinc from the cyanide bath if there is an excess of free cyanide. This is a condition which therefore must be rigidly avoided. A solution* suggested for this purpose is—

Copper cyanide	25 to 35	gm. per litre
Sodium cyanide	17 to 25	,,
Sodium carbonate . . .	not exceeding 36	,,

The composition leaves a minimum of free cyanide. The solution is worked at a temperature of 100° to 115° F. at a current density of 15 amperes per sq. ft. The usual tank voltage will then be of the order of 3 volts. Under these conditions a six-minute deposit gives a thickness of 0·0001 in. with a current efficiency of 60 per cent. This is considered to suffice when an

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* *Monthly Review, Amer. Electro-platers' Soc.*, Oct., 1935.

acid copper deposit is to follow. In the absence of a subsequent sulphate coat, the time of deposition should be increased to 18 minutes with a thickness of 0·0003 in. It is also recommended that the articles should, after removal of grease, have a brief (not more than a few seconds) dip in a weak acid solution. This may be of hydrofluoric, hydrochloric, or sulphuric acid to produce a slight etch. These acids should only be of the order of a few per cent in strength.

Stripping Copper Deposits. The stripping of copper deposits is not often necessary. Acid dip methods are not usually possible owing to the severe attack of the acids necessary to remove the copper from the basis metal. Electrolytic methods are therefore to be preferred.

Solution—

Sodium cyanide . . .		12 oz.	75 gm.
Sodium carbonate . . .		12 ,,	75 ,,
Water	to	1 gal.	1 litre

The work is made the anode in this solution which may be contained in an iron tank which can constitute the cathode and worked at 150° F. This gentle treatment should leave the basis metal with a minimum of attack.

Theory of the Process. These formulae, $Na_2Cu(CN)_3$ and $K_2Cu(CN)_3$, have been definitely established by dissolving pure cuprous cyanide (CuCN) in an excess of the alkali cyanide (NaCN or KCN) and the excess of cyanide or free cyanide determined (page 240).

Dissociation proceeds as follows—

$$CuCN.2NaCN \rightleftarrows 2Na^{\cdot} + Cu(CN)_3^{--}$$

Earlier theory suggested that the sodium ions at the cathode reacted with the molecular double cyanide thus—

$$2Na + 2(CuCN.2NaCN) = 2Cu + 6NaCN$$

precipitating copper on the cathode as the result of a secondary reaction. These reactions fully account for the quantitative relationships of the deposited copper, and the fact that free cyanide is formed at the anode whereas it is required at the cathode. The more modern conception is that the complexion $Cu(CN)_3$ is further dissociated thus—

$$Cu(CN)_3^{--} \rightleftarrows Cu^{\cdot} + 3CN^-$$

to a relatively small degree so that, although the original double cyanide is fairly concentrated, the concentration of the cuprous ions is only of the order of milli-normal, and that these cuprous ions are deposited preferentially to the sodium, and copper therefore appears as the product of the primary reaction. It must be remembered that, however slight the degree of dissociation, the removal of the cuprous ions leads to the instantaneous dissociation of more of the double cyanide, so that the concentration of the cuprous ions, though small, is maintained.

In addition, there will be the usual chemical reactions associated with the use of alkali cyanides in warm solutions. These have already been referred to in Chapter V.

Non-Cyanide Solution for Depositing Copper on Iron. Prior to the introduction of the alkaline cyanide copper solution there were many attempts to deposit copper on iron and thus impart to that rapidly rusting metal the degree of permanence characteristic of copper. As is well known, many of these solutions were compounded with copper sulphate to which alkali was added in the presence of organic compounds as Rochelle salt ($NaKC_4H_4O_6$), thereby forming soluble complex compounds. In these cases it is only necessary to impart the thinnest film of copper so long as it is continuous and offers no possibility of access of the acid in the sulphate bath which must subsequently be used to obtain a substantially thick deposit. This thin deposition is referred to as "strike plating" and Brown and Mathers* proposed the following solution for this purpose—

Copper sulphate	60 gm. per litre
Sodium hydroxide	50 ,, ,,
Sodium potassium tartrate . . .	160 ,, ,,

This solution works tolerably well with a current density of 4 to 5 amperes per sq. ft. The current efficiency exceeds 100 per cent calculated on divalent copper due doubtless to the fact that some cuprous ions are present.

Another solution proposed by Dr. Elsoner is—

Potassium bi-tartrate (cream of tartar). . .	100 gm.
Water	1 litre

to which is added copper carbonate to saturation, filtering off

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* *Trans. Amer. Electrochem. Soc.*, lxix, 39, 1936.

excess of the copper carbonate, and then making the solution alkaline with potassium carbonate. The permissible C.D. is of the order of 2—2·5 amperes per sq. ft.

These solutions, too, have their application in the attempt to plate copper on to silver mirrors obtained on glass. Such silver deposits are necessarily very thin and are quickly removed in the ordinary acid bath. With the organic alkaline baths satisfactory deposits can be obtained upon this film of silver and may be subsequently thickened in the acid solution.

Ethanolamine Solution. More recently solutions have been proposed and worked out by Brockman and Brewer* containing notable quantities of the ethanolamines. The most satisfactory example of these compounds is the triethanolamine or tri-hydroxy-ethylamine $[N(CH_2.CH_2OH)]_3$. This compound is obtainable at chemical supply houses. The solution is as follows—

Copper sulphate	15 gm. per litre
Sodium oxalate	10 „ „
Triethanolamine	22 c.c. „

A current density of 3·6 amperes per sq. ft. applied for 50 to 70 seconds gives deposits substantial enough to be transferred to the acid solution without fear of stripping. The solution, too, is non-poisonous, while from it, copper can be deposited at a much higher current efficiency than previous solutions for the flash plating of copper on steel. The permissible rate of deposition is greater than previous alkaline baths and this constitutes an advantage.

Thiosulphate Solution. The possibility of sodium thiosulphate solutions was suggested by Gernes in 1932. More recently Gernes, Loring, and Montillon† have more closely examined solutions of this type with successful results. Such solutions have the great advantage of being non-poisonous. The following composition is recommended—

Sodium thiosulphate ($Na_2S_2O_3 . 5H_2O$) . .	2 lbs.	200 gm.
Cuprous chloride (Cu_2Cl_2)	3 oz.	20 „
Sodium bisulphite ($NaHSO_3$)	1½ „	10 „
Water	to 1 gal.	1 litre.

Satisfactory bright deposits are obtained on iron and steel at 25° C. and a C.D. of 1 amp./dm.^{2} (approx. 10 amp./sq. ft.)

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* *Trans. Amer. Electrochem. Soc.*, lxix, 535, 1936.

† *Trans. Amer. Electrochem. Soc.*, 1940, lxxvii, 177.

with a cathode efficiency of 85–90 per cent. There should be little or no cupric compound present and the solution is stable so long as the ratio of "thio" to cuprous chloride does not fall below 10 : 1. No deposition takes place by simple immersion.

ANALYSIS OF CYANIDE COPPER SOLUTIONS

Only two estimations are usually required, the free cyanide and copper.

Free Cyanide. This follows the usual procedure for cyanides.

Take 20 c.c. of solution, dilute, warm and add a few drops of KI titrate with N/10 $AgNO_3$ to produce the first faint turbidity.

$$\text{Now} \quad 1 \text{ c.c. N/10 } AgNO_3 = 0{\cdot}013 \text{ gm. } KCN$$
$$= 0{\cdot}0098 \text{ gm. } NaCN$$

Hence cyanide content as KCN—

$$= \frac{N \times {\cdot}013 \times 1{,}000}{20} \text{ gm. per litre}$$

$$\text{as } NaCN = \frac{N \times {\cdot}0098 \times 1{,}000}{20} \text{ gm. per litre.}$$

Copper. Take 10 c.c. solution. Add 5 c.c. conc. H_2SO_4 and a few drops of str. HNO_3. Heat to decompose all cyanide compounds and to expel nitric acid. Continue heating until white fumes appear. These are sulphuric acid following the expulsion of the cyanide and HNO_3. Cool and dilute. The solution now contains copper sulphate. Neutralize free H_2SO_4 with solid Na_2CO_3 and dissolve turbidity with acetic acid. Add 10 c.c. 10 per cent KI and titrate with N/10 sodium thiosulphate solution, finishing with starch solution as indicator. To ensure completion of the reaction, add a further small quantity of KI. Note c.c. "thio" used, say N.

$$\text{Now} \quad 1 \text{ c.c. "thio"} = 0{\cdot}00636 \text{ gm. Cu.}$$

Hence copper content of solution is—

$$\frac{N \times 0{\cdot}00636 \times 1{,}000}{10} \text{ gm. per litre.}$$

All cyanide solutions will contain considerable quantities of carbonates. There is little need to estimate these in the case of the copper solution, but, if required, the procedure will be that given for carbonates in silver solution.

Rochelle Salt. The increasing use of this type of solution calls for a method for the estimation of its characteristic constituent. The following method recommended by Mr. Myron Diggin requires some careful manipulation, but should not be beyond the analyst who usually deals with the analysis of electro-depositing solutions. The method calls first for the elimination of the copper, afterwards precipitating the tartrate compound as insoluble acid potassium tartrate ($KHC_4H_4O_6$) and from the standard alkali required to reconvert it into Rochelle salt, calculating the amount originally present in the solution. The procedure is as follows—

Ten c.c. of the solution is transferred to a 250 c.c. flask. Add 10 c.c. of conc. HCl and 15 c.c. of distilled water. Boil until the solution becomes greenish blue and is free from turbidity. This destroys the cyanide compounds. Dilute and while still warm precipitate the copper from the acid solution by the addition of 10 c.c. of a 15 per cent solution of sodium sulphide. Filter and wash the ppt. with water containing H_2S. This is to ensure the retention of the copper in the ppt. form as it is liable to oxidation back into the soluble form. The filtrate and washings now contain the Rochelle salt free from copper. Boil to eliminate H_2S and by the addition of K_2CO_3 make the solution just alkaline to litmus. Evaporate to a small bulk, say to 20–25 c.c. Add 7 c.c. glacial acetic acid and 100 c.c. of 95 per cent alcohol. The acetic acid converts the Rochelle salt into potassium hydrogen tartrate which is only sparingly soluble in water (hence the reason for keeping the bulk of the solution small) and still less soluble (or practically insoluble) in alcohol. The mixture is allowed to stand for 15 minutes with stirring, after which it is filtered, washing four times each with 25 c.c. of alcohol. This eliminates all free acetic acid. Transfer ppt. and paper to a 150 c.c. beaker, add a few drops of thymolphthalein (as an indicator, similar to phenolphthalein) and titrate with decinormal sodium hydroxide (NaOH). The titration is conducted in a hot solution until the first permanent blue colour is obtained. This marks the reconversion of the insoluble potassium bitartrate into Rochelle salt as follows—

$$KHC_4H_4O_6 + NaOH = KNaC_4H_4O_6 + H_2O$$

The Rochelle salt in common use is the crystalline form ($KNaC_4H_4O_6 . 4H_2O$) with a molecular weight of 282 and equivalent, therefore, to 40 of NaOH.

Now 1 c.c. . IN . 1NaOH contains 0·004 gm. NaOH, equivalent to 0·0282 gm. Rochelle salt.

Hence gm. Rochelle salt per litre is—

$$\text{c.c. . IN . NaOH} \times 0{\cdot}0282 \times \frac{1000}{10}$$

and as ounces per gallon—

$$\text{c.c. NaOH} \times 2{\cdot}82 \times \frac{4{\cdot}54}{28{\cdot}4}$$

Hence oz. Rochelle salt per gallon

$= \text{c.c. . IN . NaOH} \times 0{\cdot}451$ (per 10 c.c. of solution used)

Note. The end point of the titration is less definite in the presence of undue amounts of iron, in which case a smaller volume of the solution can be taken for the analysis, making due correction in the final calculation.

CHAPTER XIII

DEPOSITION OF SILVER

WHITENING — Electro-silvering — Metal content of the solution — Anodes — Vats — Cathode connections — Quicking — Deposition of silver on lead and tin alloys—Steel work—Bright plating—Doctoring—Rate of deposition—Weight and thickness of silver deposits—Automatic plating—Throwing power—Electrolytic polishing—Applications of silver deposition—Troubles in the silver bath—Decarbonating—Recovery of silver—Stripping silver deposits—Analysis of solution

SILVER-PLATING can claim to be one of the oldest applications of electrodeposition on any scale. As a substitute for the old type of Sheffield plate which was composed of sheets of copper and silver soldered and sweated together, there has been no serious rival. The silver-plating industry has, in fact, been built on the ease with which base metals can be rendered free from the attack of corrosive substances in foods, and the lustre readily obtained upon even thin deposits of the metal. Stainless silver alloys have been eagerly sought, but so far have not matured as a material from which tableware can be commercially produced and appreciatively used.

Whitening. The production of very thin deposits of silver on base metals without the use of an external source of energy, and usually by boiling the cleaned work in a suitable silver solution, has had a large vogue for very cheap work. This practice is, however, passing, there being the much greater demand for deposits which will withstand the usual wear and tear of service. So thin is the usual simple immersion deposit that the term whitening adequately describes it. In the solution there must be a silver compound and a solvent for it. Many and varied are the compositions which have been proposed and used. Two are given as follows—

(1)	
Silver chloride	7·5
Potassium cyanide	37·5
Sodium carbonate	37·5
Common salt	15
Ammonia solution ·880	60
Water	1000

All parts by weight.

(2)	
Potassium bitartrate	80
Common salt	80
Silver chloride	Q.s. *
Water	1000

***Q.s. means in sufficient quantity.**

In either case the soluble salts are dissolved in a small quantity of the water and the silver chloride or other similar silver compound added. When dissolved, the solution can be made up to the required amount, with the remainder of the water. There is, in any case, considerable latitude in these compositions.

In use, the solution is warmed and the cleaned work immersed until nicely white. No great advantage can accrue from lengthened treatment.

By the use of a little water the dry materials may be mixed to a paste and applied to the cleaned work by means of a soft rag.

A variation of this method appeared some years ago, when in with the materials was mixed a metal powder, which, in contact with the metal being treated, served as an anode, and this enabled thicker deposits to be made. Some type of polishing powder was also added to the mixture, giving a better finish to the deposit.

Electro-Silvering. Silver deposition by means of current is the method now almost invariably used. By it, deposits of almost any thickness can be produced, the silver in the solution being regenerated by the solution of the silver anodes used.

A number of silver compounds are available. Solutions may be made up directly from the metal or from the nitrate. In either case the resulting compound in the solution is the double cyanide of silver and potassium (or sodium according to which cyanide is used). A silver potassium cyanide may be purchased containing 30 per cent silver. In this compound there will be enough potassium cyanide to hold up the silver and serve as free cyanide. The composition of the material is of the order of $2AgCN.KCN + 5KCN$. The use of the metal or the nitrate is, however, an alternative.

Metal Content of the Solution. This is most easily expressed as ounces troy per gallon, or grams per litre. Solutions for ordinary work not involving thick deposits may contain 2 oz. metal per gallon. For heavy deposits, as much as 4 oz. will be deemed desirable. Commercial solutions are in operation containing as much as 6 oz. per gallon. The excessive cost and probable accompanying wastage of silver involved with these rich solutions can only very seldom be justified.

Grain silver (fine—not sterling) can be bought at the present time at 24d. per oz. One ounce of the metal is equal to 1·574 oz. of silver nitrate, a salt which at present is of the order of 2s. 0d. per oz. This gives comparative costs of the metal and the corresponding amount of nitrate as 1 : 1·5. It is usually cheaper to buy the metal and convert it into nitrate. It involves the cost of the acid—not heavy—and the trouble. For small quantities it may be regarded as more convenient to start with the nitrate.

OTHER CONSTITUENTS. Either sodium or potassium cyanide is next required. Chemical formulae show that silver requires about its own weight of sodium cyanide to produce the double cyanide, and about 1·2 times its weight of potassium cyanide. An addition of 50 per cent more cyanide is required for free cyanide.

There has been much discussion about the advisability of the addition of either sodium or potassium carbonates. Whether intentionally added or not, they invariably form by the decomposition of the continually added free cyanide, and solutions are known to work better for their presence. Indeed, many commercial solutions to-day contain as much as 100 gm. of potassium carbonate per litre, equivalent to 1 lb. per gallon. Carbonates increase the conductance, yield more finely crystalline deposits, and increase the throwing power of the solution. This being so, they should constitute a definite addition when making a solution. The following will serve as a good solution—

	per gal.	per litre
Silver	2 oz.troy	13·7 gm.
Sodium cyanide	3 ,, avdp.	18·6 ,,
or		
Potassium cyanide . . .	4·3 ,, ,,	26·7 ,,
Sodium carbonate . . .	6·4 ,, ,,	40·0 ,,
or		
Potassium carbonate . . .	8·0 ,, ,,	50·0 ,,

Advantages accruing from the use of potassium salts are their greater conductance and solubility. Against these may be placed the larger quantities required for the same amount of chemical work and their higher cost. The rule may be observed that the salts shall either be sodium or potassium but not the two mixed. This is urged by the practical plater, though it is not very obvious why, except that when these cyanides and carbonates are estimated we should know more exactly the actual amount of material in the solution.

Of the quantities of cyanides recommended, two-thirds are required to form the double cyanides and the remaining third to act as free cyanide.

In the course of time carbonates accumulate in the solution, and it may become necessary to remove them, as suggested in the case of the copper cyanide solution. This will be referred to later.

Some idea of the very wide range of composition of silver-plating solutions can be gathered from the analyses of Brook* of a large number of solutions once in satisfactory service in the Sheffield district.

For silver solutions, potassium cyanide at one time completely held the field. The war period produced a scarcity of this compound, and sodium cyanide provided an excellent substitute. The use of the sodium compound has since prevailed in America, while in this country platers conservatively returned to the use of the potassium salt. Dr. E. B. Sanigar† has made a close research upon the relative advantages of the two classes of compounds. Spoons were plated in the different solutions. They were finished by expert finishers, inspected by qualified and unbiassed inspectors, both of whom reported no difference between the deposits obtained from the two classes of solution. All possible tests, except, perhaps, those of actual service, were made, but the evidence seemed to indicate clearly that deposits from the two solutions were indistinguishable.

A comparatively recent addition to silver plating baths which is finding favour in the United States, is potassium nitrate, which is made up to 10 to 15 per cent. Advantages claimed for this addition are: (1) increased conductance, (2) improved anode efficiency due to the NO_3 ion, (3) brighter deposits, and (4) a decrease in the amount of free cyanide required to keep the anodes clean. This innovation is due to Promisel and Wood‡ who also point out that, although the presence of chlorides in the bath somewhat increases the hardness of the deposit, they cannot be recommended on

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* *Trans. Far. Soc.*, xvi, Pt. 3, 1921.

† *J. Electrodepos. Tech. Soc.*, 1929, iv, 147.

‡ *Trans. Electrochem. Soc.*, 80, 1941, 459.

account of the increased tendency to corrosion of iron and steel plated in such a solution.

Anodes. Anodes for the silver bath should be of fine silver, again *not* sterling. Sterling silver contains 7·5 per cent of copper. If copper finds its way into the silver solution, it is, fortunately, not readily deposited. In fact, the bath would need to be unduly rich in copper and poor in silver for any appreciable quantity of copper to be deposited.* This, however, is no reason for allowing its accumulation in the bath. It should be regarded as one of those fortunate safeguards against accidental or unforeseen circumstances. The anodes should be annealed to render them more easily attacked and so maintain the silver content of the bath. They must not be suspended by any attackable metal which will be exposed to the solution. There are many obvious ways of avoiding this.

On working, they become dull owing to the temporary formation of the insoluble silver cyanide, which, however, dissolves in the free cyanide. Occasionally a slight black deposit occurs on them, due, possibly, to the formation of an oxide (Ag_2O_2). Usually, however, there is no great difficulty experienced with them. Their life and uniform solution depend to a very large extent upon the mechanical and thermal treatment which they have undergone in the process of preparation. Nowadays, this preliminary treatment may be such as admits of the uniform solution of the silver until the sheet is reduced to the thinness of a transparent film with very little disintegration, thus considerably reducing scrap.

Vats. Several materials are available for the construction of silver-plating vats. Glass or porcelain makes a clean container for the solution on the small scale. Enamelled iron on the larger scale is possible but, more usually, lead-lined wood tanks, or vessels of mild steel are serviceable. In any case, either of these materials should be wood-lined. This is mainly to prevent the possibility of short-circuiting. Where large work is being handled there is the possibility of current passing from the anode to the conducting lining and from it to projections from the work. These prominent portions of the cathode thus receive more than their share of the current, and obtain a thick and rough deposit in addition to some attack of the lead lining occurring. Indeed, it has been possible to detect lead

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* *Trans. Far. Soc.*, vi, 1910, Pt. 1.

in some of these rough deposits. The bare lead lining is safe only when all the electrodes are well distanced from it. A lining which thus receives some of the current and passes it on to the cathode constitutes a secondary or bipolar electrode. These have some use in electrodeposition but not under the conditions here referred to. Matchboard linings would, with advantage, be treated with a weak cyanide solution before being inserted in the bath. This is to take out any soluble compounds, such as resins, which are not calculated to be of any use in the solution.

Cathode Connections. The design of the cathode bars and connections will depend largely upon the nature of the work to be handled. Very commonly, however, they are arranged upon frames, to which may be imparted a slight reciprocating motion, so that the work can be kept slowly moving, this making for an improved deposit, in addition to keeping the solution gently stirred, and, therefore, more uniform in composition.

For the metallic parts of these cathode connections stainless steel will be found to be very serviceable and is largely used.

Quicking. This is a preliminary treatment applied chiefly to copper and its alloys prior to insertion in the bath. These metals tend to decompose the solution with the simple immersion of the silver upon the surface which is undergoing attack. Such films are not adhesive and are likely to lead to subsequent stripping. To avoid this, a thin, bright film of mercury is applied by simple immersion in a suitable solution.

The process is called quicking.

Quicking solution may contain from ¼ oz. to 1 oz. of mercury per gallon. The metal is dissolved in nitric acid and excess of the acid evaporated off. The resulting solution can then be poured into a solution made by dissolving sodium cyanide in water. A slight precipitate can be neglected. Alternatively the following materials will serve—

Mercuric oxide .	1 oz.	6·25 gm.
Sodium cyanide .	3 oz.	19 gm.
Water . . .	1 gal.	1 litre

The sodium cyanide is dissolved in a small quantity of water and the mercuric oxide then readily dissolves in the cyanide solution, after which the bulk of solution is made up with water. Prior to immersing the work in the silver solution it is momentarily passed through the quicking solution, receiving a bright film of mercury, which prevents the simple immersion deposition of silver and thus promotes adhesion of the silver deposit. The process is not used for Britannia metal and similar alloys.

Deposition of Silver on Lead and Tin Alloys. These metals are treated in a manner different from that of the copper alloys. They are "struck" in a weak silver solution containing a large proportion of free cyanide. The following solution is suitable for this purpose—

Silver . . .	0·6 oz. troy.	4 gm.
or		
Silver cyanide .	0·75 oz. ,,	5 ,,
Sodium cyanide .	20 oz. avdp.	125 ,,
Water . . .	1 gal.	1 litre

The work is taken straight from the potash boil and struck in this weak silver solution, afterwards being transferred to the main silver bath for the deposition of the bulk of the silver.

Steel Work. Steel work is similarly treated, though in some cases it is passed first through a silver solution even weaker than the one given above, and afterwards through the usual strike before the main solution.

Bright Plating. It has long been known and practised, that the small addition of carbon disulphide to the silver solution changes the deposit from dull to bright. This discovery is dated back to 1843 and provides the first outstanding example of the beneficial effect of an addition agent. The quantity so added is very small, amounting to only a few grains per gallon. The usual procedure is to shake up a few ounces of carbon disulphide with a gallon of the solution when a portion passes either into solution or intimate suspension. After allowing to settle, the clear liquid is added to the main bath in small doses of one fluid oz. for every 10 gallons, at intervals which experience may determine to be necessary according to the amount of work passing through the bath. A trace of the sulphur compound passes into the silver deposit though possibly far more is lost by evaporation which takes place quicker in warm than in cold weather. In such "bright solutions" a slightly higher current density is commonly used. The subsequent deposit requires much less finishing than that from the ordinary solution.

The exact function of CS_2 as a brightener has been examined by Egeberg and Promisel* who suggest that CS_2 is not the real brightener but that it gives rise to the production of thiourea $[(SC(NH_2)_2]$ which, independently, is found to yield similar results. The brightness is explained by the formation of submicroscopic crystals of silver sulphide which induce a fine crystalline structure in the silver.

Doctoring. From time to time it becomes necessary to treat specially small areas of the work which have, for one reason or other, been unsatisfactorily plated. For this purpose a small piece of silver is covered with a porous material such as sponge or a piece of rag. The silver is made the anode and the work to be "doctored" the cathode. The anode is dipped in the plating solution and applied to the defective part, which has been suitably cleaned. The solution in the "doctor" can be replenished from time to time, and the defective area thus corrected.

Further, insides of vessels are treated by filling, after suitably cleaning, with the solution and hanging in a small silver plate or rod. Convenient arrangements can be made for treating a number of such articles together, the vessels standing on a system of bars connected to the cathode or negative terminal of the machine. This method is largely applied.

Rate of Deposition. There has been much discussion as to the relative permissible rates at which silver may be safely deposited. Much depends upon the metal content of the solution. When this is high the rate of deposition can be increased. Usual practice in the large silver-plating shops, however, has followed the comparatively slow rate of about 3 amperes per sq. ft. This should be possible when the silver content is as low as 1 oz. per gallon, while with a stronger solution kept in motion, as is commonly practised, a rate of 6 amperes per sq. ft. may easily be maintained. Higher rates have been suggested but not generally adopted. Silver-platers should not be hidebound by anything which is of the nature of conservatism. They should take the line of experiment with the guidance of experience of the past. Such suggestions for

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* *Trans. Amer. Electrochem. Soc.*, 1938, lxxiv, 211.

more rapid deposition have been made by Mason* who recommends at least 8 amperes per sq. ft. and more recently by Mesle.†

A number of factors, however, must be borne in mind. In the first case, the weight of silver deposited per ampere-hour is far greater than that usual for the common metals owing to the high equivalent of silver. Secondly, there is the oft-overlooked fact that on the type of work usually silver-plated irregularities of shape lead to inequalities in C.D. over the surface when the important factor is that of the excessive C.D. on prominent and exposed parts. Such variations are often far greater than might be expected, and, in Mesle's paper, diagrams, showing the distribution of C.D. as determined by local thicknesses of the deposit, supply some answer to the demand for any considerable increase in the usual rate of depositing silver.

Weight and Thickness of Silver Deposits. The weight of silver deposited from the ordinary solution falls not far short of the theoretical value. An ampere-hour represents 4·024 gm. silver. One ounce troy is therefore deposited by 31·1 ÷ 4·024 = 7.7 ampere-hours. Allowing for a little inefficiency, this may be taken as 8 ampere-hours. Calculations can be safely based on this figure.

The thickness of silver deposits varies considerably. There appear to be no definitely accepted standards, so much depending upon the character of the work and the service it is called upon to undergo. On all types of irregular work, the deposits vary in thickness.

It may, however, be taken that there is a definite attempt on the part of many platers to maintain a high quality by adequate thicknesses, the general character of which is indicated in Table LVII.

A lower grade of plating might be of the order of 0·00063 in. or ⅝ mil. obtained by a C.D. of 3 amperes per sq. ft. during 1⅓ hours. This represents about ½ oz. troy per sq. ft.

In view of the very varying types of work, there may be equally wide differences of opinion as to the desirable weight required. For table ware the weight is more usually reckoned by the number of articles per oz. troy. It is to be feared that

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* *Trans. Far. Soc.*, xvi, Pt. 3, 1921.

† *Proc. 1st. I.E.C., E.T.S.*, March, 1937.

TABLE LVII

THICKNESS OF SILVER DEPOSITS

Grade	Dwts./Doz. Spoons		No. Spoons 1 Sq. Ft.	Dwts. 1 Sq. Ft.	Thickness Inch
A1	Table	30	10	25	0·0075
	Dessert	20	14	24	
	Tea	10			
A	Table	20		16	0·001
	Dessert	15		16	
	Tea	8			
B	Table	15		12	0·00075
	Dessert	10		12	
	Tea	5		12	

there is still much under-deposition, which militates against reasonable wear.

The formulation of exact standards is obviously a difficult matter. In the United States, however, it is specified that two grades of plating shall give deposits of 0·0008 in. (equal to 12·8 dwt. per sq. ft.) and 0·0006 in. (equal to 9·6 dwt. per sq. ft.). On the backs of the bowls of spoons and similar parts receiving the greatest wear, a thickness of 0·0012 in. is required.

As may be agreed between the two parties, the plater and the purchaser, these weights are checked by appointed inspectors. The silver deposits are stripped from the articles and the loss in weight ascertained. An acid strip is used for copper alloys, while for steel and the white metals the silver is stripped by making the weighed work the anode in a solution of sodium cyanide and weighing up the stripped articles. Alternatively for copper alloys, the silver is stripped in weak nitric acid, and from the strip solution the silver is estimated by chemical analysis. To check the thickness at the thickest parts, a further thick copper deposit is put on. The spoon, for example, is then cut through, the section being polished to remove scratches and the thickness of the silver measured by means of a suitable scale with the aid of a microscope.

Automatic Plating. One large application of silver plating is that of musical instruments. These are of many forms and sizes with widely varying areas. Nevertheless Savage and Pfefferle* have given an account of the accomplishment of automatic operation which includes, in addition to all the rinses, cleaning, coppering, sometimes nickelling and silver striking prior to the actual silver plating.

Throwing Power. Special methods for investigating throwing power have been adopted by different observers and while these may give interesting data in their special application it is, we think, preferable to use standardized methods, thus making results comparable in every case. One such method is adopted by Nicol† in the case of silver plating solutions. The cathode consists of a brass tube cut into four equal sections as shown in Fig. 79. A disc having an area equal to that of one section is placed immediately in front of the section nearest to the anode. These sections were enclosed in a gutta percha sleeve through which their connecting wires passed, these being arranged so that by convenient switches the individual currents in the sections and disc can be measured in the milliammeter (MA.) These currents were used as measures of the throwing power in place of the much more tedious method of weighing the individual deposits, a method

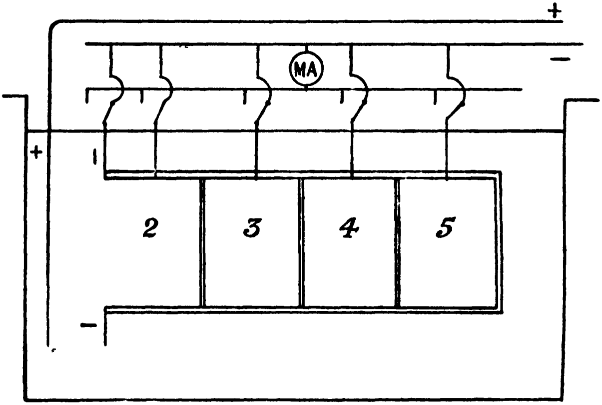

FIG. 79. THROWING POWER TEST.

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* *Amer. Electroplaters Soc.*, 1941.

† *J. Electrodepos. Tech. Soc.*, 1940, xvi, 15.

allowable for the particular purpose of comparing throwing power with varying amounts of potassium carbonate. The following results were obtained by this method—

TABLE LVIII

THROWING POWER OF SILVER SOLUTION

Potassium Carbonate		No. 1 Disc	Sections			
Oz./Gal.	Gm./l		2	3	4	5
2·4	15	720	250	3·5	0·8	0·7
4·8	30	710	235	20·0	1·0	0·8
7·2	45	700	250	20·0	1·0	0·8
9·6	60	650	280	65·0	2·4	1·4
12·0	75	640	290	70·0	3·4	1·6
14·4	90	640	290	75·0	4·5	1·8
16·8	105	640	280	75·0	5·5	2·0

These figures (milliamps.) serve to show a striking improvement in throwing power at 9·6 oz. potassium carbonate per gal. and a quicker and more striking comparison might even be obtained by dividing the figures for the disc successively by those for the sections, and these figures for section 4 (to avoid extreme sections) are in order: 900, 710, 700, 270, 190, 142 and 116 respectively.

Electrolytic Polishing. The production of a film of insoluble silver cyanide on silver anodes during the plating operation is a common phenomenon and is due to the temporary lack of free cyanide which normally re-forms at the cathode. The film usually disappears on standing. It is not so readily formed in the presence of a large proportion of free cyanide, nor usually with stirring nor with elevated temperature. It therefore first occurs in whatever depressions, however small, there are on the anode surface. This temporarily shields these depressions from solution and diverts the bulk of the current on to the more elevated parts or points of roughness. This is the process by means of which Gilbertson and Fortner* explain the considerable brightening effect on silver anodes with the presence of only a limited amount of free cyanide. The process can be carried out to produce a very marked amount of lustre on silver surfaces.

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* *Trans. Electrochem. Soc.*, **81**, **1942**, **199**.

Applications of Silver Deposition. The deposition of silver, however, goes far beyond the requirements of the "electroplating" industry. Silver has properties which extends its usefulness in directions other than that of domestic ware. Chief among these are its high degree of reflection, its permanence in air at ordinary and elevated temperatures, and also its high conductance.

A number of these applications have been pointed out by Laister.* Chemically, noble metals are those which are most permanent under atmospheric and other similar corrosive conditions. Of these metals silver is by far the cheapest. This point may be stressed by recalling the extremely thin deposits and therefore amounts of the metal required to impart the necessary amount of durability, bringing it somewhere in the same category as cadmium and chromium plating.

Its high reflective power fits it for reflector purposes which find a number of uses in warfare. More recently still, it has been shown that a very thin deposit of indium on a silver deposit, followed by heat treatment, effects the diffusion of the indium into the silver, thereby considerably increasing its tarnish-resisting property.

Its conductance also brings silver into new spheres of usefulness. Combined with its non-oxidizability at high temperature, it is of service as a coating for many switch contacts where arcing is likely to occur. Again, radio equipment utilizing alternating current opens up possibilities of silver as a conductor. It is well known that alternating current is not conducted through the entire section of a conductor uniformily, but that by far the larger proportion concentrates at the surface. This is known as "skin-effect." This is not conspicuous at the frequencies around 50 which are in common use industrially, but with the high frequency work of radio communication it can be reckoned that the current only penetrates to a depth of three ten-thousandths of an inch in a silver conductor. With a deposit of 0·0005 in. the electrical properties will be as good as those of solid silver, and hence it is that apparatus of this type is finding its way into the plating shop. It remains for the plater to know exactly the requirements of the particular new application and to operate his process to meet them.

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* *J. Electrodepos. Tech. Soc.*, 1943, 18, 69–74.

Troubles in the Silver Bath. It cannot be maintained that there are serious difficulties attaching to the working of the silver solution. Lack of free cyanide, with consequent inefficient solution of the anodes, is the most likely. Insoluble single cyanide of silver then collects on the anodes and offers undue resistance, and hinders the maintenance of the correct current density. This is an error which can easily be remedied. Silver solutions are commonly kept in motion, and the agitation gained by the use of air introduced below the anodes is advantageous in keeping the anodes clean. At the same time, there should not be sufficient free cyanide to maintain the anodes bright. They should work dull, and clear when the current is discontinued. Over prolonged periods of rest they may be removed from the bath. A satisfactory suspension of the anodes in the bath is effected with nickel wire. Anodes are occasionally found to acquire a thin black deposit, the origin of which is not generally agreed upon. This can, however, be removed by occasional scouring. Blistering of the deposit is due to lack of cleanliness. Silver solutions, like all others, should be kept free from suspended matter. This may be removed by continued filtration and circulation, solution being drawn from the bottom of the tank and passed through a canvas filtering bag to the surface. This motion also prevents stratification of the solution, which occurs with stationary solutions, and which leads to thicker deposits at the lower ends of work.

Such suspended matter is always likely to be responsible for rough deposits.

Decarbonating. Though advantages accrue through the presence of carbonates in the silver bath, there is a limit to the amount which may be regarded as desirable. Sooner or later the carbonates will have accumulated to such an extent that their removal, either entirely or in part, must be effected. This is commonly done by the addition of barium cyanide which reacts as follows—

$$K_2CO_3 + Ba(CN)_2 = 2KCN + BaCO_3$$

The barium carbonate is precipitated and may be removed after allowing to settle. A simple knowledge of these chemical formulae will indicate that for every 138 grm. of potassium carbonate to be removed 189 parts by weight of barium cyanide must be added, and this will produce 130 parts of potassium cyanide in the solution. Corresponding quantities can be worked out for sodium cyanide. The removal of a large amount of carbonate at one operation may therefore result in the production of an undesirably large amount of potassium cyanide. The difficulty can be got over by the frequent use of small doses of barium cyanide, this compound replacing some proportion of the usual free cyanide addition, or the addition of other barium compounds such as the chloride can be made, so that potassium chloride remains in the solution. This is a good conductor, and thus serves some useful purpose in the solution. Alternatively, the excess carbonates can be removed, without the addition of further chemicals, by concentrating and cooling so that the bulk of the carbonates crystallize out.

Recovery of Silver. Usually the plater is not required actually to recover the silver from his residues. He can, however, do something towards utilizing them with economy. Quantities of old solutions can be evaporated by a steam coil and excess of carbonates separated off. The liquid can then be treated with muriatic acid, and warmed to convert the whole of the silver to chloride, which can be filtered, washed, and added to other silver-plating solutions, thus increasing, as may be required, their metal content. The addition of acid to the solution without the separation of the carbonates is inconvenient, owing to the usually large amount of these compounds likely to be present, and the considerable evolution of carbonic acid gas and frothing. Methods of recovering the silver by fusion are considered outside the electro-plater's province.

In large plants the addition of zinc turnings to the drag out tank has proved very successful in the complete precipitation of the silver.

Stripping Silver Deposits. Acid and electrolytic strips are available.

For a base metal of copper and its alloys the acid strip is largely used. This may consist of—

Sulphuric acid (Sp. Gr. 1·84)	19 volumes
Nitric acid (Sp. Gr. 1·42)	1 volume

In making the mixture the sulphuric acid is added to the nitric acid and the mixture heated to about 80° C. The work is immersed after drying. Silver is attacked by the acids, the copper base being protected by the sulphuric acid. The completion of the stripping is seen when the whole of the surface has assumed a dark stain, which can subsequently be removed by the ordinary acid dip.

Steel and white metal goods are better treated electrolytically. A solution of 4 to 6 oz. of sodium cyanide per gallon (25 to 40 gm. per litre) is made and, preferably after warming, though the solution may be used cold, the work is made the anode, using some old silver or even iron as cathode. The silver is anodically dissolved, and is thus removed without attack on the basis metal.

ANALYSIS OF THE SOLUTION

Constituents of the silver solution requiring frequent analysis and control are the silver, free cyanide, and the carbonates.

Free Cyanide. This method is exactly the same as that for the copper cyanide solution. Take 20 c.c. of the silver solution and dilute to 150 c.c. Add a few drops of potassium iodide solution and slightly warm. Titrate with N/10 $AgNO_3$ to the first permanent turbidity.

Now—

$$1 \text{ c.c. N/10 } AgNO_3 = \cdot013 \text{ gm. } KCN$$
$$= \cdot0098 \text{ gm. } NaCN$$

Hence—

$$\text{c.c. N/10 } AgNO_3 \times \cdot013 \times \frac{1000}{20} = \text{gm. } KCN/\text{litre}$$

and

$$\text{c.c. N/10 } AgNO_3 \times \cdot0098 \times \frac{1000}{20} = \text{gm. } NaCN/\text{litre}$$

Silver. A very common method is based on the separation of the silver as sulphide from other metals contained in the solution by means of H_2S, subsequently redissolving the silver sulphide in nitric acid and titrating with a standard potassium or ammonium thiocyanate solution.

Ammonium thiocyanate precipitates silver from its acid solutions thus—

$$\underset{170}{AgNO_3} + \underset{76}{NH_4CNS} = AgCNS + NH_4NO_3$$

A normal solution of NH_4CNS therefore contains 76 gm. of the salt per litre. The solution is not, however, directly made in this manner. An approximate solution is prepared and then standardized with pure silver or silver nitrate as it is not possible to depend upon the purity of the purchased ammonium salt.

Prepare a solution of NH_4CNS to contain from 8 to 9 gm. of the salt per litre. This should be of a little more than decinormal strength. Charge a burette with this solution. Take 10 c.c. N/10 $AgNO_3$ in a conical flask. Dilute with distilled water and add a few drops of a solution of iron alum. (Iron alum is ferric ammonium sulphate. The ferric iron it contains reacts with excess of NH_4CNS after the silver has been precipitated, giving the characteristic red colour which provides the indicator.) Add a little nitric acid and warm the solution, subsequently titrating it with the thiocyanate solution from the burette until the first permanent red colour is obtained.

Assume that, as an average of a number of titrations—

10 c.c. N/10 $AgNO_3$ require 9·1 c.c. NH_4CNS.

The thiocyanate solution is stronger than the deci-normal silver nitrate. It can be reduced to exactly N/10 strength by the addition of water in the proportion of 0·9 c.c. to each 9·1 c.c. of the solution. Dilute a quantity of the solution in this manner and shake, after which the N/10 NH_4CNS produced will have a silver value of 0·0108 gm. silver per c.c.

The estimation of silver now proceeds as follows. Take 10 c.c. of the silver solution in a conical flask, dilute, warm and pass excess H_2S. Filter off ppt. of Ag_2S and wash well with hot, distilled water. (Copper, the most likely metal contamination in the solution is not pptd. and is thus got rid of.) Transfer the paper with the ppt. back to the flask and dissolve the black ppt. of Ag_2S in warm dilute HNO_3 forming $AgNO_3$. Using a few drops of iron alum as indicator titrate with the N/10 NH_4CNS to the first indication of permanent red colour. Assume this reading to be 12·5 c.c.

Then, 1 c.c. N/10 $NH_4CNS \equiv$ 0·0108 gm. Ag.

and the silver content of the solution

$$= \frac{12 \cdot 5 \times 0 \cdot 0108 \times 1000}{10}$$

$$= 13 \cdot 5 \text{ gm. per litre}$$

Estimation of Carbonates. The method is as follows—

Carbonates are pptd. by the addition of $BaCl_2$.

$$K_2CO_3 + BaCl_2 = BaCO_3 + 2KCl$$

Take 50 c.c. of solution and add excess of $BaCl_2$, that is, until there is no further sign of precipitation. Filter and wash the ppt. and then transfer back to the flask with the paper and dissolve the $BaCO_3$ in an excess of semi-normal HNO_3. Titrate back the excess of acid with semi-normal sodium carbonate and thus obtain the exact amount of acid required to dissolve the carbonate.

Then

$$\begin{array}{cccc} 2HNO_3 \equiv & BaCO_3 \equiv & K_2CO_3 \equiv & Na_2CO_3 \\ 2 \times 63 & & 138 & 106 \end{array}$$

Assume

$$N/2\ HNO_3 \quad \text{used} = 25 \text{ c.c.}$$
$$N/2\ Na_2CO_3 \quad \text{used} = 5 \text{ c.c.}$$

Then c.c. $N/2\ HNO_3$ required to dissolve the $BaCO_3$

$$= 25 - 5 = 20 \text{ c.c.}$$

Now 1 c.c. $N/2\ HNO_3$ contains 0·0315 gm. HNO_3

$$\equiv 0·0345 \text{ gm. } K_2CO_3 \text{ and}$$
$$\equiv 0·0265 \text{ gm. } Na_2CO_3.$$

Hence

$$K_2CO_3 \text{ content} = \frac{20 \times 0·0345 \times 1000}{50}$$
$$= 13·8 \text{ gm. per litre.}$$

$$\text{or} \quad Na_2CO_3 \text{ content} = \frac{20 \times 0·0265 \times 1000}{50}$$
$$= 10·6 \text{ gm. per litre}$$

CHAPTER XIV

DEPOSITION OF GOLD

Gold alloys—Methods of deposition—Simple immersion—The single cell process—Electro-gilding—Working the solution—Variations of colours of deposits—Carat plating—Conserving and recovering gold—Mercurial gilding—Applications of gold deposition

The deposition of gold attracted early attention, primarily from the known resistance of this metal to all types of corrosion, and also from its exceedingly pleasing appearance. While very small amounts of gold find application in the several cheap alloys used in many ordinary varieties of jewellery, the still smaller amount which by the several processes of deposition can be applied to do all that is necessary is surprising. If the nitric acid test is anything of a standard then it would appear that films of as little as one-millionth of an inch render good service.

Gold Alloys. It may be worth recording here that gold as the fine metal, is too soft for everyday use. Hence it is frequently alloyed with other metals to impart hardness and improve its wearing qualities. The proportion of gold in the alloy is referred to in twenty-fourths or, as they are commonly called, *carats*. The standard of the once familiar gold coinage was 22 carat, meaning that 22/24 of the metal was fine gold. These values are marked on the goods by the Government Assay Office after test, and known as *hall marks*, qualities as low as 9 carat being so treated in this country as against 10 carat in the United States of America. Many so-called gold products are only surfaced with these alloys, the inner base metal being of the copper-zinc type, with colours approximating to that of the gold alloy so as to become less prominent when the gold covering may be worn through.

Methods of Deposition. Four main methods of producing gold films are in operation—

Simple Immersion, in which exchange with the base metal provides the reason for precipitation. Such deposits are notoriously thin, but the high specific gravity of the deposited gold may be responsible for the unusually good properties of these films.

SINGLE CELL PROCESS, in which the current used is generated by a zinc anode suspended in a common salt solution contained in a porous pot, the work constituting the cathode when hung in a suitable gold solution containing also the porous cell. The plating plant in this case is self-contained. Slightly thicker deposits are possible than with simple immersion.

ELECTRO-GILDING in which, following usual practice, there is an external source of electrical power.

MERCURIAL GILDING, the gold being applied as a pasty amalgam. Each of these processes will be referred to briefly.

Simple Immersion. There is still a large amount of work which, by reason of low price, is treated by simple immersion. During the history of the process many different solutions have been employed with constituents to which it might be difficult to assign a definite function. Simplicity of composition would seem to be a recommendation for a solution of this type.

The solution contains little gold, which is replenished from time to time by further additions. A general composition may be as follows—

Sodium cyanide . . .	40 gm.
Sodium carbonate . . .	50 ,,
Water	1 litre

To this solution gold is added to choice, possibly to the extent of 6 dwt. per gallon or 2 gm. per litre. The fine gold is dissolved in aqua regia (a mixture of strong hydrochloric and nitric acids usually in the proportion of 3 : 1 by volume) and excess of acid evaporated off. The gold chloride is dissolved in water, precipitated by ammonia, producing a brown precipitate of gold fulminate. This is filtered, but not allowed to become dry, as it is explosive in the dry condition. The fulminate is washed into the above solution, when, with warming, it readily dissolves.

In operation the solution is kept hot, say up to 80° C., and the work, cleaned in the usual manner, immersed in it. While almost every metal will turn out gold from this solution, the most satisfactory deposits are obtained on copper and its alloys, and other metals are, therefore, flashed with copper or brass prior to gilding.

The Single Cell Process. The gold solution for this method is usually weaker than for simple immersion. It contains several other constituents which probably play some part in the production of denser deposits. Potassium or sodium ferrocyanides are notable constituents. A solution may be made as follows—

Sodium ferrocyanide	$3\frac{1}{2}$ oz.	20 gm.
Sodium phosphate	$1\frac{2}{3}$,,	10 ,,
Sodium sulphite	$\frac{1}{12}$,,	·5 ,,
Water	1 gal.	1 litre

This solution is made up and gold fulminate added to give a content of 3 to 4 dwt. of gold per gallon. The solution is boiled for a short time, and any deposit may be filtered off and neglected.

The cell arrangement is simple. A zinc sheet or rod is suspended in a saturated salt solution, contained in a clean porous pot, standing in the gold solution. The cleaned work is suspended in the gold solution, its suspension wire being connected to the zinc. Then zinc passes anodically into the salt solution while gold is deposited on to the work as cathode. The gold solution is replenished by occasional additions of gold fulminate.

Electro-Gilding. This is the method most commonly employed for the deposition of appreciable amounts of the metal, any desired thickness being applied at will. Solutions for this purpose contain very varying amounts of the metal, from a few dwt. per gallon upwards. The figure is often largely determined by the high cost of gold, and, consequently, the initial outlay with possible losses.

All electro-gilding solutions are of the cyanide type though the final composition may be achieved through different stages.

The methods of preparation are few and relatively simple. Starting with the metal in the "fine" state, this is dissolved in a minimum amount of aqua regia—a mixture of nitric and hydrochloric acids, both strong. It suffices to start with hydrochloric acid and make occasional additions of nitric acid. Strongly acid fumes are given off, the operation being carried out with good ventilation. When the metal is dissolved, excess of acid is evaporated off, very great care being taken not to overheat the gold chloride residue, which is readily decomposed by slight elevation of temperature. The gold chloride is redissolved in a small proportion of water, and re-evaporated to get rid of last traces of acid. Two methods of procedure may now be followed.

(*a*) The gold is precipitated with ammonia, a yellowish-brown product, known as fulminate of gold, being obtained. This is filtered and washed with water; care being taken that it does not become dry, as it is then explosive. A solution of potassium or sodium cyanide of suitable strength is prepared and the fulminate washed and dissolved in it. This provides the solution.

(*b*) Alternatively, the gold chloride can be directly added to the cyanide solution, when the usual yellow colour of the chloride disappears by the transformation of the salt into the double cyanide (AuCN.KCN). By this method a small proportion of alkali chloride remains in the solution. The amount is too small to be regarded as detrimental, especially in view of the impurities usually introduced by the frequent additions of free cyanide.

Using either of these methods the following quantities may be taken as some guide—

Gold	½ oz. troy	3·4 gm.
Total KCN	3 oz. av.	19·0 ,,
Water	1 gallon	1 litre

The solution, however prepared, is best heated before operating it.

Additions of sodium phosphate and a reducing agent are common, the former substance acting not primarily as a conducting salt but giving rise to complex compounds which reduce the metal ion content and thereby increase the density of the deposit.

Working the Solution. This is a solution which, from its widely varying composition, is not susceptible of exactly stated conditions of operation. Two main results have usually to be achieved: (1) the desired thickness, apart from current efficiency, as this is usually very low, and (2) colour.

The colour of gold deposits varies with many conditions. With cold solutions and low C.D. the colour is pale and unattractive. With increased C.D. and at a higher temperature (up to 60° C. and over) the colour assumes a more pleasing shade, generally regarded as a warmer tone. Excessive current induces burning, with a "foxy" and powdery deposit. This is essentially a case in which the personal judgment of the operator is of the greatest value. In any case, both the P.D. and C.D. are low, and usually best left not specified.

Internals are gilt by filling the vessel with the solution and applying an internal anode, while awkward corners and badly plated spots are easily "doctored." A gold anode is to be recommended. It dissolves quantitatively, and should not be allowed to remain in the solution when not in use. Generally the anode efficiency exceeds cathode efficiency, the solution becoming enriched with metal. Many gilders, therefore, prefer to work with a small insoluble anode, which may be of platinum, and make occasional additions of gold salts.

Variations of Colour of Deposits. Additions to the solution may effect large changes in the colour of the deposit. Co-deposited copper produces a redder shade—"red or rose gold"—while the addition of small proportions of silver solution effects a greenish tint in the deposit known as "green gold." Again, the addition of nickel cyanide or zinc cyanide very much reduces the colour of the gold to what is called "white gold." Dead gilding is effected by depositing the gold on a surface obtained either by severe pickling, sand-blasting, or copper deposition from the sulphate bath. The judicious application of dead and bright deposits may be used to much decorative advantage.

Where thicker deposits are required, recourse to quicking is advantageous with occasional scratch-brushing, after which operation the suspension wire should be applied in another position, as wire marks are liable to be very prominent.

Carat Plating. In the production of coloured deposits, success in the maintenance of an exact shade is a matter of the most careful control. These difficulties led to the investigation of the deposition of gold alloys, or as it is termed, "plating to carat."*

Thus a satisfactory and consistent 18 carat green gold may be obtained from the following solution—

Au as $NaAu(CN)_2$	2·00	gm. per litre
Ag as $NaAg(CN)_2$	0·75	,,
NaCN, free	4·00	,,
Na_2CO_3 anhydrous	5·00	,,
Na_3PO_4	20·00	,,
K_2SO_3	5·00	,,

* Pope: *Proc. 1st I.E.C.*, *E.T.S.*, March, 1937

The solution is worked warm and at a low current density. The metal content is replenished from the anodes while redder deposits are obtained by replacing the silver with copper.

Conserving and Recovering Gold. The high cost of the metal necessitates every care to prevent loss. A small volume of first rinsing water should, therefore, be religiously used and returned to the bath as make-up water. Stripping of gold deposits is effected with ease by making the work anode in a weak cyanide solution, say 5 per cent sodium cyanide, with a small iron cathode. The gold rapidly disappears from the anode, and the solution can be reserved for the recovery of its gold contents. This, with old solution and a certain amount of sweep, will always be taken over by an assayer, who has no difficulty in extracting the metal content. In order to reduce the bulk of solution to be handled, the cyanides may be decomposed with acid, HCN being expelled. The solution then receives an addition of ferrous sulphate, which, in the course of a few hours (the mixture may be allowed to stand overnight), deposits the gold as a brown powder, which is recovered by sedimentation, filtering and cupelling with lead or other type of furnace treatment.

Mercurial Gilding. In this process a pasty amalgam is made by adding mercury to heated gold and squeezing out excess of mercury through chamois leather.

Its application to the article to be gilded is made by cleaning the article in the usual manner, and rubbing it over with a wire brush which has first been dipped in a solution of mercuric nitrate. This serves a similar purpose to quicking, leaving a film of mercury on the surface of the metal. The gold is applied by passing the wire brush over the amalgam and then over the work. This applies an even layer of amalgam. To increase the final thickness of the gold deposit, this operation is repeated a number of times, after which the work is rinsed and dried. The mercury is now expelled by heating in a muffle or over a dull charcoal fire. Mercury volatilizes at 390° C., leaving the gold as a pale yellow deposit, which is rendered more uniform by scratch-brushing. The colour of the deposit is enhanced by passing the work through a mixture of alum, nitre, and salt in the form of a paste. The work is now dried over the dull fire, and heating continued until the residue of salts just fuses. It is then plunged into water to remove the fused salts, after which it is rinsed. This colouring operation can be repeated at will.

Applications of Gold-Deposition. In addition to the usual processes of electro-gilding, a number of special processes have been carried out in which films of deposited gold of extreme thinness have been made and utilized. In the manufacture of the fine wires from which ornamental metallic braids are produced, brass wire is, in some cases, drawn so that 1 oz. of metal produces 1,300 yds. of wire. Before the last stages of drawing are effected, the wire is gilt so that only 2 pennyweights of gold cover 1 lb. of the wire. A simple calculation will show that the thickness of the gold film is of the order of 1½ millionths of an inch, or that one ounce of gold serves to satisfactorily gild 120 miles of wire.

The production of gold leaf by electrolysis has been attempted. In the process, silver was first rolled down to a thin foil which was then gilt on one side only. The silver was subsequently dissolved away by nitric acid leaving the thin gold film floating in the liquid, the deposit being subsequently dried, cut to the usual 3¼ in. square leaves and assembled in the form of the usual books. These leaves were of the order of one 1/250,000th of an inch thick so that 1 oz. of gold covered an area of 200 sq. ft.

Still more recently, films of gold have been produced by electrodeposition which were of the order of four ten-millionths of an inch in thickness, so thin—and yet impermeable to gases—that print could readily be read through a succession of five of these deposits. These were produced by Müller by the deposition of the required film of gold on a silver foil strip. The deposit was then covered by a further deposit of silver and in this sandwich form could then be cut and mounted into the position finally required. The silver was then dissolved by some suitable process leaving the extremely thin gold deposit suitably mounted.

Again, a considerable quantity of the precious metal is obtained or, in the final stage of extraction refined, by electrolysis, yielding a product of the highest purity.

These are examples which possibly lie outside the recognized range of ordinary gold plating, but they well illustrate the manipulative skill called for in some of these electrodeposition processes, and quantities handled in others.

CHAPTER XV

DEPOSITION OF NICKEL

INTRODUCTION—Original solution—Modern solutions—Buffering reagents—Nickel electrotyping solutions—Current densities and thickness of deposits—Rapid nickel-plating—Anodes—Purity of nickel anodes—Maintenance of solution—Removal of iron—Removal of chromium—Preparation of work for nickel-plating—Brass, copper, etc.—Iron and steel—Castings—Anodic acid etch—Zinc, tin, and lead alloys—Treatment of die castings—Black nickelling—Barrel plating—Common defects in nickel-plating—Porosity—Pitting—Peeling—Nickel undercoat for chromium—Heavy nickel deposition—Protective value of nickel deposits—Production of nickel sheets—Composite coatings

Introduction. For many years the deposition of gold and silver monopolized the field of electrodeposition, and it was not until the early 'eighties that the deposition of nickel, especially on iron and steel for protective purposes, came to be suggested and practised. About that date, the advantages of this deposit were urged by Adams, and since that time the method has been considerably practised, and during recent years has obtained a considerably extended vogue, mainly on account of a large amount of scientific research work carried out, this resulting in a fuller appreciation of the possibilities of what are becoming somewhat standardized solutions of well-known properties, replacing the original solution which, for many years, was used more or less empirically, with results which fell far short of perfection.

Original Solution. The original solution was composed of—

Nickel ammonium sulphate .	12 oz. .	75 gm.
Water	1 gal. .	1 litre

The solution was brought to such acidity as was detected by means of litmus without the reaction being too marked. Excess acidity was counteracted by the addition of ammonia, and the solution strength kept up by reference to hydrometer readings, which in those days constituted a stock method of solution testing. Seldom, if ever, is this solution used to-day. Not that the solution is valueless, for it rendered excellent service over many years, but it fails to meet the requirements of modern industry. Its rate of deposition was low, usually not exceeding 4 amperes per sq. ft., and a long time, therefore, was required to effect substantial deposits. These were hard and not so pliable as might be desired. Nevertheless, the formula was slavishly retained for many years, until research broke through conservatism, and it was shown that with single nickel sulphate as the main constituent of the solution, deposits could be made more rapidly, were softer, and therefore more amenable to subsequent treatment, were more ductile, and therefore adapted themselves to slight bending in service. Later, a number of additions have been made with marked advantages.

The extensive use of both nickel sulphate (single nickel salts) and nickel ammonium sulphate (double nickel salts) has necessitated some specification* of their composition in order to guarantee freedom from undesirable impurities.

Modern Solutions. While the process of simplification does not show the way for the reduction of nickel solutions to a single one, or two, yet much has been done in this direction within the past few years. Two types of solutions for general use, therefore, are given as follows—

LIGHT SOLUTION

(*a*)	Double nickel salts	4 oz.	25 gm.
	Single nickel salts	8 oz.	50 ,,
	Water	1 gal.	1 litre
(*b*)	Single nickel salts	1½ lb.	150 gm.
	Magnesium sulphate	3½ oz.	22 ,,
	Boric acid	1½ ,,	9 ,,
	Sodium chloride	1 ,,	6 ,,
	Water	1 gal.	1 litre

HEAVY SOLUTION FOR RAPID PRODUCTION

Single nickel salts	3 lb.	300 gm.
Nickel chloride	3 oz.	19 ,,
Boric acid	2 oz.	12·5 ,,
Water	1 gal.	1 litre

The first two of these solutions are recommended for general use where special qualities of the deposit are not aimed at. The solutions are simple in manipulation, are commonly used cold, and require about 5 to 6 amperes per sq. ft. The deposits

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* B.S.I. Specification 564, 1931.

are more workable than that obtained by the use of double salts alone. The third of these solutions is now largely used, with some variations of proportions of constituents according to the experience of workers. Each constituent serves a particular function.

Chlorides are regarded as being of importance in assisting the solution of the anode. While common salt was the first addition, nickel chloride is now more commonly used. Nickel anodes available to-day are very much superior to those of former practice in their solubility under the influence of the current.

Acidity of Nickel Solutions. This factor, once only roughly defined and tested, though regarded as of some importance, is now considered as one of considerable importance. The subject has already been dealt with in some detail in Chapter VII. Here it remains only to be said that experience has shown that a pH of 5·6 to 6·2 generally meets the case in nickel-plating, this range, with its fairly easy and quick computation, being much more accurate than that of applying methyl orange and litmus papers. It is to be noted, however, that an increase of temperature increases the acidity, thereby lowering the pH value. This reduction at a temperature of 40° to 50° C., may be as much as 0·35 degree on the pH scale, and care should be taken to ensure comparative tests when working with a warm solution. The changes of acidity in the nickel solution are due to irregular working of the electrodes.

Unfortunately there is no simple rule for adding acid and alkali to correct pH. A given quantity of acid will give a different decrease in pH in different solutions in which, mainly on account of the variation of the SO_4^{--} ions, there will be different degrees of dissociation of the added acid. Corrections can, however, be made in the following manner. For decreasing pH a standard acid may be made by diluting concentrated sulphuric acid to 100 times its volume. Take 10 c.c. of the plating solution, add the required indicator, brom cresol purple it may be, and add the standard acid until the solution acquires the tint corresponding to the required pH. A simple calculation will then show that for each c.c. of this standard acid added to 10 c.c. of the plating solution, 16 fl. oz. of the concentrated acid should be added to each 100 gallons of the bath.

Similarly for increasing pH, a standard ammonia solution is made by diluting the ·880 solution to 100 times its volume. This is now used to correct the pH of a 10 c.c. sample of the solution and for each c.c. of standard ammonia used, add 16 fl. oz. (suitably diluted) of the ·880 solution to each 100 gallons of the bath.

As it is not always possible to control the working of these exactly, it is desirable to have some other method of, as it were, steadying the pH of the solution. This is done by the use of *buffering reagents.*

Buffering Reagents. Boric acid figures so largely in nickel-plating solutions that a word or two must be said with regard to its purpose. As has already been pointed out (Chapter II), this acid dissociates only very feebly, and thus cannot be regarded as contributing to the conductance of the solution. By reason of this feeble dissociation it serves another useful purpose, viz., that of a buffering agent. By this term is meant a substance which opposes changes in pH value. In the presence of boric acid the addition of alkali to the nickel bath effects far less change in the pH value than in its absence. The need for constancy of the pH value of the nickel solution has already been emphasized. With variations in the current efficiency of the cathode, alkali may be produced which ordinarily would be dissociated with the reduction of acidity. Boric acid absorbs this alkali and thus maintains a more uniform pH value. Substances of this type are said to *buffer* the solutions, and serve a particularly useful purpose in all plating solutions where low acidity only is permissible and must be maintained. The salt of a weak acid similarly takes up acid formed at the anode.

Nickel Electrotyping Solutions. While dealing with nickel solutions for various purposes, it may be well to make reference to those in use for the purpose of electrotyping. Here the special requirement is that of the deposition of nickel over a graphited surface. This is not possible with a solution containing nickel sulphate only. The addition of an ammonium salt at once produces satisfactory deposits, and the problem remains to determine the best materials, quantities, and conditions.

This matter has been explored by the U.S. Bureau of Standards, recommendations being made for solutions for depositing upon wax and also upon lead. For wax the composition suggested is as follows—

Nickel sulphate . .	12 oz.	75 gm.
Ammonium chloride . .	1 „	6·25 „
Water	1 gal.	1 litre

After the wax is covered with nickel, and also in the case of lead moulding, a stronger solution is recommended as follows—

Nickel sulphate . .	1·4 lb.	140 gm.
Ammonium chloride .	2½ oz.	15 „
Water	1 gal.	1 litre

Ammonium sulphate is not recommended, as its presence reduces the solubility of the nickel sulphate.

Current Density and Thickness of Deposit. The rate of nickel deposition has in recent years been considerably accelerated. With the old double nickel sulphate solution the rate of deposition rarely exceeded 3 to 4 amperes per sq. ft. and the time required to obtain a sufficiently substantial coating was of the order of three hours, a batch in the morning and another in the afternoon being the usual procedure. To-day solutions vary in strength from 100 to 300 gm. of the single nickel salts per litre. With 100–150 gm. per litre, the solution is frequently used cold when current densities approximating to

TABLE LIX

THICKNESS OF NICKEL DEPOSITS

Current efficiency 95%

Current Density	Thickness in Mils in			
Amp./Sq. Ft.	30 Min.	60 Min.	90 Min.	120 Min.
5	0·13	0·25	0·38	0·51
10	0·25	0·51	0·76	1·01
15	0·38	0·76	1·14	1·52
20	0·51	1·01	1·52	2·03
25	0·63	1·26	1·90	2·53
30	0·76	1·52	2·28	3·04
40	1·01	2·03	3·04	4·06
60	1·52	3·04	4·56	6·08
80	2·03	4·06	6·1	8·12
100	2·54	5·07	7·6	10·14

6 amperes per sq. ft. are used. With the stronger solution used warm, however, there is the possibility of increasing the current density up to 60 or even 80 amperes per sq. ft. with a considerable reduction of time to obtain satisfactory thickness and increasing the number of batches of work put through the solution per day. A more usual rate of deposition is of the order of 20 amperes per sq. ft. Table LIX shows the thickness of deposits obtained under the different conditions in each case with a current efficiency of 95 per cent, and these figures are more viivdly expressed in Figs. 80 and 81 from which, without calculation, the thickness of deposit for any intermediate conditions can be readily derived.

An alternative table (LX) shows times required for nickel (and also cobalt) deposition.

TABLE LX

TIMES REQUIRED FOR NICKEL AND COBALT DEPOSITS (C.Eff. = 95%)

Amp. per Sq. Ft.	Time to Produce Thickness of				
	·00005″	·0001″	·0005″	·001″	·002″
10	6	12	1	2	4
20	3	6	30	1	2
30	2	4	20	40	1·20
40	1·30	3	15	30	1·0
50	1·12	2·24	12	24	48
Gm. per sq. ft.	1·035	2·07	10·35	20·7	41·4

Above thick line = hours and minutes.
Below thick line = minutes and seconds.

The determination of the thickness of nickel and other deposits has recently received considerable attention, the methods used being the applications of (*a*) direct measurement with the micrometer, (*b*) methods involving chemical treatment, and (*c*) methods based on the wearing away of the

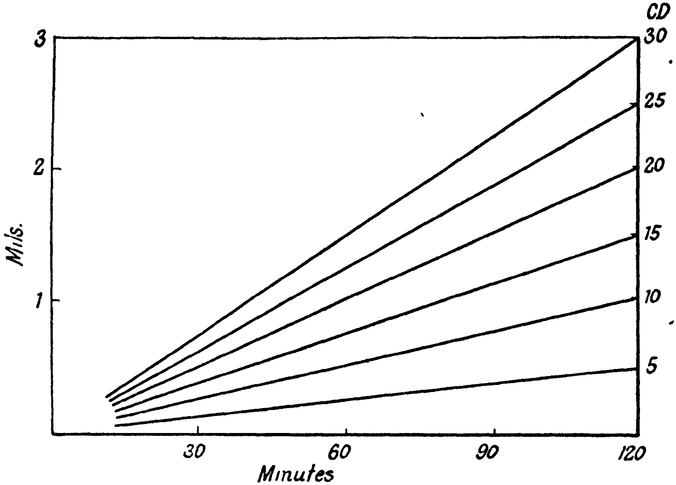

FIG. 80. THICKNESS OF NICKEL DEPOSITS

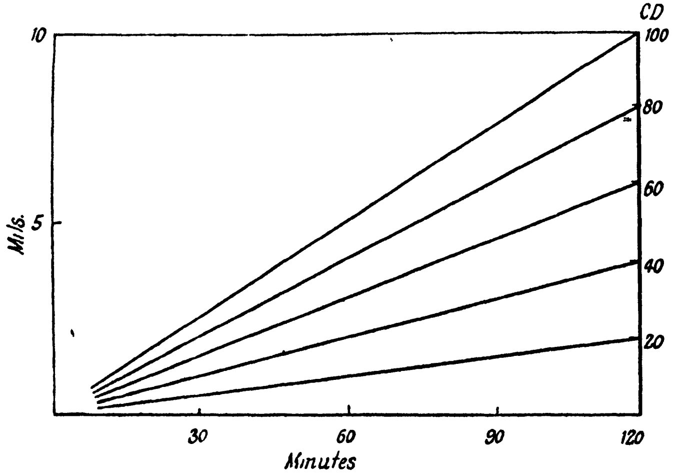

FIG. 81. THICKNESS OF NICKEL DEPOSITS

deposit by either mechanical or chemical processes. These are dealt with in some detail in Chap. XXII.

A simple method is that of taking a test piece with a thin coating of chromium on to which the required nickel deposit is made. A subsequent thin coat of chromium puts this deposit into stress enabling it to be readily stripped from the chromium below. The removed deposit is then measured with the micrometer.

Rapid Nickel-plating. For mass production purposes where large numbers of components are required to be well plated a very much quicker rate of deposition has been adopted with considerable success. There appears to be nothing very special in the solution or its method of operation. Normally a solution for this purpose contains from 200 to 250 grm. of the single salts per litre, with other usual additions, and is worked warm, higher temperatures favouring more rapid deposition. The cleaning operations involve electrolytic alkali, followed by anodic pickling, care being taken to rinse thoroughly before transferring to the nickel bath. Under these conditions current densities up to 80 amperes per sq. ft. requiring about 15 to 20 minutes' deposition are very serviceable, the anodic pickling leaving a surface which admits of the closest contact between the base and deposited metals.

Anodes. These may be of cast or sheet metal. Cast anodes are more easily dissolved, but subject to disintegration. Rolled anodes dissolve less freely and give rise to acidity but involve less scrap. Oval shaped nickel bars are sometimes advocated to diminish scrap. They seem to offer the possibility of greatly reduced surface with wear.

There is some tendency for pure nickel anodes to assume a "passive" state, which reduces their rate of solution. To correct this, what are termed *depolarized* anodes have been introduced. This metal is of a high order of purity, but contains sufficient oxide to prevent passivity. The nickel depositor has thus some choice of anode material. Experience goes a long way in the selection of the most suitable type.

A type of nickel anode now finding favour is designed to obviate the nuisance caused by the anode throwing off particles of nickel oxide or nickel. This "Auto-Filter" nickel anode is claimed to form a thin skin, continuous and adherent, which prevents the escape of particles which usually pass into the solution and cause trouble. The skin thus acts automatically as a filter, while the anodes are claimed to have a very high efficiency. A special heavy type filter bag is also provided for protecting the anodes from damage during service.

A scarcity of the metal, however, might considerably impede the industry. This has to some extent been the experience recently on the Continent* though the supply of nickel compounds was not adversely affected. To overcome the difficulty electro-depositors had resort to the production of their own anodes by depositing nickel on cathodes of lead using also lead anodes. Nickel is deposited on the lead cathodes, while an equivalent of acid forms at the anode. This is continuously neutralized by the addition of nickel carbonate thus maintaining the metal content of the solution. The lead cathodes with their nickel deposit then become the anodes of the usual depositing tanks and, after losing most of their nickel, can be again thickened up by transferring to the anode production tank.

Purity of Nickel Anodes. Time was when nickel anodes seldom exceeded a purity of 96 per cent, while they were more often of the order of 92 per cent. The nickel-plating industry was possibly retarded by the lack of more exact knowledge of the metallurgy of the metal and methods for its extraction in a purer form. To-day, purity is a matter which has called for consideration with the progress in the methods of deposition, and has with other materials used in electrodeposition, been taken up by the British Standards Institution,† which in drawing up a specification co-ordinates the requirements of the consumer with the possibilities of the manufacturer.

For nickel anodes the following particulars are, among others, called for in the specification referred to—

Nickel (with cobalt) not less than 99·0%
Nickel ,, ,, ,, 98·5%

Maximum impurities—

Iron	0·75%
Copper	0·25%
Silicon	0·1%
Manganese	0·1%
Carbon	0·3%
Zinc	0·01%

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* Springer: *Proc. 1st I.E.C., E.T.S.*, March, 1937.

† B.S.I. Specification 558, 1934.

This specification carries the assurance that the requirements can be met by the manufacturer.

Maintenance of Solution. With the efficiency of the present types of nickel anode and their longer life the maintenance of the composition of the nickel solution is not the difficult problem of that of years ago. Formerly anodes were very much less efficient with the continuous formation of free acid which from time to time had to be neutralized by periodic additions of either ammonia or, later, nickel carbonate. In modern practice, anode and cathode efficiencies are both more nearly alike and not far from ideal. Over long periods of working, therefore, the pH may remain fairly constant. Such variations as do occur may frequently be traced to undesigned additions of either acid or alkali owing to inefficient rinsing of work as it comes from either the acid etch in the case of ferrous metals, or alkaline cleaners in the case of non-ferrous metals. In fact such faulty operations may usually be detected by these pH variations in the nickel solution.

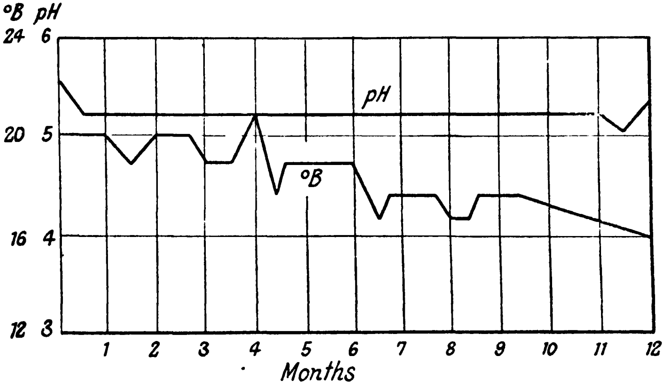

FIG. 82. RECORD OF A NICKEL SOLUTION OVER A PERIOD OF ONE YEAR

The accompanying curve (Fig. 82) shows the variation of pH and density of a nickel solution over a period of one year. The solution measured 1,000 gallons and continuously carried 250 amperes through a 24-hour day for the whole of this period. This represents 250 × 24 × 360 = 2,160,000 ampere-hours or over 2,000 ampere-hours per gallon. The constancy of the pH curve may be taken as an indication of the efficacy of the buffering agent. With regard to the fall in density, the loss of salts may be taken as roughly proportional to the decrease in density, which in this case was from 20° B to 16° B or from 1·160 to 1·126 specific gravity (Fig. 82).

The fractional loss may be taken as—

$$\frac{160 - 126}{160} = 0{\cdot}212$$

representing a life of the original salts of nearly five years and an annual loss of salts on 1,000 gal. containing 3 lb. per gal. of 636 lb. of nickel salts with their accompanying chemicals. With careless operation the pH curve might have varied considerably from time to time with different classes of work brought from an acid etch or an alkaline cleaner.

Removal of Iron. With solutions now worked at relatively low pH there is the tendency for the accumulation of iron, especially with steel work on portions of which no deposit is required or produced, such for example as tubular work which has been left uncorked. No advantage of any kind can be claimed for the presence of this iron and its removal becomes a matter of importance. Where stirring and filtration is used, the removal of iron is a fairly simple matter of reducing the acidity by the addition, with stirring, of a suitable quantity of nickel carbonate paste or sodium carbonate solution, and when the pH of 6 or more is reached iron salts hydrolyze and are precipitated. The removal is facilitated by using rather an excess of carbonate and agitating with air, the iron then being more readily precipitated together with, possibly, a small proportion of nickel. The solution is circulated through the filter and finally an addition of acid is made to bring the pH back to its required figure.

Removal of Chromium. The presence of chromium compounds in the nickel solution may give rise to a smoky appearance to the deposit. Such compounds may be removed by the addition of 1 lb. of ferrous sulphate to each 100 gals. of solution and after standing for some hours an addition of nickel carbonate is made to bring the pH up to 4·8 keeping the mixture at 160° F. for some hours. It is then filtered and acid added to reduce the pH to 2·9 or other required value and, if needs be, filtered again through activated carbon.

PREPARATION OF WORK FOR NICKEL-PLATING

The work which normally comes to the nickel-plater may be classified into a few groups—

(A) Brass, Copper, Bronze, Gun-metal, Delta Metal, etc. These metals may be either (1) stamped or spun, or (2) cast.

STAMPINGS, ETC. These usually have a sufficiently prepared surface to be sent to the polisher for liming. If machine or heat treatment marks are present, these must be removed by emery bobbing or emery brushing. Subsequent to buffing, the following sequence of operations will be followed—

(*a*) Removing grease with either the electric cleaner, potash or soda, or the phosphate cleaner; (*b*) rinsing in warm water; (*c*) the application of a bright dip; (*d*) rinsing; (*e*) brushing with lime or whiting, and ample rinsing prior to passing to the nickel bath. Weak cyanide solutions are sometimes used but experience is proving that these are best omitted. The bright dip must be used with caution in order to minimize subsequent finishing.

The bright dip has the advantage of increasing the adhesion of the deposit to the base metal. This has recently been shown by Hothersall* to be due to the action of the bright dip in removing from the surface of the work the thin layer of flowed or "amorphous" metal produced in the polishing processes which he found in certain cases is susceptible to hydrogen embrittlement during nickel plating. If this "flowed" layer is not removed, stripping is liable to occur due to the failure of the weaker layer of embrittled metal.

Hothersall† has also originated a method of securing the removal of the flowed layer, which has the very important advantage over the old bright dip process that the original polish of the work is little impaired. The new process is applicable to the treatment of copper, brass, bronze, and gun-metal, and consists in etching the degreased work anodically at a current density of 10 amperes per sq. ft. in an acid solution of ammonium citrate prepared by dissolving 50 gm. of citric acid in water neutralizing with ammonia and adding a further 20 gm. of citric acid dissolved in water, finally diluting to 1 litre. The bath is used at room temperature and treatment for 30 seconds is sufficient. The cathodes should be of nickel

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* *J. Electrodepos. Tech. Soc.*, 1932, vii, 115.

† *Ibid.*

sheet or foil. After etching, the work is thoroughly rinsed with running water and transferred to the nickel bath without delay.

CASTINGS. These are characterized by porosity, an altogether undesirable feature from the platers' point of view, the pores secreting liquids which, if not thoroughly removed, will assuredly lead to subsequent corrosive action, with peeling of the deposit. Preliminary grinding with felt bobs and successively fine grades of emery is effected to develop a surface for the polisher. The same result may alternatively be obtained by rumbling in a barrel with steel balls and soap or by sand-blasting. The choice of method will, to some extent, depend upon the nature of the original castings. Subsequently, the work can be treated as though it were a stamping, except that, wherever rinsing is applied to remove any liquid, the operation must be thorough to avoid the subsequent risk of spotting out. Cyanide solutions are again wisely omitted in the treatment.

It has been pointed out by Caplan* that a good casting is essential to good plating. The expedient of tinning to fill up pores is in every way unsatisfactory. Excess sand should be removed before the work comes to the polishing shop.

Anodic etching is applied in many cases, the copper alloys in a 5 per cent cyanide solution, and iron and steel in sulphuric acid of 50° B. The time of etching varies with different classes of work, cast iron requiring only from 15 to 20 seconds. Subsequently, until required in the nickel bath, the work is kept in a 5 per cent cyanide solution, and prior to plating is rinsed and passed through a 10 per cent sulphuric dip and rinsed.

(B) Iron and Steel. SHEET METALS. The mechanical and heating operations which these metals have usually undergone necessitate the careful removal of the oxide films found on the surface. Sulphuric and hydrochloric acids are used for this purpose. The latter is in common use. Some prefer to start with the strong acid and use this until its acid content has been reduced to nearly zero, after which the pickle is thrown away. Others prefer to decide on a particular strength of acid, and from time to time make further additions to maintain this strength while at the same time throwing away an equal volume of the older acid. Very little scouring

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* *J. Electrodepos. Tech. Soc.*, 1934, ix.

should suffice to complete the cleaning. Grease in quantity may be removed in one of the modern types of de-greasers, and for the production of a matt surface sand-blasting is often resorted to.

Where nickel is being applied directly to iron and steel a process of anodic pickling is resorted to, the work being made anode in a sulphuric acid of about 60° B. with or without a few ounces of chromic acid per gallon. Nitric acid is also being used as an alternative to the chromic acid.

Castings. For iron castings the general rules applicable to brass castings must be followed. Grinding must be applied to remove the lowest pits and when sand-blasting is used it may be necessary to pickle the metal in hydrofluoric acid to remove imbedded particles of sand. Much depends upon the quality of the castings, and if these are of good quality it may be necessary only to pickle without the application of the mechanical processes of sand-blasting or grinding. After pickling, however, it is well to give a light scouring with lime to neutralize remaining acid, and inhibit subsequent spotting out.

Anodic Acid Etch. The preparation of steel surfaces for nickel-plating is also accomplished in what is called an anodic acid cleaner. This is composed of moderately strong sulphuric acid of 60 to 70 per cent strength corresponding roughly to 50° to 55° B., to which is added potassium dichromate ($K_2Cr_2O_7$) to the extent of 3 oz. per gallon, or say 20 gm. per litre. On a 6-volt circuit a current density of 100 amperes per sq. ft. will first be obtained, this soon falling to 20 amperes per sq. ft. The lead lining of the tank can be used as the cathode and a treatment of about one minute suffices to remove the oxides, the anodic oxygen removing the grease and scale and also rendering the surface passive. The satin surface developed provides a perfect "key" for the subsequently deposited nickel. The method is largely used in mass production work with but a very small percentage of stripping.[*]

Metals carrying passive films, as for example stainless steel, offer difficulties of adhesion of deposited nickel, necessitating the removal of the film prior to plating. This preliminary treatment involves immersion in concentrated hydrochloric acid when the subsequent deposition of nickel is made from a

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[*] Laban: *J. Electrodepos. Tech. Soc.*, 1930, [illegible]

chloride solution. For other nickel solutions, however, the preliminary dip contains, in addition to the acid, some ferric chloride and arsenic trioxide. In any case it is advisable for the nickel bath to contain some chlorides with a low pH value. The nickel deposits will subsequently lend themselves to chromium plating in the usual type of solution.*

(C) **Zinc, Tin, and Lead Alloys.** After preliminary polishing with a Vienna lime and stearine compo, the work is cleaned with a mild alkali such as soda ash or soda phosphate solution. Strong alkalis cannot be used, as they attack these metals. They are then scoured with lime or whiting, and transferred to the cyanide copper bath.

Zinc work, if only slightly covered with oxide, may be pickled in weak sulphuric acid for a few seconds only. It is permissible to immerse Britannia metal and lead in weak nitric acid for a very short time. Tin requires special treatment in polishing, the usual lime and stearine compo not being suitable. A drier compo, such as tripoli, is here more serviceable.

Most zinc castings are of the type known as die castings. These may at times require grinding on flat bobs to remove the deepest blowholes, different grades of emery being used for this purpose. Subsequently a final polish with tripoli compo can be imparted.

Treatment of Die Castings. The choice of solutions for nickel-plating die castings is not one made without reference to the scientific side of the subject. Zinc is a very active metal. Ordinarily it turns nickel out from its solutions. An attempt to nickel zinc or its alloys under ordinary conditions results in a black streaky deposit, due largely to the simple immersion deposition. The conditions of the solution and deposition must, therefore, be such as minimize this possibility of simple immersion deposition. Raising the current density is a step in the right direction, but the solution requires modification.†

A lower nickel ion concentration is required without necessarily decreasing the nickel content of the solution. A sulphate solution is, therefore, preferred to a chloride solution. The addition of sodium or magnesium sulphates is advantageous

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* **Hoefner**: *Monthly Rev. Amer. Electroplaters' Soc.*, 1933, 20 (1) 22-26

† **Laban**: *J. Electrodepos. Tech. Soc.*, 1935, vi, viii; **Wright and Taylor**: *Ibid.*, viii, 8.

in that with its common SO_4 ion it reduces the concentration of the nickel ions. This is also effected by the addition of citrates which effect the formation of complex ions. Minimum stirring keeps the nickel ion concentration at the cathode low, and this is further facilitated by the addition of some colloids. The solution is one of design rather than accident.

For nickel-plating die castings, therefore, solutions contain notable proportions of sodium citrate ($Na_3C_6H_5O_7$) or sodium sulphate. Two solutions in successful commercial operation are as follows—

(1)	Double nickel salts	10 oz. per Imp. gal.	62·5 gm. per litre
	Common salt	7 ,, ,, ,, ,,	43·7 ,, ,, ,,
	Boric acid	2 ,, ,, ,, ,,	12·5 ,, ,, ,,
	Sodium citrate	1 ,, ,, ,, ,,	6·25 ,, ,, ,,
(2)	Single nickel salts	9 oz. per Imp. gal.	56 gm. per litre
	Ammonium chloride	1·5 ,, ,, ,,	9·4 ,, ,, ,,
	Boric acid	2 ,, ,, ,, ,,	12·5 ,, ,, ,,
	Sodium sulphate (cryst)	32 ,, ,, ,, ,,	200 ,, ,, ,,

Even with these solutions very definite methods must be followed if the deposition is to be assured of success. In some cases it is regarded as good policy to put on an undercoat of copper from the cyanide solution. A large amount of work, however, is treated by direct plating of the nickel on to the die castings.

Striking the work is to be recommended to prevent the possibility of the solution of the zinc. For this purpose a C.D. of 25 to 30 amperes per sq. ft. may be used for 20 to 30 seconds, after which the C.D. is reduced to normal for the period of deposition, which may be from 30 to 40 minutes, according to the finish required.

Again, the acidity of the solution must be kept down, not allowing the pH value to be less than 5·5 to 5·8. The sodium sulphate is recommended because it is cheaper than the magnesium salt. The added sulphate improves throwing power by reducing the concentration of nickel ions around the cathode. Were it not for the spotting out troubles, which invariably occur with cyanide solutions, it might be suggested that it is better to copper the work first. Many practical platers regard direct nickelling as the safer procedure.

Black Nickelling. This process has been largely applied. Formerly an alkaline solution containing arsenic was used, but presented the difficulty of maintenance in order to obtain uniform results. According to a Technological Paper issued by the United States Bureau of Standards, the best results were produced from the following solution—

Nickel ammonium sulphate	approx.	10	oz. per gal.	60	gm. per litre
Zinc sulphate . .	,,	1¼	,, ,, ,,	7·5	,, ,, ,,
Sodium thiocyanate . .		2½	,, ,, ,,	15	,, ,, ,,

The solution is worked cold at a low voltage of 0·5 to 0·7 volt giving not more than 1 ampere per sq. ft. An increase in current density diminished the blackness of the deposit, which became greyer in colour.

The analysis of the deposits gave results of the following order: 40 to 60 per cent nickel, 20 to 30 per cent zinc, 10 to 14 per cent sulphur and 10 per cent organic matter. While, therefore, the deposit is not entirely of metal, it is largely metallic. Nickel anodes of the type which do not dissolve readily are used, so that the solution does not acquire more nickel than is deposited. Additions of zinc sulphate and sodium thiocyanate are required from time to time. Quite thick deposits can thus be built up.

Barrel Plating. The conditions of barrel plating are markedly different from those of vat plating. In the vat there is usually a large volume of solution and area of anode, relative to the surface of the work plated. In the barrel the proportionate volume is much smaller, as is also the area of the anode. With the rapid conditions employed in the barrel, there is the definite tendency to the impoverishment of the solution with increase of acidity. These conditions are corrected by periodically—daily, if not more frequently—changing the solution with other from the main vat.

Common Defects in the Nickel Solution. The nickel solution is possibly the most susceptible to deviations from the path of good working, and many defects may arise. Some of those more usual may here be referred to.

If the work appears to receive little or no deposit and is discoloured there is the greatest possibility that the current is too low, this being brought about by unexpectedly high resistances of poor contacts, thin connecting wires, and the like. The remedy for this is obvious. On the other hand poor cleaning may be, to some extent, responsible. The trouble is also met with metals containing zinc, but may be overcome by striking with a high current density.

Alternatively the work may appear to be well nickelled, but the deposit is rough and dull. This is commonly the result of too high a current density, which is easily remedied, or it may be that the bath is too alkaline. A check of the pH will be necessary. Again, poor conductance may account for a similar trouble, this fault being rectified by the addition of nickel sulphate or common salt. These additions depend, to some extent, upon the composition of the bath.

The deposit may show evidence of peeling. This is most usually due to too high a current density, at least on prominent parts of the work, probably while the more remote parts are being covered. An obvious remedy for this is to increase the inter-electrode distance, making less difference between these two parts of the work. Alternatively, peeling may be occasioned by the presence of a previous deposit of nickel. It is correct practice to remove all prior coatings of nickel before attempting to put on a new deposit, the old deposit carrying a thin film of insoluble oxide difficult to remove, and effecting a separation between the two coats of nickel. Complete stripping prior to replating is essential. The same difficulty may also arise from too high a C.D. generally, or, again, by too great acidity or too low pH value. This latter fault can best be remedied by the addition of nickel carbonate, the excess acid being taken up as nickel sulphate without the addition of unnecessary constituents. There is also the possibility of the presence of films of oxides of the base metals due to faulty cleaning, with its obvious remedy.

Another common fault is the tendency to the production of black streaks on the deposit. This is usual with work containing notable quantities of zinc, and metals of this class, including die castings, require special treatment. The presence of zinc in the solution also gives rise to the same trouble. Such zinc content might arise from the use of galvanized vessels in the preparation of the solution. If the trouble is slight it may possibly be remedied by working the solution for a time with a high current density on to iron cathodes, the zinc thus being deposited out, although with excess of nickel. If this trouble is more severe it may possibly be removed by addition of calcium carbonate, precipitating the zinc as carbonate.

with again some nickel, which will have to be sacrificed. A serious contamination with zinc may, however, not be amenable to either kind of this treatment, and may necessitate throwing away the solution.

Spotting out occurs frequently with nickel deposits, mainly due to imperfect methods of cleaning, but these remedies are treated elsewhere. Finally, dark burnt deposits may be due to too high a C.D., too low a metal concentration, or too low a temperature. These several possibilities can readily be separately explored and remedied. In the winter, when the solution is cold after a week-end rest, a bucket of hot water may do all that is required. Solutions, whether warm or cold, are continuously evaporating, and occasional additions of water are necessary.

Porosity. The thin deposits of nickel usually put on for protective purposes often fail to protect by reason of the presence of numerous small pores. These admit the corrosive media with fatal results. Porosity is due to a number of causes. Irregularities on the surface of the metal and the settling of suspended impurities are the two chief causes. Some of these difficulties may be obliterated in thicker deposits, and a thin porous deposit may improve on thickening. With a view to preventing accumulation of fine particles in suspension in the nickel solution anodes are often bagged. Pores also result from the clinging of gas bubbles to the surface. As the gas is disengaged the metal beneath becomes coated with nickel, and what, with clinging hydrogen, might have developed into a pore, is eliminated. Generally speaking, porosity is a term applied to microscopic channels running through a deposit and terminating with the base metal, thus admitting the presence of corrosive influences. Porosity, in the initial stages of deposition, may thus be eliminated by continued deposition, hence the usual requirement of a definite thickness of deposit.

Pitting. There is some confusion as to the use of this term as distinct from porosity. Pitting may be regarded as the presence of macroscopic (seen with the naked eye) holes or channels running either right through or terminating in the thickness of the deposit, which have for the most part been occasioned by the clinging of hydrogen bubbles. If the holes go right through the deposit corrosion of the base metal may occur. If the holes terminate within the deposit no such corrosion will occur. A further distinction between pitting and porosity is that the former is generally very local and obvious, while porosity is more general, and very much less obvious.

The porosity of nickel deposits has been one of the sorest problems of the nickel-plater. Many causes have been suggested, with methods for the elimination of the defect. Only recently, however, has the subject been explored with any degree of scientific precision.

A porous deposit provides a source of weakness in that it permits the entrance of corrosive moisture to the underlying metal. Corrosion begins and proceeds between the base metal and the nickel coating leading to the flaking off of the latter.

A number of causes have definitely been assigned for this defect. In the first place much pitting is occasioned by the sticking of small hydrogen bubbles on the cathode surface. The points of sticking are imperfections on the surface of the metal. They might, in some cases, be removed by machining, and while this may not be possible in numerous cases, the required uniform surface is producible by a preliminary deposit of copper of about 0·0004 in. thickness. This will be appreciated when it is remembered that in the solution of ordinarily impure zinc the hydrogen is evolved at such points of impurity, and the zinc is rendered immune from corrosion in acid by covering these points with mercury. As a step towards the elimination of hydrogen the addition of nickel nitrate, hydrogen peroxide, and other oxidizing substances finds some vogue.

But the presence of hydrogen is in itself attributable to the presence of an excess of acid. If the pH value of the solution is of the order of 3–4, considerable quantities of hydrogen may be deposited. The pH figure should be more nearly 5·5–6·4 and this is a figure which should be frequently tested for, the test being so simply carried out and of such great value.

Another cause is traceable to the presence of suspended impurities. These may become attached to the cathode, and prevent deposition. Alternatively, they may, in some cases, become covered with metal and give rise to roughness. Their removal can be effected by filtration. This is now well established procedure. It does not involve occasional emptying the bath. Continuous filtration can be easily effected, the solution being taken from the bottom of the tank by pumps or the air lift, and delivered back to the tank through simple cloth filter bags.

The study of this defect has been the subject of several investigations by Macnaughtan and his associates. Thus Macnaughtan and Hothersall* were able to differentiate clearly between two distinct types of pitting, one associated with surface imperfections in the basis metal and the other with the condition of the solution. They also showed that pitting of the former type could be readily eliminated by the use of a composite coating of nickel-copper-nickel.

It was at first thought that pitting of the second type always resulted from the presence of impurities in the solution. It was later found, however, that cases of pitting occurred in highly purified solutions, and in a subsequent paper the authors express the opinion that in such cases the presence of flocculated basic material at the cathode face by absorption into the gas-liquid interface increased the adhesion of the hydrogen bubbles on the cathode surface and thus caused pitting in the deposit. In support of this view they describe numerous experiments in which pitting has occurred in pure solutions under conditions favourable to the production of flocculated basic material at the cathode face.

In general the occurrence of pitting is favoured by the presence of chlorides or the absence of alkali metal salts in the solution, whilst operating the solution at a low pH (pH 3·0 or less) will usually ensure freedom from the defect.

Peeling. Nickel deposits are notoriously prone to peel away from the basis metal. Two reasons may be given for this. The first is that of lack of cleanliness, and therefore a poor grip between the deposited nickel and the metal beneath. The remedy for this is obvious. Of all solutions, those for the deposition of nickel are absolutely void of any cleansing properties, and scrupulous care must, therefore, be exercised in guaranteeing the cleanest surface possible for the reception of the nickel.

But there must be some added tendency to pull the nickel away and cause it to curl up in the all too familiar way. This tendency arises from the fact that most deposited nickel is in

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* *Trans. Faraday Soc.*, **xxiv.**

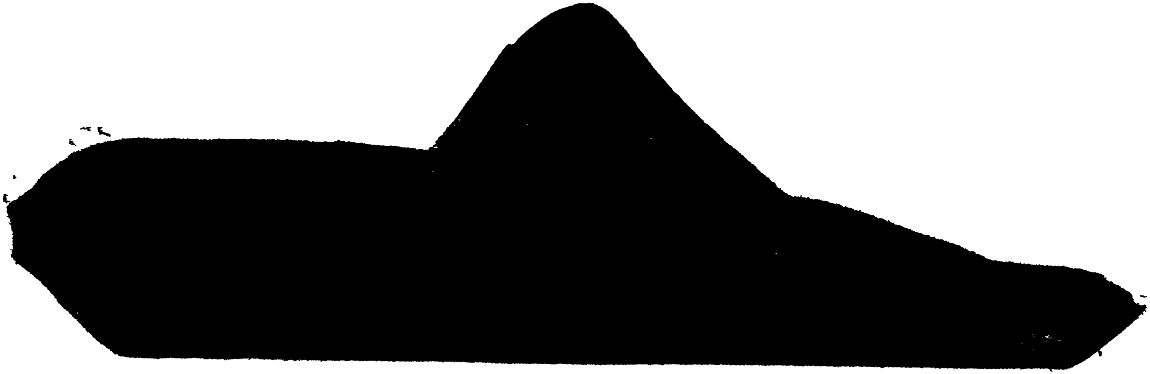

Fig. 83 Zinc Deposit, Curled After Deposition

a condition of stress. There are, in the deposit, forces tending to make the deposited surface shrink, and this causes the deposit, if it has the freedom, to curl. A deposit of nickel on one side of a cathode shows this property at once. The defect occurs in other deposited metals in which co-deposited hydrogen may be absorbed. A very striking example is seen in the accompanying photograph, Fig. 83, which shows a deposit of zinc. This was when deposited quite flat. After removal from the aluminium cathode on which it was deposited, it slowly began to curl. This has been going on for some years, and there is every indication that the deformation is still proceeding. Appreciating this possibility, we can understand the source of peeling in nickel deposits and take steps to prevent it.

First, attention must be given to the preparatory cleaning of the work. Secondly, steps must be taken to minimize these stresses during deposition. It has been shown clearly that the trouble can be got over by using solutions of low acidity with, therefore, less likelihood of the deposition of hydrogen, and further at temperatures of between 35° and 40° C. (95° to 104° F.).

Nickel Undercoat for Chromium. Nickel has come to be recognized as the most suitable metal upon which to deposit chromium, the nickel providing a coating which withstands corrosion, and upon which chromium can be readily and adhesively deposited. For this purpose special properties are required by the nickel coating. Nickel deposits are usually hard and brittle, but as an undercoat for chromium a softer and tougher metal is required, one which will give somewhat to the stresses imposed upon it during the deposition of the chromium. Such deposits are less liable to peel during deposition or to strip afterwards.

A solution recommended for this purpose is the following—

Single nickel salts	3 lb. . . .	300 gm.
Nickel chloride	3 oz. .	19 ,,
Boric acid	2 oz. . .	12·5 ,,
Water	1 gal. . .	1 litre

In order to secure a bright deposit with less buffing costs the solution is worked at a temperature of 100°–110° F.

Deposits from ordinary solutions, though capable of receiving good finishes, are often found to be quite ineffective for chromium plating. Some of the defects of the usual nickel deposit are (1) poor adhesion due to faulty cleaning; (2) brittleness due to co-deposited hydrogen; and (3) oxidation of the nickel surface.

Fortunately, the chromium plating solution shows some cleansing properties in that it readily dissolves many metallic oxides, though it is unsatisfactory to leave the solution to effect this removal.

The production of the required physical properties of the nickel deposit demand attention to three factors chiefly. These are (1) temperature, (2) current density, and (3) acidity.

At an elevated temperature higher current densities can be effectively used, while still retaining comparatively soft deposits. Acidity needs careful control. This is, to some extent, effected by the introduction of a little chloride in the solution to promote anode corrosion. and thus prevent the formation of acid. Moreover, the presence of fluorides in the solution is well recognized to exert a control over the pH value. Equal quantities of acid added to two nickel solutions, differing only in the addition of fluorides to one of them, cause a smaller increase in acidity (or a lowering of the pH value) in the bath containing the fluorides. Boric acid provides the required degree of acidity, and, moreover, acts like fluorides in preventing marked changes in the pH value. Such reagents which exert a steadying effect on the pH value have already been referred to as buffering reagents.

With such precautions there is no difficulty in providing a nickel coating which is suitable for the subsequent chromium deposit, and such a nickel deposit should preferably precede the deposition of chromium on all grades of brass. In the case of iron and steel these metals may either be directly nickelled and then chrome-plated or they may receive an initial thin film of nickel, followed by sulphate copper, then nickel, and finally chromium. Another advantage of the nickel coating is the modifying effect upon the somewhat blue tone of the chromium, and the fact that in recesses, where the throwing power of the chromium solution is poor, the nickel colour is far preferable to the possibility of a red copper base being discerned.

In the early stages of chromium-plating development there seemed to be the recognition of the need for prior nickelling in a solution of this stronger type. While this solution, as a type, is still of extensive application, there is abundant evidence that one of the compositions given on page 269 is in every way serviceable though slower, and a large amount of work is to-day being satisfactorily turned out from this weaker solution.

Heavy Nickel Deposition. One very large and important application of nickel deposition is that of the salvaging of worn machine parts, thus bringing them back into service with greater speed, more economy, and enhanced properties than new parts. The process originated during the European War. Then the idea of building up worn parts by the deposition of iron was first tried out. It was natural that iron should be selected as the metal to function for this purpose. The deposition of iron, however, was by no means so well understood, and difficulties early presented themselves leading to a change over to the metal nickel as most nearly like iron. The process soon justified itself. Its results were so eminently satisfactory that it soon became established practice to introduce deposited nickel into the manufacture of the parts which were to receive excessive wear.

The hardness of deposited metals is much greater than the same metals in their usual metallurgically prepared forms. Evidence of this is to be found in Table LXX on page 435. Moreover, the method could be employed on the spot, thus saving a lot of delay in transport. It has since been continued on an increasing scale and now provides a useful tool in engineering construction.

Machine parts which have been reduced in diameter through excessive wear are first machined to take out marked unevenness and to secure concentricity. They are suitably cleaned in hot alkali or an electrolytic cleaner, the usual trichlorethylene cleaners being too small for some of the large pieces which come up for treatment. The parts not requiring deposition are now "stopped off" to prevent useless deposition. This is done by immersing the whole of the part in a bath of suitable wax, for which purpose paraffin wax was first employed, but has more recently been superseded by other waxes including those of the chlorinated naphthalene type. For this waxing process the parts requiring deposition are protected. The waxing may require two immersions to obtain the required thickness. After cooling the whole of the piece, that portion which is to be plated is again lightly cleaned in a lukewarm cleaner and, after rinsing, introduced into the nickel plating solution in which it receives a deposit sufficiently rapid to reduce time to a minimum without the risk of the development of undue roughness on the more extreme portions. This may require hours, days, or in special cases even weeks, until the deposit is definitely thicker than the finished dimension. After rinsing, the wax is removed by re-immersion in the wax pot and allowing to drain. The deposit is then machined down to finished dimensions and is ready for replacement for service. It is then found to be far more serviceable on account of the increased hardness of the deposited metal.

Similar examples of deposition are concerned with chromium in which case the deposit is exceedingly hard, the chromium being applied on the top of the nickel or in some cases alone.

Cadmium by reason if its endurance against corrosive conditions has been used in the same way.

Further, in special cases it has been found feasible to apply the metal to exact finished dimension without resort to any subsequent machining or grinding process, the deposition conditions being controlled to ensure all the required smoothness. In some such cases the bearing itself may provide the plating tank with a small revolving anode centrally disposed.

By the more ordinary process, large parts weighing a number of tons have been treated, necessitating the use of lifting cranes for holding the part while in the deposition tank. One can easily visualize the massive proportions of the tanks and their equipment for this purpose.

Protective Value of Nickel Deposits. It is difficult to assess exactly the value of nickel deposits. Assuming that the process of deposition has produced an apparently sound adherent deposit, there remains the question of permeability to corrosive influences. Few deposits can be regarded as absolutely perfect. Few are entirely free from porosity. Generally, increasing the thickness reduces porosity, though the deposit need not necessarily be all nickel. By tests on somewhat the same lines as those referred to under the treatment of zinc deposits, it is possible to make rough comparisons of the relative values of different deposits. Generally these deposits may be compounded with copper and nickel, usually, where iron and steel are concerned, comprising a thin deposit of nickel on the base metal, followed by an appreciable thickness of copper from the acid bath. This deposit is then polished prior to putting on the final coating of nickel. Of such a composite deposit 1 mil (= 0·001 in.) should provide a satisfactory coating equal to all the usual conditions of service. Such a deposit requires about 20 ampere-hours per sq. ft. of the two deposits reckoned together.

Production of Nickel Sheets. The processes of nickel deposition go beyond the range of electro-plating and building up, and touch the realm of electrolytic refining and the adaptation of the metal. In the latter case, the production of nickel sheets by deposition has been described by Wynne-Williams.* The structure of sheet metal required for a number of mechanical operations is different from that usually obtained by deposition. Ductility is an important, even an essential, asset. Such structure can, however, be produced by control of the conditions of deposition, and sheets of nickel up to 12 ft. long and 4 ft. wide are produced by deposition upon suitable steel rollers which admit of easy stripping. Such sheets may go up to 0·048 in. in thickness. In the paper referred to, the usual conditions for this type of deposition are laid down, these including high current density, rapid rotation of the partly submerged cylinder, low pH and a relatively hot solution continuously filtered. There appears to be no very special composition of solution essential to the process which has attained commercial importance.

Composite Coatings. Owing to the difficulty of removing or neutralizing alkaline solutions retained in the pores of metal castings, most workers prefer to use the acid copper bath for flash coppering prior to nickelling or chromium plating. As the acid copper bath cannot, however, be used for direct plating on to iron, it is the practice in this instance to flash the article in an ordinary nickel solution for just sufficient time to assure a complete coating of nickel, rendering the basis metal immune from attack by the subsequent copper bath.

The article is then transferred to the acid copper bath to receive a substantial coating of close-grained copper, after

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* *J. Electrodepos. Tech. Soc.*, 1936, xi, 143.

which it is rinsed, and transferred to the nickel bath to receive the desired coating of nickel. By this means much trouble due to subsequent spotting out can be avoided.

The most satisfactory type of chromium deposit on iron is a composite coating comprising nickel, copper, nickel and chromium.

CHAPTER XVI

DEPOSITION OF NICKEL (CONTD.)

CONDITIONS influencing the hardness of nickel deposits—Anodic polishing——Stripping nickel deposits—Bright nickel plating—Schlotter solution—Hinrichsen solution—Analysis of nickel plating solutions—Estimation of chlorides—Estimation of nickel, cyanometric method—Alternative method—Dimethylglyoxime method—Estimation of ammonium compounds—Estimation of iron compounds—Estimation of sodium formate—Estimation of cobalt sulphate—Volumetric estimation of cobalt—Alternative method for nickel-cobalt solution—Estimation of boric acid—Estimation of sodium naphthalene trisulphonate

Conditions Influencing Hardness of Nickel Deposits. In the electrodeposition of nickel the cathode efficiency is invariably somewhat less than 100 per cent. In the absence of other dischargeable ions the small proportion of the current which is not utilized in depositing nickel is of necessity used in the discharge of hydrogen ions. The hydrogen thus produced at the cathode appears in part as gas bubbles which, if conditions are favourable, may adhere to the cathode and thus cause pitting in the deposit.

A more fundamental aspect of this discharge of hydrogen ions, however, lies in its effect upon the acidity of the electrolyte in the immediate vicinity of the cathode. Hydrogen ion discharge implies a reduction of acidity or a tendency for alkaline conditions to develop in the electrolyte.* A number of factors will determine the extent to which this tendency will proceed, some of which will be considered later. For the moment it is desired to consider the effect of such alkalinity upon the conditions at the surface of the cathode.

When a solution containing nickel ions is made progressively more alkaline, a point is reached at which hydrolysis, that is a decomposition by means of water, of the nickel salt takes place with the result that some of the nickel is thrown out of the solution in the form of a basic compound. The physical nature of this material as well as its chemical composition will vary according to the conditions of precipitation,

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* *Trans. Amer. Electrochem. Soc.*, xxv, 335, 1914.

more particularly in respect of the composition and acidity of the solution.

Macnaughtan and his co-workers have made a close study of this subject, the results of which have appeared in a series of papers before the Faraday Society. The principal findings are summarized below.

In a study of the effect of acidity on the hardness of electrodeposited nickel, Macnaughtan and Hammond* found that in a number of typical electro-plating solutions the hardness of the nickel decreased rapidly as the acidity of the solution increased, until a critical pH was reached, below which no further diminution in hardness took place. In its place there was a very slow increase. Curve *I* (Fig. 84) shows the relation between the hardness of the deposit (Brinell number) and the acidity of the electrolyte in a solution containing nickel sulphate, potassium chloride, and boric acid, and is typical of the results obtained.

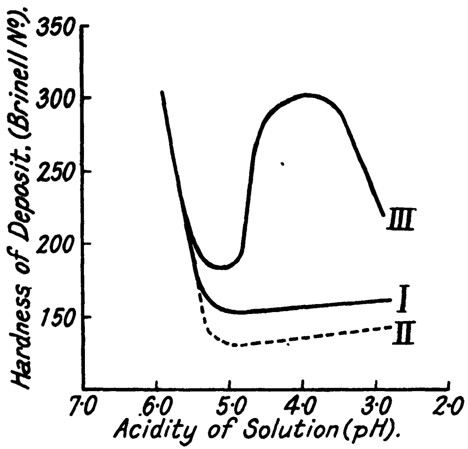

FIG. 84. EFFECT OF PH OF NICKEL SOLUTION ON HARDNESS OF DEPOSITS

In a subsequent paper Macnaughtan, Gardam, and Hammond† describe the results of systematic variations in the composition of the electrolyte, their experiments aiming at

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* *Trans. Faraday Soc.*, xxvii. 633, 1931

† *Trans. Faraday Soc.*, xxix. 792, 1933.

explaining the functions of the individual constituents in nickel-plating solutions in determining the mechanical properties of the deposits obtained, and also the incidence of certain defects, notably pitting. In particular, alkali metal ions and chlorine ions were found to exert a marked effect both on the mechanical properties of the deposit and on the incidence of pitting. Thus the omission of the potassium ion from the solution described above resulted in a marked reduction of the hardness of the deposits below the critical pH. This is shown in Curve *II*, Fig. 84.

Moreover, the absence of the potassium was found to cause a pronounced increase in the amount of pitting. The ions of the other alkali metals were found to function in a similar manner. Thus the presence of alkali metal ions in a nickel-plating solution has two principal effects: (1) harder deposits are obtained, and (2) the tendency of the solution towards pitting is diminished.

The effect of omitting chlorine ions was still more striking. When the pH of the solution was lowered below the critical value in the absence of chlorine ions, a sudden marked increase in the hardness of the deposits was obtained, this rise in hardness being subsequently replaced by a rapid diminution after a certain pH was reached. See Curve III, Fig. 84.

It was also found that the presence of chlorine ions in a nickel solution tends to increase the liability to pitting.

Thus alkali metal ions have a hardening effect on the deposit and tend to prevent pitting, while chlorine ions have the converse effect, viz. to soften the deposit and increase the tendency to pitting.

The authors explain these results in the following manner: The basic material produced at the cathode by the discharge of hydrogen ions may appear (1) in a colloidal form; (2) as a coagulated precipitate; or (3) as a mixture of both these forms. The presence of certain colloidal materials is well known to produce a refinement of crystal size in the deposit and thus the presence of colloidal basic material at the cathode surface will produce hardening in the deposit. The presence of colloidal material is favoured by (1) a high pH of the solution, and by (2) the presence in the solution of alkali metal ions, the latter stabilizing the colloid, and hence the influence of these conditions in promoting harder deposits.

Not all of the basic material produced at the cathode surface remains in the colloidal form, a proportion appearing as a flocculated precipitate which can have no influence on the hardness of the deposit. Flocculation of the basic material which is first formed in the colloidal form is brought about by the presence in the solution of negatively charged anions which neutralize the positive charges of the colloid and thus cause it to flocculate. Of these anions the monovalent chlorine ion, by reason to its close approach to the cathode, is the most effective, hence the influence of chlorine ions in diminishing the hardness of the deposit.

Positive evidence in favour of the above theory has been provided by Macnaughtan and Gardam* who have been able to recognize the absorbed basic materials in heat-treated electrodeposited nickel and to correlate the amount present with the conditions of deposition by observing its effect in restricting grain-growth on low temperature annealing. The authors have also investigated the hardness, tensile strength, and ductility of various types of electrodeposited nickel both before and after annealing.

Anodic Polishing. As a method of improving the appearance of dull nickel deposits, anodic treatment in a sulphuric acid solution has been developed by Hothersall and Hammond.† The deposit is made anode in sulphuric acid of 75 per cent strength at a temperature of 20–40° C. The acid is made by mixing 60 volumes of the concentrated acid with 40 volumes of water. At a high C.D. of 250 amp./sq. ft. from ·5 to 2·5 minutes serves to remove the rough surface and leave one which is markedly brighter. The nickel removed in the process is slight, amounting to ·00005 inch from a ·001 inch hard deposit, and ·00015 inch from a ·001 inch soft deposit. The resulting surface can be described as intermediate between the usual dull and bright deposits.

Stripping Nickel Deposits. Nickel deposits may be removed by either electrolytic or dipping methods.

Electrolytic. Solution—

Sulphuric acid (66° B) . .	2 gal.
Glycerine	2 oz.
Water	1 qt.

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* *Trans. Faraday Soc.*, xxix, 755, 1933.

† British Patent No. 504026, 1941.

The solution is used cold with either (*a*) the lead lining of the tank as cathode or (*b*) lead plates serving the same purpose. Usually 6 volts will be required for the purpose and where materials are being handled in quantity there is some chance of the economic utilization of the nickel which passes into the solution.

This method is capable of a number of variations by the alteration of the proportions of the acid and water, variation of temperature and sometimes the addition of a small amount of copper sulphate which is claimed to reduce the attack on the basis metal.

Dipping. Solution—

Sulphuric acid (conc.) . . .	2 vols.
Nitric acid (conc.) . . .	2 ,,
Hydrochloric acid (conc.) . .	$\frac{1}{16}$ vol.
Water	1 ,,

It should be almost unnecessary to add that the sulphuric acid should be added to the nitric acid and *not* vice versa, while the water may preferably be added to the nitric acid before the addition of the sulphuric acid. The acid mixture may be used cold, though with an elevation of temperature to 160° F. the action is accelerated. Again, many variations are possible with an acid mixture of this type.

Bright Nickel Plating. Considerable interest has recently been taken in this new development in the art of nickel plating, the advantages for which are numerous.

In the first place, there will be the necessity for the production of a high finish prior to plating. Subsequently there will be no loss of nickel by final buffing and the time of deposition can therefore be proportionately reduced, it being usually reckoned that 20 per cent of the metal is removed in this final process. Bright deposits represent very fine crystal structure with which is also associated greater hardness. Where chromium-plating follows, added advantages accrue by cutting out the operations of drying, unwiring, polishing, rewiring and degreasing before passing to the chromium bath.

With these and other advantages in mind, it becomes possible to draw up what might be regarded as the ideal properties of such a solution. These have been set out as—*

(1) The maintenance of brightness to reasonable thickness as contrasting with mere flash deposits.

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* *J. Electrodepos. Tech. Soc.*, 1936, xi, 199.

(2) Good physical properties including those of adhesion, hardness, ductility, and lack of porosity.

(3) Good chemical properties, for example, resistance to corrosion and protection for the base metal upon which the bright deposit is made.

(4) A good undercoat for chromium which would increase the throwing power of the solution now in use, so that more uniform deposits could be made than those obtaining in present practice with polished or dull deposits.

In addition, the composition of the solution should be such as admits of relatively easy and exact chemical control, and the solution should preferably be capable of operation at current densities exceeding those already in use. Good throwing power would be an added qualification.

While this does not exhaust the list of desirable features of such a solution it suffices to emphasize the importance of the subject in progressive nickel plating.

The Schlötter Solution. In numerous earlier attempts at bright nickel plating a measure of brightness was from time to time obtained with, however, only very moderate thickness, not more than mere flashing. Generally, all deposits must start bright inasmuch as they start with thin layers of only a few atoms thick. As deposition proceeds these atoms build up as large crystals and a surface made up from such crystals effects the scattering of the light which falls upon them. The object with bright plating will therefore be very considerably to limit the size of the crystals which, very closely packed together in the deposit, produce a relatively smooth surface from which light is in a very large measure reflected, producing brightness. Schlötter contends that for this to take place, the crystal size must be kept down to a ten-thousandth of a millimetre or one two-hundred-thousandth part of an inch. Reduction of crystal size is effected by the co-deposition of colloids and these again were formerly of large molecular weight which, while hindering crystal growth, were in themselves still too large molecularly to achieve the best results. Now the tendency is towards the use of additions of smaller molecular weight. Thus in the Schlötter patents one of the original compositions of the solution was as follows—

Nickel sulphate		160 gm.
Nickel benzoldisulphonate		30 ,,
Boric acid		30 ,,
Water	to	1 litre

the solution being adjusted to a pH of 2·5 to 4·5.

With this or a similar solution, the claim was made for the production and retention of brightness with quite thick deposits, the size of the crystal structure being determined by X-ray analysis.

In a more modern form, a Schlötter solution contains—

Nickel sulphate	.	175 gm.
Nickel chloride	.	85 ,,
Boric acid	.	20 ,,
Sodium naphthalene trisulphonate	.	35 ,,
Water	to	1 litre

The method for determining the addition agent is given later and necessitates some careful analysis, well, however, within the range of any analytical chemist.

The unusually large amount of nickel chloride would seem to be unnecessary and experiments indicate that it could with advantage be reduced.

The permissible current density with the maintenance of brightness exceeds that of the usual dull nickel solutions and very satisfactory work has been done with this type of solution.

As with most solution formulae, there is the possibility of some variation in composition, and in more commercial work it is possible to make the needful additions of brightening agent in the form of a mixture with nickel salts.

The Hinrichsen Solution. In this country, however, considerable progress has been made with a solution of the following type introduced by Hinrichsen.*

This contains—

Nickel sulphate	240 grm. per litre
Cobalt sulphate	15 ,,
Boric acid	30 ,,
Nickel chloride	45 ,,
Sodium formate	35 ,,

The solution is worked with nickel anodes with periodical additions of cobalt sulphate and sodium formate as determined by analysis. These additions can, however, be regulated by a knowledge of the ampere-hours passed through the solution and registered by an ampere-hour meter.

The solution is worked at a temperature of 135° F. and a pH of 4·5. Current densities of from 40 to 80 amperes per sq. ft. are easily attained, and the deposit and solution meet all the requirements previously set out.

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* Brit. Pat. No. 461126, 1937.

A consideration of the process would lead to the suggestion of the accumulation of nickel in the solution when nickel anodes are used and additions of cobalt sulphate made. Experience has, however, shown that with the usual proportion of cobalt in the alloy deposit the accumulation of nickel sulphate is approximately equal to that of the cobalt sulphate addition, and is almost exactly counterbalanced by the loss by drag-out so that there is no undue accumulation of the nickel salt.

The possibility of using a cobalt-nickel alloy anode does not seem to call for consideration in view of the easy regulation of the composition of the cobalt content by the addition of cobalt sulphate. It must, however, be said that solutions of these special types need more care in their control than do those of the more ordinary types.

The success which this solution has achieved is sufficient to justify the claim that the problem of bright nickel has been satisfactorily solved without suggesting that there is no possibility of further progress.

Where numerous small parts are being treated and necessitate wiring, the saving of time can be easily imagined. Alloy deposition is well known to conduce to smaller crystal growth, and, with it, greater lustre. The deposit is advantageously whiter than nickel and less attacked by corrosive media.

ANALYSIS OF NICKEL PLATING SOLUTIONS

The following constituents are frequently required to be determined and controlled: nickel salts, ammonium compounds, chlorides, boric acid, and the pH. The determination of the pH is dealt with elsewhere (page 125).

In the following analysis and the calculations based thereon, as also in many other examples in which a high degree of accuracy is not required, some approximations are made, such for example as the adoption of 59 as the atomic weight of nickel in place of the more accurate figure of 58·6. These unimportant approximations are done solely with a view to simplifying calculations. Seeming slight discrepancies between these and figures in many analytical treatises are thus to be accounted for.

Estimation of Chlorides. For this purpose N/10 $AgNO_3$ is required. Take 10 c.c. of the plating solution. Dilute with distilled water. Add two drops of a neutral solution of potassium chromate giving a pale yellowish green colour. Run in the silver nitrate a little at a time with gentle shaking. Silver chloride is pptd. and when this is complete the next drop of $AgNO_3$ gives a red colour with K_2CrO_4 due to the formation of Ag_2CrO_4. This marks the end of the titration.

Then

$$\underset{58\cdot5}{NaCl} + \underset{170}{AgNO_3} = AgCl + NaNO_3$$

from which it will be seen that 1 c.c. N/10 $AgNO_3$ = 0·00585 gm. NaCl. The calculation is simple. Assuming, however, that the only chloride present is that of nickel, then—

$$\underset{117}{2NaCl} = \underset{238}{NiCl_2.6H_2O}$$

from which—

$$1 \text{ c.c. N/10 } AgNO_3 = 0\cdot0119 \text{ gm. } NiCl_2.6H_2O$$

Hence—

$$\text{Titration readings (c.c.)} \times 0\cdot585 = \text{gm. NaCl per litre}$$

and

$$\text{Titration readings (c.c.)} \times 1\cdot19 = \text{gm. } NiCl_2.6H_2O \text{ per litre}$$

In the stronger nickel solutions this change of colour may be less conspicuous. Concurrently, the curdy and white AgCl ppt. becomes pink by the absorption of the Ag_2CrO_4 and, at the same time, breaks down to the granular or even powdered form.

Estimation of Nickel: (1) *Cyanometric Method.* This is based on the conversion of the nickel salt into the double cyanide as follows—

$$NiSO_4 + 4NaCN = Ni(CN)_2.2NaCN + Na_2SO_4$$

Solutions required are (1) N/10 $AgNO_3$, and (2) a solution of sodium cyanide of approximately the same normality. In the titration of silver nitrate and cyanide the following reaction occurs—

$$\underset{170}{AgNO_3} + \underset{\underbrace{2 \times 49}_{98}}{2NaCN} = AgCN.NaCN + NaNO_3$$

so that deci-normal sodium cyanide contains 9·8 gm. NaCN per litre. No sample of the cyanide would be sufficiently pure to make up the solution directly. An approximate solution is made by dissolving from 10 to 11 gm. of good sodium cyanide in water and making up to one litre. This is standardized against the N/10 $AgNO_3$. To do this take 10 c.c. NaCN solution and dilute considerably with water. Add a few drops of KI and warm. Run in the silver nitrate solution from a burette until there is the first permanent turbidity. If the sodium cyanide is stronger than N/10, the c.c. of silver nitrate will exceed 10. Assume the figure to be 11·5. The NaCN solution is now diluted by the addition of 1·5 c.c. water to each 10 c.c. NaCN, which will bring it down to N/10 and therefore exactly equivalent (c.c. for c.c.) to the silver nitrate.

Now the addition of NaCN to nickel solution first produces a greenish yellow ppt. of nickel cyanide which dissolves in excess of NaCN to form the soluble double cyanide. This solution of the ppt. cannot, however, be carried out with volumetric exactitude. The procedure therefore is to add an excess of the standard NaCN and titrate back the excess with $AgNO_3$.

To make the test, dilute the nickel solution to one-tenth of its original strength. Take 10 c.c. of the dilute solution (= 1 c.c. original solution). Add standard NaCN, 10 c.c. at a time, until the ppt. first formed redissolves, forming a yellow solution. Note c.c. NaCN added. Dilute, warm, add a few drops KI solution and titrate with N/10 $AgNO_3$ to produce the first permanent turbidity. Note c.c. $AgNO_3$ added. Typical figures are—

Dilute nickel solution = 10 c.c.
N/10 NaCN = 20 c.c.
N/10 $AgNO_3$ = 5 c.c.

Hence c.c. NaCN for reaction with nickel salt = 20 − 5 = 15.

Now $AgNO_3 \equiv 2NaCN$

$4\ NaCN \equiv NiSO_4.7H_2O$

Hence $2AgNO_3 \equiv NiSO_4.7H_2O$

$2 \times 170 \qquad 281$

from which it will be seen that

1 c.c. N/10 NaCN = 0·01405 gm. single nickel salts.

Hence one litre of the nickel solution contains—

$$15 \times 0{\cdot}01405 \times 1{,}000 = 211 \text{ gm. single nickel salt}$$

Alternative Method. A variant of this method is that of the direct titration of the nickel solution with a standard potassium or sodium cyanide solution. For this purpose a standard KCN solution is made so that it contains 32·5 grams KCN per litre. This necessitates making a solution somewhat stronger, titrating with N/10 $AgNO_3$ and diluting to obtain the exact strength. Based on the reaction—

$$\underset{170}{AgNO_3} + \underset{130}{2KCN} = AgCN\,.\,KCN + KNO_3$$

a decinormal KCN contains 13 gm. KCN per litre. The solution now required will be 2·5 times as strong and 10 c.c. will require 25 c.c. N/10 $AgNO_3$ to carry out the above reaction.

The nickel solution is diluted to one tenth of its strength and 25 c.c. taken. Nickel solutions may contain small amounts of acid and this is neutralized using methyl red as the indicator. The neutral solution is then titrated with the standard KCN from a burette until the ppt. first formed is just redissolved. The reaction is quite sharp, one last drop of KCN solution serving to remove the last trace of cloudiness to produce a clear yellow solution.

The nickel content of the solution is then given by the formula—

$$\text{Ni (oz. per gal.)} = {\cdot}47\ (\text{c.c. KCN} - {\cdot}05)$$

It is, however, just as well to know how these figures are obtained. First then the ·05 allows for the unavoidable excess to clear the solution. Next, as

$$\underset{59}{Ni} = \underset{260}{4KCN}$$

$$\text{Hence} \quad 1 \text{ c.c. KCN} = \frac{32{\cdot}5}{1000} \times \frac{59}{260} = {\cdot}007375 \text{ gm. Ni.}$$

In the test we have taken 25 c.c. dilute solution which contains 2·5 c.c. of the original strength. Hence each c.c. KCN used represents ·007375 gram of nickel in 2·5 c.c. solution. Expressing this in terms of ounces per gallon we have—

$$\frac{{\cdot}007375}{2{\cdot}5} \times \frac{4540\ (\text{c.c./gal.})}{28{\cdot}4\ (\text{gm./oz.})} = {\cdot}47$$

(2) *Dimethylglyoxime Method.* A gravimetric method is based on the use of a reagent called dimethylglyoxime of which the formula is $C_4H_8N_2O_2$. Even in the most dilute solutions nickel salts give with this reagent a characteristic red ppt. of nickel dimethylglyoxime $[Ni(C_4H_7N_2O_2)_2]$ which is quantitatively formed even in the presence of any other metal. The method is therefore useful for the determination of nickel in the bright plating solutions containing cobalt sulphate from which it can be precipitated without co-precipitation of cobalt. Carried out carefully the method is capable of great accuracy but involves more time and work than the cyanometric method.

The dimethylglyoxime solution is made up to 1 per cent of the reagent in alcohol and the process carried out as follows—

10 c.c. of the plating solution is taken and diluted to 100 c.c.

10 c.c. of the diluted solution (equivalent to 1 c.c. of the original solution) is transferred to a 600 c.c. beaker and diluted to 400 c.c. with distilled water. About 3–5 gm. of tartaric acid is added to prevent the ppt. of any iron present with the subsequent addition of ammonia and the solution heated to 80° C. Now add 100 c.c. of the dimethylglyoxime solution and sufficient ammonia solution to make the mixture just alkaline. Boil for a short time and allow to stand in a warm place for half an hour. The ppt. is now filtered off in a weighed Gooch crucible, and after washing with hot distilled water, is dried at 110–120° C. It is now weighed and reheated to the same temperature until a constant weight is obtained with two successive weighings to ensure complete freedom from moisture. From the formula of this red ppt. it will be seen that it contains 20·31 per cent of its weight of nickel.

Example—

1 c.c. of the original solution gave ·217 gm. ppt.

Hence—

gm. $NiSO_4.7H_2O$ per litre

$$= \frac{\cdot 217 \times 20\cdot 31 \times 281 \times 1000}{100 \times 59}$$

$$= 210 \text{ gm./litre}$$

This method of analysis determines the whole of the nickel content of a solution expressed as nickel sulphate. Where nickel chloride is present the amount determined from the chloride test is recalculated as nickel sulphate thus—

$$\underset{238}{NiCl_2 . 6H_2O} \equiv \underset{281}{NiSO_4 . 7H_2O}$$

and deducted from the total amount of nickel sulphate as determined by the dimethylglyoxime test. Alternatively and more simply, the weight of nickel ppt. from 1 c.c. of solution multiplied by 203·1 gives the gm. of nickel per litre.

For general purposes, however, the volumetric (or cyanometric) method is to be preferred.

Estimation of Ammonium Compounds. These occur in nickel solution by the use of double nickel salts or by the addition of ammonium chloride as a conducting or anode-corroding agent. In whatever form they may have been introduced, it is impossible to determine subsequently the manner of their introduction owing to the ionization of all the compounds in the solution. The usual procedure therefore is to determine the amount of ammonia which can be extracted from the solution, and then express it either as the sulphate or as double nickel salts or ammonium chloride according to knowledge of the original formula from which the solution was made up and later additions. This usually suffices and is, as a matter of fact, all that can be done. The allocation of the basic and acidic radicals is not a matter of great importance.

The *estimation of ammonia* is based on the following reactions—

(1) All ammonium compounds are decomposed on boiling with alkalis—

$$\underset{132}{(NH_4)_2SO_4} + 2NaOH = \underset{34}{2NH_3} + Na_2SO_4 + 2H_2O$$

The ammonia is collected in a known quantity of standard acid, and from the un-neutralized portion the amount of ammonia absorbed is calculated.

(2) The nickel compounds will be completely pptd. as nickel hydroxide and will not interfere with the evolution of the ammonia.

(3) The apparatus will include a flask for boiling off the ammonia and a condenser and receiver containing the standard acid. A standard alkali will also be required to determine the

excess of acid. Semi-normal acid and alkali are suitable for the purpose.

An estimate of a suitable quantity of nickel solution must first be made in order to keep the quantities within reasonable limits. Introduce this into flask *A* (Fig. 85) and add excess of caustic soda of which the quantity and strength need not be known. The predetermined quantity of semi-normal H_2SO_4 is added to the receiver *B*, the last portion being allowed to flow through the tube *C* containing broken glass or glass beads. Also add a few drops of methyl orange to *C*. This serves as a check against loss of ammonia by lack of sufficient acid for absorption. To ensure ease of boiling without "bumping," a few heavy pieces of broken glass are added to flask *A*, the contents of which are now boiled until one-third to one-half of the contents have distilled over. By this time the whole of the ammonia should have gone over. The contents of *C* are washed into *B* which will show a red colour due to excess of acid. This is now titrated back with semi-normal alkali.

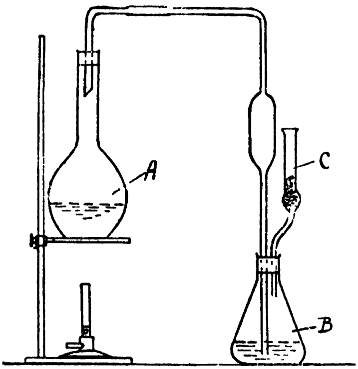

FIG. 85. ESTIMATION OF AMMONIA

Data and calculation—

Nickel solution taken = 25 c.c.
N/2 acid = 50 c.c.
N/2 alkali used = 31 c.c.

Now $$1 \text{ c.c. N/2 acid} \equiv 0{\cdot}0245 \text{ gm. } H_2SO_4$$

$$0{\cdot}0245 \times \frac{34}{98} = 0{\cdot}0085 \text{ gm. } NH_3$$

Hence $$\begin{aligned} 50 - 31 &= 19 \text{ c.c. N/2 acid} \\ &= 0{\cdot}0085 \times 19 \\ &= 0{\cdot}1615 \text{ gm. } NH_3 \end{aligned}$$

Hence 25 c.c. Ni solution contain 0·1615 gm. NH_3

Now
$$\underset{34}{2NH_3} \equiv \underset{132}{(NH_4)_2SO_4}$$
$$\equiv \underset{395}{NiSO_4.(NH_4)_2SO_4.6H_2O}$$

Hence 1,000 c.c. Ni solution contain $\frac{1,000}{25} \times 0{\cdot}1615 \times \frac{132}{34}$

$$= 25{\cdot}1 \text{ gm. } (NH_4)_2SO_4$$

or

$$\frac{1,000}{25} \times \frac{0{\cdot}1615}{1} \times \frac{395}{34} = 75 \text{ gm. double nickel salts}$$

Estimation of Iron Compounds. As a common impurity in nickel plating solutions iron may be determined in the same manner as in the acid copper bath (see page 226). Take 50 c.c. of the plating solution and warm with a few drops of conc. HNO_3 to oxidize ferrous compounds into the ferric form. Dilute to about 150 c.c. and add an excess of NH_4OH. Both iron and nickel compounds are affected by this addition but nickel compounds remain in solution as complex compounds while the iron is pptd. as ferric hydroxide. This is filtered, well washed with hot water, dried and ignited to Fe_2O_3.

Then
$$Fe_2O_3 \equiv 2FeSO_4 . 7H_2O$$
$$160 \equiv 2 \times 278$$

Hence—

$$\text{Wt. } Fe_2O_3 \times 20 \times \frac{556}{160} = \text{gm. ferrous sulphate per litre}$$

A greater degree of accuracy is obtained by dissolving the ferric hydroxide ppt. (after some washing) in warm dil. HCl and reprecipitating with ammonia.

Estimation of Sodium Formate. The principle of this estimation can be simply stated. In acid or neutral solution sodium formate ($H.COONa.H_2O$) is oxidized as follows—

$$H.COONa.H_2O + O + H_2SO_4 = NaHSO_4 + CO_2 + 2H_2O$$

Oxalic acid ($H_2C_2O_4 . 2H_2O$) is similarly oxidized—

$$H_2C_2O_4 . 2H_2O + O = 2CO_2 + 3H_2O$$

Potassium permanganate ($KMnO_4$) usually provides the oxygen—

$$2KMnO_4 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 3H_2O + 5{\cdot}O$$

Hence—

$$\underset{316}{2KMnO_4} \equiv \underset{630}{5(H_2C_2O_4\,.\,2H_2O)} \equiv \underset{430}{5H.COONa.H_2O}$$

A decinormal solution of oxalic acid contains 6·3 grams of the crystalline acid per litre, while one of potassium permanganate contains 3·16 gm. per litre. The former compound is usually bought in a reliably pure form and made up to decinormal strength by weighing and accurate measurement, while potassium permanganate solutions are made up to approximate strength only and ultimately standardized against the accurately prepared oxalic acid.

Prepare an N/10 oxalic acid solution by dissolving 6·3 gm. of the pure crystallized acid in water and making up to a litre. $KMnO_4$ solution is now made by completely dissolving from 3·25 to 3·5 grams of the salt and making up the solution to one litre.

Standardization of the $KMnO_4$ is done by taking 10 c.c. of the oxalic acid solution into a flask, diluting somewhat and adding dilute sulphuric acid. The solution is warmed to about 60° C. and a little of the $KMnO_4$ solution added from a burette. The $KMnO_4$ should immediately be decolorized. If not, the solution is not warm enough. Heat a little further and continue the addition of permanganate until there is the first trace of permanent violet colour. Repeat the titration for the sake of a more accurate figure. Let the average of several titrations be 9·5 c.c. $KMnO_4$ which is therefore somewhat stronger than the N/10 oxalic acid and therefore requires dilution by adding 5 c.c. of water to every 95 c.c. of $KMnO_4$. Do this and make a further titration to check the accurate balance of the two solutions. Then—

$$\begin{aligned} 1 \text{ c.c. N/10 } KMnO_4 &\equiv {\cdot}0063 \text{ gm. } H_2C_2O_4\,.\,2H_2O \\ &\equiv {\cdot}0043 \text{ gm. } H.COONa.H_2O \end{aligned}$$

For the analysis take 10 c.c. of the bright nickel solution and dilute to 100 c.c. Take out 20 c.c. of the diluted solution (= 2 c.c. of the original solution) and from a burette carefully add about 30 c.c. of the permanganate solution. Warm the mixture to boiling point. Cool and add an excess of dilute sulphuric acid. There is an excess of $KMnO_4$ some of which is now in the form of a brown manganese hydrate ppt. This is removed by the addition of a known excess of oxalic acid solution. For this purpose add 20 c.c. oxalic acid solution. The brown ppt. and violet colour disappear and there is now present an excess of oxalic acid. Titrate this with a further quantity of $KMnO_4$ from the same burette and note the total quantity of $KMnO_4$ used.

Example—

Total $KMnO_4$ soln. used	= 37·1 c.c.
Oxalic acid soln. used	= 20·0 ,,

Then

$KMnO_4$ soln. used for the oxidation of sodium formate	= 17·1 ,,

Hence

$$H.COONa.H_2O \text{ present} = \frac{17{\cdot}1 \times {\cdot}0043 \times 1000}{2}$$

$$= 29 \text{ gm./litre}$$

or c.c. $KMnO_4 \times 2{\cdot}15$ = gm./litre sodium formate crystals

This analysis is one of easy manipulation and gives consistently good results.

Estimation of Cobalt Sulphate. This analysis calls for some accurate work involving the use of a special reagent called α nitroso-β naphthol. This reagent is obtainable from the usual chemical supply houses and is dissolved to form a 2 per cent solution in acetic acid of 75 per cent strength.

For the analysis, 10 c.c. of the solution is taken and diluted to 100 c.c. From this solution 50 c.c. is taken (equivalent to 5 c.c. of the original solution) and further diluted to 100 c.c. with distilled water. The solution is acidified with HCl and brought nearly to boiling. 50 c.c. of the special reagent solution is added and the mixture kept boiling for 10 minutes. It is now allowed to stand for one hour and filtered, the ppt. being washed first with hot water, then with 12 per cent HCl until the washings are nearly clear, and finally with hot distilled water. The ppt. is now dried and ignited strongly, when it is transformed into cobalt oxide Co_3O_4.

Example—

5 c.c. of solution gave ·021 gm. Co_3O_4

Now $$\underset{177}{Co_3O_4} \equiv 3\,\underset{843}{(CoSO_4 . 7H_2O)}$$

Hence

$$CoSO_4 . 7H_2O = \frac{·021 \times 843 \times 1000}{177 \times 5} = 14·7 \text{ gm. per litre}$$

Volumetric Estimation of Cobalt. The gravimetric estimation of cobalt just described involves some careful work and is not altogether susceptible of easy accuracy. There is always some tendency for the co-precipitation of nickel. This can to some extent be guarded against by dissolving the ignited cobalt oxide in hydrochloric acid diluting and making the solution slightly alkaline and adding a solution of dimethylglyoxime. A red ppt. indicates the presence of nickel which, if in sufficient quantity, can be filtered off, followed by the re-determination of cobalt in the filtrate. This is a somewhat tedious operation. An alternative volumetric method is free from such nickel contamination.

The method is based on the oxidation of the cobalt compounds with sodium perborate in an alkaline medium when a subsequent reaction with potassium iodide releases iodine in proportion to the cobalt present.

The analysis is carried out by taking 10 c.c. of solution into a flask of at least 250 c.c. capacity. It is diluted to 100 c.c. with distilled water and 7 c.c. of 20 per cent sulphuric acid added. About 5 gm. of sodium perborate is added when a ppt. appears which afterwards clears. Sodium hydroxide is now added to render the mixture alkaline, when it is boiled for about 15 minutes. During this process there is a green ppt. of nickel hydroxide. The solution is cooled to room temperature and about 5 gm. of potassium iodide added, followed by 25 c.c. of sulphuric acid of the same strength as that previously added. This dissolves up the nickel hydroxide leaving the solution with a brown colour due to liberated iodine. To express the reaction in equation form it will suffice to show the oxidized cobalt compound as Co_2O_3 which reacts with KI as follows—

$$H_2O + Co_2O_3 + 2KI = 2CoO + I_2 + 2KOH$$

Hence $$\underset{59}{2Co} \equiv \underset{127}{2I}$$

The brown solution of iodine is now titrated with decinormal sodium thiosulphate of which—

$$1 \text{ c.c.} = {\cdot}0127 \text{ gm. I} = {\cdot}0059 \text{ gm. cobalt.}$$

Hence each c.c. of "thio" per 10 c.c. of plating solution represents—

$$\frac{{\cdot}0059 \times 1000 \times 281}{10 \times 59} = 2{\cdot}81 \text{ gm. } CoSO_4 \, . \, 7H_2O\text{/litre}$$

or

$$\frac{2{\cdot}81 \times 4{\cdot}54}{28{\cdot}4} = {\cdot}45 \text{ oz. per gallon.}$$

The technique of this method is easily acquired and repeated tests carried out on exactly similar lines serve to give comparable results as we are usually concerned with slight changes of composition from the original formula in order to ascertain needful additions to maintain original strength.

Alternative Method for Nickel-cobalt Bath. Take the equivalent of 1 c.c. of the bath and dilute to 100 c.c. Add small quantities of ammonium chloride, sodium pyrophosphate and potassium iodide. Fill a burette with potassium or sodium cyanide solution prepared and standardized to contain 27·54 gm. of KCN or 20·74 gm. of NaCN per litre. Add a small volume of ammonia to the test solution so that it smells faintly of the gas. Run in cyanide solution from the burette until the ppt. first formed—single cyanides—just disappears yielding a clear yellow solution. This can be done with the precision of a single drop. Then

$$\text{c.c. cyanide} \equiv \text{oz. nickel} + \text{cobalt/gallon.}$$

The amount of nickel is then obtained by deducting the cobalt obtained from one or other of the determinations described.

This method is approximate to the extent that cobalt behaves a little differently from nickel when pptd. and redissolved by cyanide. This difference is not large and is measured on a relatively small content of cobalt. It can only amount to a much smaller error on the much larger nickel content.

To check the strength of the standard cyanide solution used it will be seen that

$$\begin{array}{cc} Ni \equiv & 4NaCN \\ 59 & 196 \end{array}$$

$$\therefore \quad 1 \text{ c.c. NaCN} = \frac{20{\cdot}74}{1000} \times \frac{59}{196} = {\cdot}000625 \text{ gm. Ni} + \text{Co}$$

$$= {\cdot}000625 \times \frac{4540}{28{\cdot}4} = 1 \text{ oz./gal.}$$

Determination of Boric Acid (*Method* 1). Pipette 5 c.c. of the nickel solution into a beaker and add 200 c.c. water. Add sufficient Na_2CO_3 to completely ppt. the nickel (50 c.c. N/2 solution should suffice). Filter off the nickel hydroxide or basic carbonate ppt. by means of a filter pump, and thoroughly wash the ppt. To the solution, add methyl orange and sufficient N/2 HCl to bring the solution to neutrality. Now add about 10 gm. of glycerine or mannitol and 1 c.c. of 0·5 per cent phenolphthalein solution as indicator. The boric acid is now titrated with N/10 NaOH to produce a permanent pink or violet colour. At this stage, add a further quantity of 3 gm. of glycerine or mannitol. If the pink colour disappears, continue the titration with the alkali to reproduce the colour.

In the presence of glycerine or mannitol, the neutralization of boric acid with NaOH is as follows—

$$\underset{62}{H_3BO_3} + \underset{40}{NaOH} = NaH_2BO_3 + H_2O$$

from which it is easily seen that 1 c.c. N/10 NaOH is equivalent to 0·0062 gm. boric acid. Further methods will now be described which, avoiding the tedious pptn. and filtration of nickel compound, are rapid and more serviceable for routine work.

(*Method* 2.) The following rapid method is due to Longfield* who, as the result of some 3,000 tests, regards the method as accurate to within ¼ oz. per gallon. The test is carried out in a medium of glycerine which, as it usually contains traces of acid, is first neutralized with N/10 sodium hydroxide until phenolphthalein as an indicator just comes to a pink or violet colour.

100 c.c. of this neutral glycerine is warmed to 150° F. (66° C.) and 0·02 gm. of methyl red is added and dissolved in it. This constitutes the indicator for the test.

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* *Mon. Rev. Amer. Electroplaters' Soc.*, May, 1936, xxiii, No. 5, pp. 23–4.

Take 5 c.c. of the nickel-plating solution. Add 25 c.c. of neutral glycerine. Nickel solutions with a low pH introduce acidity which must now be removed. This is done by adding methyl orange and titrating with N/10 sodium hydroxide. For nickel solutions with a pH between 5 and 6 this would appear to be unnecessary.

For the actual titration for boric acid, it is convenient to have a glazed plate provided with a number of depressions or small cups. Into these cups small quantities of 5 drops each of the indicator are placed. The glycerine and nickel solution mixture is now titrated with N/10 sodium hydroxide testing drops of the solution by stirring with the indicator in the cups. The presence of boric acid gives rise to a red colour to the indicator and the titration is continued until the mixture of solution with the indicator produces only an orange colour. The fading of the red colour is readily observed. The exactly required orange colour may not be so easily determined, but this difficulty can be got over by noting the quantities of sodium hydroxide added for successive shades of colour as a yellow colour indicates an excess of alkali. In the record of this test the following note then appears: "Since 6 c.c. of the N/10 sodium hydroxide solution equals 1 oz. boric acid per gallon, the number of c.c. used in the titration divided by six will give the ounces per gallon of boric acid in the nickel-plating solution." This note calls for some explanation. Now boric acid titrates with NaOH in the presence of glycerine according to the following equation—

$$\underset{40}{NaOH} + \underset{62}{H.H_2BO_3} = NaH_2BO_3 + H_2O$$

$$\text{Now 1 c.c. N/10 NaOH} = 0{\cdot}0040 \text{ gm. NaOH}$$
$$= 0{\cdot}0062 \text{ gm. } H_3BO_3$$

Suppose in the titration of 5 c.c. nickel solution we used 5 c.c. N/10 NaOH. Then the following simple calculation gives the boric acid in ounces per gallon—

$$\frac{5 \times 0{\cdot}0062}{5} \times \frac{4540}{28{\cdot}4} = 1$$

Hence dividing the c.c. N/10 NaOH per 5 c.c. nickel solution by 5 gives the ounces of boric acid per gallon. The quotation given above is American and refers to the American gallon, which is five-sixths of the Imperial gallon. A little thought will show the reason for the figure of 6 c.c. in the quotation, which is correct for the American gallon, while the figure of 5 applies for the Imperial gallon. In other words, each c.c. N/10 NaOH per 5 c.c. nickel solution represents one-fifth of an ounce of boric acid per gallon.

The method has the advantage of speed and simplicity, and the accuracy to $\frac{1}{4}$ oz. per gallon is all that can be required for most purposes.

(*Method* 3.) This also avoids the need for the separation of the nickel compound and also gives a sharp end point. It utilizes a test reagent made up in the following manner: Dissolve 60 gm. of sodium citrate in 400 c.c. distilled water and add 600 c.c. of pure glycerine. Thoroughly mix by shaking, and add 0·2 gm. of phenolphthalein dissolved in 10 c.c. alcohol. Now add from a burette sufficient N/10 NaOH to produce a faint violet colour. This quantity of reagent will suffice for about 40 boric acid determinations.

To make the test, take 1 c.c. of the nickel solution which has been brought to a neutral condition by the addition of either acid or alkali, both of which will need to be of only deci-normal strength. To this add 25 c.c. of the test reagent solution, and titrate again with N/10 NaOH till the green colour changes to blue (compounded by the green of the solution and violet of the phenolphthalein now made slightly alkaline). This end point is sharp. Let v = c.c. N/10 NaOH added.

Now 1 c.c. N/10 NaOH = 0·0062 gm. boric acid

Hence boric acid in the nickel solution

$$= v \times 0{\cdot}0062 \times 1{,}000 \text{ gm. per litre}$$

which can be quickly converted into oz. per gal.

This method of quickly estimating the boric acid may follow that of the estimation of nickel given on page 306. After the cyanide titration for nickel, remove alkalinity by titrating with ·1N . H_2SO_4 using methyl red as indicator. Then add 10 to 25 c.c. of neutral glycerine. Add a few drops of phenolphthalein as indicator and titrate with ·1N . NaOH to the first permanent trace of violet colour. Call the volume of ·1N . NaOH used b c.c. Then

$$H_3BO_3 = {\cdot}40 \times b \text{ oz. per gallon}$$

This formula again requires explanation. The neutralization of boric acid follows the course

$$\underset{62}{H_3BO_3} + \underset{40}{NaOH} = NaH_2BO_3 + H_2O$$

So that 1 c.c. ·1N . NaOH = ·0062 gm. H_3BO_3
and 1 c.c. ·1N . NaOH per 2·5 c.c. solution represents

$$\frac{\cdot 0062 \times 4540}{2\cdot 5 \times 28\cdot 4} = \cdot 4 \text{ oz. } H_3BO_3 \text{ per gallon}$$

Estimation of Sodium Naphthalene Trisulphonate. This reagent is the one most commonly used in the Schlötter solutions for bright nickel. Its formula is

$$C_{10}H_5(SO_3Na)_3$$
$$\text{Mol. Wt.} = 434$$

By oxidation with sodium peroxide the carbon and hydrogen are burnt off and the remainder converted to sodium sulphate. The estimation follows these lines and is carried out as follows—

Take 2 c.c. of the plating solution. Evaporate to dryness in a nickel crucible on a water bath. Dry over a small flame without spitting. Cool. Add about 5 gm. of sodium peroxide. Place lid on the crucible and gently raise the temperature to fusion. During the process the trisulphonate is oxidized to sulphate and some of the nickel compound is converted to oxide. Continue heating until the "melt" is quiet. Cool. Transfer crucible and lid to a beaker and cover with about 100 c.c. of distilled water gently adding a little strong HCl to dissolve the nickel oxide. Remove, with rinsing, the crucible and lid. The solution is now clear and contains an excess of HCl. Heat to boiling and add an excess of hot $BaCl_2$. Boil for some minutes and allow to settle. Filter through a good filter of known or negligible ash, washing with hot water until the washings do not respond to the chloride test with silver nitrate. Dry and ignite the ppt. of $BaSO_4$ in a porcelain crucible. Weigh to get the weight of $BaSO_4$ after allowing for any filter ash.

Make a smilar test with 2 c.c. of the solution without the preliminary ignition with sodium peroxide, treating with HCl and $BaCl_2$ and filtering the $BaSO_4$ and weighing in the usual manner. This gives the $BaSO_4$ due to the metal sulphates in the solution. The amount is less than after ignition with sodium peroxide, the difference being due to the sulphonic compound.

Then

$$\frac{\text{Excess } BaSO_4 \text{(in first test)} \times \cdot 62 \times 1000}{2}$$

= grams sodium naphthalene trisulphonate per litre.

The factor ·62 is obtained as follows—

$$\underset{434}{C_{10}H_5(SO_3Na)_3} = \underset{699}{3BaSO_4}$$

$$1 \text{ gram } BaSO_4 = \frac{434}{699} = \cdot 62 \text{ gm. sulphonate compound.}$$

CHAPTER XVII

DEPOSITION OF ZINC

INTRODUCTION—Electro-zincing—The sulphate solution—Anodes—Operating conditions—Rate of deposition—Throwing power—Addition agents—The chloride solution—The alkaline solution—Operating conditions—Additions to the solution—Preparation of work—Comparison of "acid" and "alkaline" zinc deposits—Deposition of zinc on aluminium—General observations on zinc deposits—Testing zinc deposits—Analysis of solutions

Introduction. Zinc in industry finds its widest application as a protective coating for large quantities of iron and steel. The zinc is applied by three methods. In hot galvanizing, the iron and steel is cleaned and passed through a bath of molten zinc. A substantial coating is thus applied. Though widely used, the process fails for some purposes, in that the deposit is uneven and in some parts distinctly lumpy. It, moreover, necessitates the article being raised to a temperature of at least 460° C., not always desirable.

Cold galvanizing, or electrodeposition, has the advantages of being carried out at the ordinary temperature, the production of a more uniform deposit, the avoidance of the need for cleaning the threads of screws, etc., with that of being able to put on any desired thickness of deposited metal.

Sherardizing is a method of applying zinc to iron and steel by imbedding the cleaned metal in zinc powder and raising the temperature to about 300° C., well below the melting point of zinc. The coating is uniform, the temperature definitely lower than that in hot galvanizing, and the process is being increasingly applied.

Electro-Zincing. The electrodeposition of zinc is easily accomplished, two solutions being largely used for this purpose. In the so-called "acid solution," zinc sulphate is the main constituent, while the "cyanide" solution is of a composition somewhat similar to that of the cyanide copper solution. Each of these solutions has its definite field of application. The deposit from the sulphate is brighter than that from the cyanide, but the latter solution throws far better. In the "acid" solution there is some discrimination as to the anode impurities which pass into the electrolyte, and are subsequently deposited on the cathode. In the cyanide solution most metals readily pass into the solution and are deposited from it. For resistance to corrosion the deposit needs to be as pure as possible. Zinc anodes of a high order of purity can easily be obtained, but if any difference is permissible, anodes in the cyanide solution should be rather purer than those for the sulphate solution. Further, the sulphate solution is unsuitable for cast iron, and this is probably due to the tendency to the deposition of hydrogen on the impurities of the cast iron.

The Sulphate Solution. This may be constituted as follows—

Zinc sulphate . .	3 lb.	300 gm.
Common salt . .	2 oz.	13 ,,
Boric acid . .	3 ,,	20 ,,
Aluminiun sulphate .	4 ,,	26 ,,
Dextrine . . .	2 ,,	13 ,,
Water . . .	1 gal.	1 litre

While this composition is not of a simple type, each constituent has its particular function. The zinc compound supplies the metal to be deposited. Common salt contributes to conductance. Boric acid controls acidity, while aluminium sulphate and dextrine function as addition agents, improving the physical character of the deposit.

These solutions must be on the slightly acid side. Without acid there is a marked tendency to the production of basic salts with the formation of spongy deposits. This was one of the early troubles with zinc deposition, before the degree of acidity had been definitely determined and controlled.

Further, in the presence of too much acid the zinc anodes containing, as they are bound to, some impurities, are corroded, though this increases the content of zinc in the bath and lowers the acidity.

On the other hand, if the acidity is low there will be some possibility of incompletely soluble anodes giving rise to acid production, as it does in the nickel bath. It would, therefore, appear that the acidity is not likely to increase alarmingly. Usually it stands between 1·5 and 3 on the usual pH scale, far more than in the case of nickel, and this may be equal to

2 to 5 gm. of free acid per litre. In such a solution both anode and cathode efficiencies are nearly 100 per cent, and the solution, therefore, persists over prolonged periods of operation.

An alternative solution is that containing—

Zinc sulphate . .	1½ lb.	150 gm.
Sodium acetate . .	6 oz.	40 ,,
Water . . .	1 gal.	1 litre

To this and other solutions, addition agents proposed include gum arabic, glucose, beta-naphthol, and gum tragacanth. With small additions of these, amounting to not more than about 1 gm. per litre a current density of up to 30 amperes per sq. ft. may be used, this sufficing to produce a deposit of 0·0005 in. in a quarter of an hour, this thickness being considered sufficient to give normal protection against corrosion.

Anodes. These should be of cast metal and as pure as possible. Impurities, if they do no worse, lead to excessive anode corrosion. Accumulating in the solution, they are likely to cause trouble in subsequent deposition.

Operating Conditions. At normal temperature the solution may be used with a P.D. of 2 to 2·5 volts, giving a current density of 10 amperes per sq. ft. This C.D. may be markedly increased without impairing the character of the deposit, and a little experimenting on the part of the operator will soon show the range of C.D. which can be used with safety. It is a simple matter to do this with a small bulk of solution. In fact it is up to the operator to trace the value of the constituents of the bath by working similar solutions without each of the constituents in turn.

Rate of Deposition. The following figures are of interest regarding the weight, thickness, and other properties of the deposit.

One ampere-hour is responsible for the deposition of 1·22 gm. of zinc. Allowing for slight cathode inefficiency this figure may safely be taken as 1·2 gm. Ten ampere-hours per sq. ft. represents a thickness of 0·66 mil, and this will, therefore, be the thickness obtained in half an hour if the C.D. can, by agitation, be pushed up to 20 amperes per sq. ft. Other similar figures can be calculated and are embodied in Tables LXI and LXII.

TABLE LXI

Thickness of Zinc Deposits from Sulphate Bath

Current efficiency = 95%

Current Density Amp./Sq. Ft.	Thickness in Mils in			
	15 Min.	30 Min.	45 Min.	60 Min.
5	·08	·16	·24	·33
10	·16	·33	·49	·66
15	·25	·50	·75	·99
20	·33	·66	·99	1·32
25	·41	·82	1·24	1·65
30	·49	·99	1·48	1·98
35	·58	1·16	1·74	2·31
40	·66	1·32	1·98	2·64
45	·75	1·49	2·24	2·97
50	·82	1·65	2·47	3·3

TABLE LXII

Thickness of Zinc Deposits from Alkaline Bath

Current efficiency = 60%

Current Density Amp./Sq. Ft.	Thickness in Mils in			
	30 Min.	60 Min.	90 Min.	120 Min.
5	·11	·22	·33	·44
10	·22	·44	·66	·88
15	·33	·66	·99	1·32
20	·44	·88	1·32	1·76
25	·55	1·10	1·65	2·20
30	·66	1·312	1·97	2·63

Hot galvanizing will, by test, be found to apply a coating of 1 oz. per ft. super. Electro-galvanizing suffices to give the same protection with about one-half of this amount of metal. This is mainly due to the fact that the deposited metal is much more pure than that applied in the hot galvanizing process. The electro-deposited coatings usually run to about

0·3 to 0·5 oz. per sq. ft. The 10 ampere-hours per sq. ft. referred to above corresponds to about 0·4 oz. per ft. super.

Mere thickness, however, is not everything in the case of a zinc coating, and there has been some diversity of opinion as to the thinnest deposits which can be relied upon to offer reasonable resistance to the corrosive conditions of service. The Washington Bureau of Standards at one time specified 1½ mils, but Hughes* suggests that considerably less, as low as three-quarters of a mil, should suffice. Much depends upon the evenness of the deposit with freedom from pores and the nature of the corrosive conditions to which the deposit will be subjected.

Throwing Power. This, in the case of the zinc sulphate solution, is notoriously low, and the solution is therefore of greater service in electro-galvanizing sheet work with which the inter-electrode distance is very uniform. Some qualitative figures have already been adduced in Chapter VII, but the low throwing power does not so much matter where plain sheet metal is being handled. For irregular work the solution does not meet the necessary requirement, and recourse must therefore be had to the cyanide solution.

Addition Agents. Quite a number of addition agents have been used to improve the character of the zinc deposit, and, therefore, to increase the rate of deposition. Among them are aluminium compounds, the several types of sugars, pyrogallol, dextrin, beta-naphthol, and gum arabic. With most of these compounds there is definite absorption, though this is not the case with aluminium compounds, there being no evidence of co-deposition. With aluminium compounds loss is occasioned by the separation of aluminium hydroxide from the colloidal state, in which it is effective for addition purposes. Organic materials, however, are absorbed, usually to the extent of about 1 lb. per ton of metal. This quantity varies considerably, but depreciation in the quantity present will be reflected in the character of the deposit, necessitating occasional further additions of these materials.

The Chloride Solution. Attempts at increasing the conductance of the zinc sulphate solution by the addition, first, of common salt and other chlorides, led to the discovery that

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***Modern Electro-plating* by Hughes, (Henry Frowde and Hodder and Stoughton), p. 76.

excellent deposits are obtainable from solutions made entirely from chlorides. The following is a typical composition of such a solution—

Zinc chloride	24 oz.	150 gm.
Sodium chloride	40 ,,	250 ,,
Aluminium chloride	4 ,,	25 ,,
Water	1 gal.	1 litre

The aluminium chloride serves the purpose of an addition agent, giving whiter and smoother deposits without the deposition of any aluminium.

Such a solution would have only about one-half of the resistance of the sulphate bath referred to above, and the resistance can be still further reduced by the addition of more salt or ammonium chloride.

A current density of 15 to 45 amperes per sq. ft. is possible with a pH value of 3·5 to 4·5.

By the application of agitation the C.D. can be considerably increased, even up to 150 amperes per sq. ft. For a deposit of 0·0006 in., about 500 ampere-minutes would be required. At 50 amperes per sq. ft., 10 minutes' deposition would suffice.

The Alkaline Solution. This, as previously stated, has the advantage of far greater throwing power than the sulphate solution. Generally, the composition of the solution is in line with that of copper cyanide, but in order to increase throwing power still further, an appreciable amount of caustic soda is added. The chief constituents of the solution are zinc sodium cyanide, sodium cyanide, and caustic soda. An aluminium compound is added as an addition agent.

These essential constituents are obtained by the use of different original chemicals. The following may be taken as a typical composition—

(1)	Zinc oxide (80% Zn)	6½ oz.	40 gm.
	Sodium cyanide	16 ,,	100 ,,
	Sodium carbonate	1½ ,,	9·5 ,,
	Caustic soda	½ ,,	3 ,,
	Potash alum	2 ,,	12·5 ,,
	Water	1 gal.	1 litre

The preparation of the solution is undertaken by dissolving the sodium cyanide in water. The solution may be warmed and the zinc oxide added. This should dissolve readily, after which the remaining constituents are added.

An alternative formula is the following—

(2)	Zinc cyanide (55% Zn)	9½ oz.	59 grm.
	Sodium cyanide .	8½ ,,	53 ,,
	Caustic soda . .	7 ,,	44 ,,
	Sodium carbonate .	1½ ,,	9·5 ,,
	Aluminium sulphate .	¾ ,,	4·7 ,,
	Water . . .	1 gal.	1 litre

The sodium cyanide, caustic soda, and sodium carbonate may be dissolved in water and the zinc cyanide and aluminium sulphate added, these readily dissolving in the resulting solution.

From the following expressions—

$$\underset{117}{Zn(CN)_2} + \underset{98}{2NaCN} \rightarrow Na_2Zn(CN)_4$$

it will be seen that 1 lb. of pure zinc cyanide requires practically ·84 lb. pure NaCN for its solution.

These two formulae look distinctly different. As a matter of fact they agree when made up, with the exception that No. (1) contains a few grams of potassium sulphate introduced in the alum. These formulae emphasize the fact, often overlooked, that on mixing, chemical changes occur between the several chemicals, resulting in the production, in this case, of an almost identical solution. Thus—

$$ZnO + 4NaCN + H_2O = Zn(CN)_2 2NaCN + 2NaOH$$

Alkaline zinc solutions thus contain both zinc sodium cyanide and sodium zincate (Na_2ZnO_2).

Analysis of one works solution gave the following results—

Zinc (as metal) = 36·8 gm. per litre.
NaCN (total) = 22 ,, ,, ,,
NaOH = 61·6 ,, ,,

$$\text{Now } \underset{196}{4\ NaCN} \equiv \underset{65}{Zn}$$

$$\text{Hence 22 gm. NaCN} \equiv \frac{22}{196} \times \frac{65}{1} = 7{\cdot}2 \text{ gm. Zinc as } Zn(CN)_2 . 2\,NaCN$$

Zinc as sodium zincate = 36·8 − 7·2 = 29·6 gm.

$$\text{Again} \quad Zn \equiv 2NaOH$$
$$65 \equiv 80$$

$$\therefore \quad 29{\cdot}6 \equiv \frac{29{\cdot}6}{65} \times 80 = 36{\cdot}4 \text{ gm. NaOH combined with Zinc.}$$

Hence free NaOH = 61·6 − 36·4 = 25·2 gm.

In this form the analysis appears as—

$Zn(CN)_2$ 2NaCN = 23·8 gm. per litre.
Na_2ZnO_2 = 65·1 ,, ,, ,,
NaOH = 25·2 ,, ,, ,,

Another equivalent or alternative composition would be—

$Zn(CN)_2$ = 13·1 gm. per litre.
ZnO = 36·9 ,, ,, ,,
NaCN = 11·1 ,, ,, ,,
NaOH = 61·6 ,, ,, ,,

These alternative formulae for a single solution can readily be deduced from the chemical equivalents of the substances concerned.

Operating Conditions. The solution may be worked either cold or warm. Cold solutions usually are better for being a little stronger, and not infrequently they contain a larger proportion of free cyanide in order to keep the anodes free from insoluble cyanide of zinc. The temperature of operation is a matter of choice and convenience.

Generally, however, a temperature of about 30° to 40° C. (86° to 104° F.) may be used. The current density permissible exceeds that of the "acid" solution, going up to even 40 amperes per sq. ft. A more usual figure is 20 amperes per sq. ft.

The solution is preferably worked in an iron tank, as is common with warm cyanide solutions. There is no inherent objection to a lead-lined tank so long as the lining is either a new one or very carefully washed after any previous solution.

Additions to the Solutions. Now it has come to be recognized that this solution, although sorely required for the purpose, fails to give satisfactory deposits on cast iron, and yet this metal calls for galvanizing by electro-deposition. After prolonged treatment with the current, either there is no deposit or one very thin and streaky is obtained. The fault evidently lies with the metal. Cast iron contains notable quantities of carbon, and it would appear that there is the preferential deposition of hydrogen at this conspicuous impurity, with the consequent loss of metal.

Methods have been proposed to overcome the trouble. One is the addition of a mercury compound to the solution. This patented method involves the use of a small amount of mercury in the anodes, say up to 1 per cent, and a corresponding quantity in the solution. This, in theory, is simple.

The mercury is easily deposited and, once there, opposes the deposition of hydrogen, thereby offering greater facility for the deposition of the zinc. This difficulty in depositing hydrogen on mercury occurs with other metals, but to a lesser degree. It is generally called *over-voltage*, meaning, in effect, a greater voltage required to maintain the deposition of certain ions over that ordinarily expected from their usual electro-chemical properties (see page 64). It is an important electro-chemical phenomenon, and one which comes into operation when impure zinc, which is ordinarily rapidly dissolved by sulphuric acid, becomes passive after amalgamation.

The small amount of deposited mercury suffices to, as it were, cover up the impurities, and hence the deposition of zinc can proceed normally.

A word of warning must, however, be uttered regarding the use of mercury in zinc deposition. For a deposit which is not to be brought into contact with other metals it may be all to the good. It will be recalled that amalgamated zinc is not hindered from dissolving electro-chemically in the several forms of voltaic cell where another metal is in contact with it through the external circuit.

There may be—indeed are—some applications of zinc deposition in which the deposit will come into contact in the process of fabrication with other metals. There is here the almost certain risk that the presence of mercury in the zinc deposit may facilitate the corrosion of the adjacent metal. There is now the feeling that mercury in the zinc is disadvantageous, and care is being advocated to ensure its absence. This will involve the testing of the several materials used in the process for the presence, even in very small amounts, of mercury. This will be described later.

The above formulae for the cyanide solution show the addition of aluminium compounds as addition agents. Dextrose is also used. The plater would do well to settle for himself by experiment the one which he regards as preferable. Both can be used satisfactorily.

Preparation of Work. Where cast iron is being treated, special attention must be paid to the preliminary treatment. One of the likely troubles is that of uneven deposits due, probably, to insufficient cleaning. The difficulty lies with the sand which adheres to the casting, and pickling in hydrofluoric acid is to be recommended. For this purpose the bought acid may be diluted to about 10 per cent of its strength, and the presence of a small proportion of sulphuric acid is to be recommended. Preferably hydrochloric acid should not be used with cast iron, as the smallest traces left in any pores in the metal are likely to lead to considerable corrosion after deposition.

If the bath is working satisfactorily it should yield an excellent bluish-white soft deposit, one which is non-porous and soft enough to withstand considerable distortion by bending, and thus maintain its continuity in service.

Comparison of "Acid" and "Alkaline" Zinc Deposits. Owing to the considerable importance of zinc deposition for protective purposes, there has been a large amount of experimental work, both on a small and large scale in order to determine the most satisfactory methods of effecting the deposition. These tests, to which reference is later made, seem to show without doubt that the cyanide deposit is to be preferred to that obtained from the acid solution. In the first place, there is retained by the base metal a film of the depositing solution. In the cyanide bath this is protective rather than corrosive, while the reverse must be stated with reference to the acid solution. Again, the cyanide solution gives more even deposits than the sulphate solution, while it possesses cleansing properties which, while not being relied upon to effect cleaning, are, nevertheless, there as a second line in case of inadvertently faulty cleaning. Above all, the vastly superior throwing power of the cyanide solution inevitably marks it out as pre-eminently suited to the deposition of the metal on all but very plain work. The solution may be regarded as more costly in make up, maintenance, and working, but these disadvantages are far more than balanced by the superior deposit.

Deposition of Zinc on Aluminium. Special interest attaches to the deposition of zinc upon aluminium as a means of protection from corrosion. The best preliminary treatment of the aluminium, or the alloy of this metal, with constituents whic impart the desirable mechanical properties, is that of removing grease and subsequently sand-blasting. By this means the troublesome oxide film is entirely removed and, after a rinse, the work is at once transferred to the zinc plating bath which, for this purpose, may conveniently contain—

Zinc cyanide .	10 oz. approx.	60 gm.
Sodium cyanide	5 ,, ,,	30 ,,
Caustic soda .	3 ,, ,,	20 ,,
Ammonia .880.	5 fl. oz. ,,	30 c.c.
Water . .	1 gal. ,,	1 litre

With this solution there is less tendency to blistering of the deposit, while the alkali is of sufficient quantity and quality to keep the anodes free from insoluble and insulating slimes.

General Observations on Zinc Deposits. Zinc is recognized to be an excellent protective for iron and steel owing to what is called its *sacrificial corrosion*. It is, however, still necessary to obtain deposits of appreciable thickness such as 0·0006 in. mentioned above.

There is no difficulty in producing these deposits. Both sulphate and chloride solutions are available, keeping the pH between 3·5 and 4·5. The throwing power, however, is not good, and cannot be appreciably increased. Addition agents have been considerably experimented with, but not with the success which might have been hoped. Dextrine seems to have proved most serviceable. The addition of aluminium salts has the advantage of buffering the solution, that is, making it easier to maintain the correct concentration of hydrogen ions or the pH value.

Generally, conductance can be largely increased by the addition of chlorides and the use of zinc chloride in place of zinc sulphate. The solution, especially with the application of agitation, can then be used with very high current densities.

One notable feature of zinc deposits is the ready diffusion of other deposited metals into them. Metals which are thus readily absorbed are copper, brass, gold, and silver. Gold deposits are so readily absorbed as to show no signs of their presence after a very short time. Experiments have shown that nickel is not absorbed, and this metal, therefore, provides a suitable undercoating for the more easily absorbed metals.

Zinc deposits usually contain hydrogen which induces brittleness. This may, however, be removed by heating for 30 minutes at 100°–200° C. and some specifications require this treatment.

The following recommendation for the thickness of zinc coatings has been made through the collaboration of Dr. Blum, the American Electro-platers' Society and the American Society for Testing Materials.

	Minimum Thickness on Significant Surface
(1) General Service . .	·0005 in.
(2) Mild Service . . .	·00015 in.

Testing Zinc Deposits. Zinc deposition is carried out for a very definite protective purpose, and it is only to be expected that tests will be applied to ensure a sufficient quantity and quality of deposit to secure the required protection. It is not proposed to discuss these tests in detail, only to enumerate them.

The mechanical tests include hammering, squeezing, grinding and bending to determine adhesion. Chemical tests include, among others, that designed many years ago by Preece, which consists of immersing the specimen in a specified copper sulphate solution to ascertain its continuity. Weak spots are soon revealed by the appearance of red dots due to deposited copper, the local currents for this purpose being set up between the anodic zinc and the exposed iron which becomes the cathode.

These tests will be referred to in some detail in Chapter XXII.

ANALYSIS OF THE SOLUTION

The Sulphate Solution. In this case the chief determination is that of the zinc or its sulphate. For this purpose considerable dilution is necessary to bring the solution down to the strengths comparable with those of the usual standard solutions. In the case of the 300 gram of zinc sulphate per litre solution, dilution to six to ten times the volume is convenient.

Estimation of Zinc. A hot acid solution of zinc reacts with potassium ferrocyanide according to the following equation—

$$3ZnCl_2 + 2K_4Fe(CN)_6 = 6KCl + K_2Zn_3(Fe(CN)_6)_2$$

the end point being detected by the formation of a brown colour with uranium acetate solution used as an external indicator.

Now Mol. Wt. $K_4Fe(CN)_6{\cdot}3H_2O = 422$

Hence 844 gm. potassium ferrocyanide $\equiv 3 \times 65$

$= 195$ grm. zinc.

It is usual to make up the solution of approximate strength and standardize it with either pure zinc or pure zinc sulphate. For this purpose make up a solution of the ferrocyanide containing 50 gm. of the crystallized salt per 1 litre.

Standardization. (1) With pure zinc. One gramme of pure zinc is weighed out and dissolved in dilute HCl and the solution made up to 100 c.c. 25 c.c. (= 0·25 gm. Zn) is taken out, diluted and heated, and the hot solution titrated with the ferrocyanide until a drop withdrawn from the flask and mixed with a drop of a solution of uranium acetate on a tile shows the first sign of a brown coloration.

Assume 21·7 c.c. of the ferrocyanide solution to have been used. Then—

$$1 \text{ c.c. ferrocyanide solution} = \frac{0{\cdot}25}{21{\cdot}7} = 0{\cdot}0115 \text{ gm. Zn.}$$

The ferrocyanide solution might now be diluted so that 1 c.c. is equivalent to 0·01 gm. Zn. For this purpose each 21·7 c.c. should be diluted to 25 c.c.

The Estimation. Dilute 10 c.c. of the solution to 100 c.c. Take 25 c.c. of the diluted solution. Further dilute, add a little HCl, warm and titrate with the ferrocyanide solution using the "spot" indicator of uranium acetate on a tile until there is produced a brown colour. Repeat the titration for concordant results.

Example. 25 c.c. diluted Zn. soln. = 16·2 c.c. $K_4Fe(CN)_6$.
Hence as

$$1 \text{ c.c. } K_4Fe(CN)_6 = 0{\cdot}01 \text{ gm. Zn}$$

zinc per litre of the bath solution

$$= \frac{16{\cdot}2 \times 0{\cdot}01 \times 100 \times 1000}{25 \times 10} = 64{\cdot}8 \text{ gm.}$$

and as

$$\underset{65}{Zn} \equiv \underset{287}{ZnSO_4.7H_2O}$$

the weight of zinc sulphate per litre is

$$\frac{287 \times 64{\cdot}8}{65} = 286 \text{ gm.}$$

Alternatively—

Since $195 \text{ gm. Zn} \equiv 844 \text{ gm. } K_4Fe(CN)_6 . 3H_2O$

$10 \text{ gm. Zn} = 43{\cdot}28$,, ,,

Hence by dissolving 43·28 gm. of pure potassium ferrocyanide and making up to 1000 c.c. the resulting solution will have a value of ·01 gm. Zn per c.c. This may be sufficiently accurate for many purposes.

The Alkaline Solution. In this solution the zinc, free cyanide, caustic soda and sodium carbonate are frequently required.

Zinc. Little need be added to the method described for the sulphate bath except to indicate that as usual it is necessary to decompose the cyanides, after which the acid solution can be treated like the sulphate bath.

An alternative gravimetric method is that of taking 5 c.c. of the solution and adding sufficient strong H_2SO_4 to decompose the cyanides. Dilute considerably, and add an excess of sodium carbonate solution to ppt. the zinc as $ZnCO_3$. This ppt. is filtered and washed thoroughly to get rid of all excess of Na_2CO_3, after which the ppt. is ignited to ZnO.

$$\text{Now} \qquad \underset{65}{Zn} \equiv \underset{81}{ZnO} \equiv \underset{117}{Zn(CN)_2}$$

$$\text{Hence} \qquad \text{Wt. of ZnO} \times \frac{1000}{5} = \text{gm. ZnO per litre}$$

$$\text{or} \qquad \text{Wt. of ZnO} \times \frac{1000}{5} \times \frac{117}{81} = \text{gm. } Zn(CN)_2 \text{ per litre.}$$

Free Cyanide. This is not directly determined by standard silver nitrate as with other solutions. The method adopted is that of adding an excess of caustic soda which converts the whole of the zinc compounds to sodium zincate (Na_2ZnO_2) so that the whole of the cyanide is converted into the sodium salt which is then estimated with silver nitrate. From the known zinc content, the amount of NaCN required to form the compound ($Zn(CN)_2.2NaCN$) is calculated and this deducted from the total cyanide gives the amount of free cyanide.

As an example take 10 c.c. of solution and dilute to 250 c.c. Take 25 c.c. of the diluted solution and add an excess of NaOH. Titrate in the usual manner with N/10 $AgNO_3$ to the first permanent turbidity.

$$\text{Then} \qquad \text{c.c. N/10 } AgNO_3 \times {\cdot}0098 \times \frac{250}{25} \times \frac{1000}{10}$$
$$= \text{gm. total NaCN per litre.}$$

Alkalis. The solution contains caustic alkali, and therefore also carbonates, the estimation of which follows the lines indicated described in detail in Chapter V.

To carry out the estimation, the bath is suitably diluted so that 1 or 2 c.c. of the bath can conveniently be measured off. Thus, by diluting 10 c.c. of the bath to 250 c.c., each 50 c.c. of the dilute solution will contain 2 c.c. of the bath. Sufficient potassium ferrocyanide solution is added to account for the estimated zinc, and more than sufficient silver nitrate to account for the total cyanide. Subsequently, the estimation of alkalis follows the lines detailed in Chapter V by titration with semi-normal hydrochloric acid. With phenolphthalein as indicator, the total caustic and half the carbonates are found, while, with the further addition of methyl orange, the remaining half of the carbonate is found, from which the quantities of caustic and carbonate are readily calculated.

Testing for Mercury. The following tests with the modifications indicated are also available for compounds and metals other than those used in the production of zinc deposits. They are well known to the analytical chemist.

In the case of cyanide solutions the cyanide contents are first decomposed by treatment with the minimum of strong acid, excess of which is boiled off by the reduction of the solution to a small volume. The usual metallic salts will not require this treatment. In the case of metals to be used as anodes a small quantity of turnings may be dissolved in the minimum amount of the relevant acid, boiling off excess of acid.

The first test involves the deposition of any mercury present on a clean copper surface, on which it will be recognized by a white deposit, which may be brightened by gentle rubbing. A slightly acid solution is required. Excess of acid is undesirable. Hence the better practice of removing excess of acid by evaporation and adding a regulated amount.

In the case of plating solutions, remove where necessary the cyanides, and after evaporation dilute the solution, adding about 3 c.c. of strong HCl. Place in the solution a small piece of copper foil, which has been cleaned by immersion in 50 per cent nitric acid for a half to one minute until it gasses vigorously. Rinse thoroughly and introduce the copper into the solution. A white deposit, which, after drying, becomes bright, is good evidence of the presence of mercury. The application of this method to salts and metals will be obvious.

Where mercury may be present in appreciable quantity the usual test of the addition of a solution of stannous chloride to an alkaline solution will indicate the presence of mercury by a grey turbidity, or, when the amount of mercury is smaller, a white turbidity.

Quantitative tests are also available but these need not be described here.

CHAPTER XVIII

DEPOSITION OF CADMIUM

INTRODUCTION—The solution—Additions to the solution—Anodes—Thickness of the deposit—Operating conditions—Anti-corrosion properties of cadmium—Nickel on cadmium—Heat treatment of cadmium deposits—Cadmium and foodstuffs—Analysis of solution

Introduction. Cadmium provides another example of a metal to which little reference is made in earlier literature. It is a recent "find" in electro-plating. It has already attained extensive use, and it may be said that, quantitatively, its value is being established. There is generally the optimism that a new procedure is more valuable than subsequent service proves. The extended use of the metal is at least one argument in its favour. Secondly, there is the fact that, electro-chemically, it lies nearer to iron than does zinc, and with electro-chemical likeness there is less likelihood of corrosion with one or other of the adjacent metals. There has been much discussion as to the relative merits of cadmium and zinc for protective purposes. For cadmium there are disadvantages in its higher cost, and in the fact that the deposit produces a dark stain on the hands, necessitating the deposit being covered with another metal. As a result, a large amount of work has been treated, first with cadmium as a rust-proof undercoat, and then with nickel to obtain the desired finish.

The Solution. Very little success has been obtained with an "acid" cadmium solution, and all the solutions in practical use are of the cyanide type. These yield very satisfactory deposits, may be worked cold, and throw well, though not so well as is the case with the strongly alkaline zinc solution.

Formulae for the solution have the usual variety, although it is satisfactory to note that in the case of every metal these formulae are being reduced to a limited number, a step in the right direction.

All cadmium solutions, therefore, contain the double cyanide of cadmium and sodium, with additions of free cyanide and alkali and some addition agent.

A good average formula may be taken as follows—

Cadmium oxide .	**5¼ oz.**	**33 gm.**
Sodium cyanide .	**12 ,,**	**75 ,,**
Water . . .	**1 gal.**	**1 litre**

This is recommended because it is easily made up. The cyanide is dissolved in water less than the final quantity, and, after warming, the cadmium oxide readily dissolves, after which the volume can be made up. At first there would not appear to be any provision for caustic soda, but the following equation shows that this is formed when the constituents of the solution are mixed—

$$H_2O + CdO + 4NaCN = Cd(CN)_2 \cdot 2NaCN + 2NaOH$$

Then if $CdO = 4NaCN$

$$\begin{array}{cc} 128 & 196 \end{array}$$

1 lb. pure cadmium oxide requires 1·53 lb. pure NaCN for its solution.

An alternative formula leading to much the same result is the following—

Cadmium cyanide [$Cd(CN)_2$]	6¾ oz.	42 gm.
Sodium cyanide . .	8 ,,	50 ,,
Caustic soda . . .	4 ,,	25 ,,
Water	1 gal.	1 litre

The following comments on the composition of the solution may be made. There is a wide range of free cyanide permissible even up to 100 per cent over that which is combined. A 50 per cent excess is shown in the above formula. Caustic soda may go up to 30 gm. per litre, rather in excess of the above figure. The throwing power, while good, is open to improvement, especially having in mind the purpose for which cadmium plating is undertaken. An excess of alkali has not the same beneficial effect as with zinc. A suggestion has therefore been made of the use of a more dilute solution in which to strike the work. Weaker solutions are usually better throwers. Such a solution would, if of the cyanide type, possess cleansing properties, and this would constitute an added advantage. After a quick strike for a few minutes at a high C.D. of say 30 to 50 amperes per sq. ft., the work is transferred to the main solution.

In common with all other baths containing cyanides the cadmium bath tends to accumulate carbonates, for the advantages of which there appears to be some limit. This has been set at about 25 gm. per litre. Soderberg and Westbrook* claim that excess carbonates can be eliminated by reducing the temperature of the solution to 0° C., when the carbonates in excess of 22·5 gm. per litre crystallize out. Occasionally it may be necessary to "seed" the crystals by the addition of a small amount of the solid carbonate, this operation being well known and practised in the production of crystalline salts.

Additions to the Solution. The foregoing solution gives with proper current control tolerably satisfactory deposits, but not altogether of the type required for commercial work and under commercial conditions of production. Some addition agent is necessary. Many have been proposed. Several very satisfactory examples are here suggested. Dextrine to the extent of ½ oz. per gallon will be found to be very serviceable. The dextrine is easily dissolved in water or some of the solution and then well stirred into the main bath. Another good addition is Turkey red oil, obtainable from any chemical supply house. For a gallon of solution 1½ oz. of oil are shaken with about one pint of the solution. It readily mixes, and can then be stirred into the bath. With this addition it will be found that an increase of C.D. becomes permissible, possibly up to 50 per cent, with an appreciable reduction in the time required for deposition.

Cadmium deposits are improved by the addition of "brighteners." A good result is obtained with nickel to the extent of about 0·2 to 0·3 gm. of nickel per gallon of solution. This is equivalent to ⅛ oz. of single salt per gallon. Dissolve this in a little water and add sodium cyanide solution until the precipitate first formed just redissolves. This solution of nickel sodium cyanide is then added to the bath. These suggestions should first be tried out on samples of say 2 gallons before applying them to large baths.

Anodes. These should be of cadmium. It will be found that the anode solution is greater than might be anticipated from the current employed, that is to say, over 100 per cent. If the cathode efficiency is either 100 or less there will be more metal passing into the solution than deposited from it. The electrode efficiency ratio may even be as high as 1·25, leading to undue concentration of the metal in the solution. This tendency is corrected by the addition of iron anodes in small

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* *Trans. Electrochem. Soc.*, 80, 1941, 429.

proportion, which experience will soon determine, possibly one of iron to four of cadmium. Excessive anode solution is thus prevented.

As an anode material, cadmium balls have a large application. These are held in wire containers and as they diminish in size further additions are made, thus maintaining approximate uniformity of anode surface.

Thickness of Deposit. Ordinarily cadmium is deposited at a far greater rate than copper. The exact figure is : 1 ampere-hour is equivalent to 2·08 gm. of cadmium. Usually the current efficiency is high, nearly theoretical, and thus the thickness of cadmium deposited per hour by a current density of 10 amperes per sq. ft. is approximately 1 mil. Table LXIII embodies relevant data on cadmium deposits.

TABLE LXIII

THICKNESS OF CADMIUM DEPOSITS

Current efficiency = 90%

Current Density Amp./Sq. Ft.	Thickness in Mils in			
	15 Min.	30 Min.	45 Min.	60 Min.
5	·11	·23	·35	·46
10	·23	·46	·70	·93
15	·35	·7	1·05	1·4
20	·46	·93	1·4	1·87
25	·58	1·17	1·75	2·34
30	·70	1·40	2·1	2·81

Operating Conditions. The operation of the bath is simple, the solution being used either warm or cold where heating is not convenient. The preparation of the metal for plating is much the same as for zinc, iron and steel going through the same pickling processes prior to plating. The deposition may be carried out at 10 to 15 amperes per sq. ft., a fine dead white deposit then being obtained. The solution requires little attention and correction. The metal content is not likely to fall short of that originally put in. The free cyanide depreciates and additions can be made from time to time.

For thin deposits lower C.D.'s are employed, say 4 amp./sq. ft. At this rate, an hour's deposit is ·00036 inch thick.

Not infrequently deposits fail to exhibit the desirable clean whiteness. In such case the plated work can be passed through a weak acid solution. This may be sulphuric or acetic, generally not more than 1 to 2 per cent strength with subsequent rinsing.

Unfortunately the deposit does not permit of much handling. It readily marks. This can to some extent be remedied by passing the finished work through a solution of a soap compounded with whale oil, the preparation being made alkaline by adding ammonia. After rinsing, the very thin layer of soap which clings—and these and other materials do cling to work far more tenaciously than is usually imagined—serves the purpose of a thin lacquer. The alkali addition (ammonia) may be regarded as a safeguard against any acid left from the slightly acid dip.

Anti-Corrosion Properties of Cadmium. From theoretical considerations cadmium might be deemed an excellent preventive against corrosion. This, in general, is true. Much less certain, however, is the minimum thickness to secure reasonable freedom from attack. Corrosive conditions vary considerably. In general it has been suggested that 0·3 mil (equivalent to 18 minutes' plating at 10 amperes per sq. ft.) should suffice. While this might serve if only we could guarantee the continuity of the deposit, there appears to be little confidence in so doing. Safer policy will be to increase the thickness to 0·4 mil (24 minutes' plating under the same current conditions). This slightly heavier deposit is of far more importance than might be judged from the merely increased thickness. It serves the purpose of filling up many pores in the deposit which otherwise might just be left open. A niggardly policy with regard to the amount of metal deposited is unwise. A simple calculation will show that 0·4 mil represents ¼ oz. of metal per foot super. The cost of the metal is very small and the saving by a thinner deposit is so negligible as to be unwise to attempt. Some consideration of the cost of the metal plated might well be taken into account when figuring out the thickness to be deposited.

Recommendations for cadmium deposits similar to those for zinc (see page 331) are—

	Minimum Thickness on Significant Surface
(1) General Service . . .	·0005 in.
(2) Mild Service	·00015 in.

While zinc provides the cheapest protective coating for iron and steel, that afforded by cadmium is markedly better and can further be improved by treatment with a weak solution of potassium dichromate with the formation of stable basic chromate of the metal, which is not only more stable but also very adherent.

Nickel on Cadmium. The deposition of nickel on cadmium has attained some vogue, cadmium supplying the protection against corrosion and the nickel giving the desirable finish. Such composite deposits have their advantages and disadvantages. For real efficiency both deposits must be perfectly sound. There is probably more certainty of this in the case of the cadmium than in the nickel deposit. Cadmium protects by reason of its being attacked more readily than the iron and steel, and reasonably thick deposits are therefore of great value.

The addition of a further coating of nickel adds a complication. If the latter deposit is at all porous then the cadmium below will be subject to attack, forming a white corrosion product which will appear in spots. For absolute protection, therefore, the nickel deposit must be non-porous. It is thus claimed that while the cadmium-nickel deposit is superior to nickel alone it may fall far short of one of cadmium alone.

Heat Treatment of Cadmium Deposits. It has been shown that by raising the temperature of a cadmium deposit on iron and steel there is absorption of the deposit in the basis metal. This is seen by the fact that although the deposit may have been made on a smooth surface, this surface, after removal of the heat-treated deposit, is roughened. As a similar phenomenon is known to occur in hot galvanizing, and also that the iron-zinc alloy formed is mainly responsible for the resistance to corrosion, it is thought that a similar advantage accrues from the heat treatment of cadmium deposit and the process is often recommended.

At the same time any hydrogen absorbed in the deposit is removed and the coating becomes more amenable to bending.

Cadmium and Foodstuffs. The protective value of cadmium and its possible contact with foodstuffs raises the question of its safety under these circumstances. Cadmium cannot be regarded as a poison in the ordinary sense. No recorded case of definite cadmium poisoning is known. Small doses produce sickness, which, at least, is unpleasant and undesirable. Further, cadmium is not attacked by either neutral or alkaline conditions, but in no case should the metal be used under circumstances in which acids arising from the decomposition of foodstuffs are likely to come into contact with the metal. If cadmium salts are used medicinally as emetics, care can, and at least ought to be exercised to prevent the contamination of foods by these salts. Prevention of trouble is better than cure, and safety first is a good motto.

ANALYSIS OF THE SOLUTION

The analysis of the cadmium solution usually concerns the free cyanide and metal content, neither of these estimations being of quite the simple type. In addition, the amount of caustic soda and sodium carbonate will be useful in cases in which the solution is being kept under close observation for testing purposes.

Free Cyanide. A simple titration with deci-normal silver nitrate would seem to be the first and reasonable suggestion. If this is tried it will be found that the end point is not so sharp as with other free cyanide tests. In place of the usual turbidity, there appears a definite precipitate which is not easily seen until the solution has stood for a time. The end point may therefore be easily exceeded. The test, however, is practicable with care.

An alternative test is with a standard solution of nickel sulphate which can be used in exactly the same manner as silver nitrate. From the following data—

$$\begin{array}{ccccccc} NiSO_4.7H_2O & \equiv & Ni(CN)_2.2KCN & \equiv & 4KCN & \equiv & 2AgNO_3 \\ 281 & & & & 260 & & 340 \end{array}$$

it can be seen that as an N/10 solution of silver nitrate contains 17 gm. per litre, a solution of nickel sulphate of equivalent strength will contain 14·05 gm. per litre, each c.c. of which will represent 0·013 gm. KCN or 0·0098 gm. NaCN. With this solution the end point is sharper and the solution therefore has this use.

Estimation of Cadmium. Several methods are available for this purpose.

(1) Weighing the cadmium as sulphide. 10 c.c. of the solution are treated with a little strong sulphuric acid with the

addition of a few drops of nitric acid and the solution evaporated down to a small bulk. This ensures the destruction of the carbonates and cyanides and leaves the cadmium in the form of sulphate. The acid is over-neutralized with solid sodium carbonate and the turbidity taken up with acetic acid. The solution is diluted, warmed and gassed with H_2S, when the cadmium is thrown down as the sulphide CdS. This is filtered through a weighed paper and well washed with water to remove all soluble salts, the ppt. being finally dried to a constant weight giving the weight of cadmium sulphide. From the fact that $CdS \equiv CdO$, the weight of cadmium as the oxide in grammes per litre is easily calculated.

(2) Alternatively, the cadmium may be precipitated directly from the plating solution by saturating it with H_2S, as cadmium sulphide is insoluble in cyanide solutions, while many other sulphides are soluble. In filtering off the sulphide, there is always the possibility of the sulphide assuming the colloidal form and thus being washed through the filter. This method is therefore not to be recommended.

(3) An approximate method involving little manipulation is carried out as follows. 20 c.c. of the solution from the bath are transferred to a 50 c.c. measuring cylinder and 10 c.c. of a strong solution of sodium sulphide solution (Sp. Gr. = 5 degrees on the Beaume or 7·4 degrees on the Twaddell hydrometer added. This precipitates the sulphide. The solution is made up to the 50 c.c. mark with water and well shaken and allowed to stand for from 12 to 24 hours when the ppt. settles down as a compact mass. This method carried out with standard solutions of cadmium shows that every 2 c.c. of ppt. correspond to approximately 1 oz. of the metal per gallon of the solution.

Ferrocyanide Estimation. Cadmium may also be estimated with ease and accuracy by the method already explained for zinc (see page 331). In this case the reaction is as follows—

$$CdCl_2 + K_4Fe(CN)_6 = K_2Cd(CN)_6 + 2KCl$$

or 422 grm. of $K_4Fe(CN)_6.3H_2O$

$$= 112 \text{ grm. Cd}$$

From this relation it is possible to make up a ferrocyanide solution somewhat stronger than is required for 1 c.c. to be equivalent to 0·01 gm. Cd. This solution is standardized against either pure cadmium sulphate ($3CdSO_4.8H_2O$) which contains 43·82 per cent cadmium, or against the pure metal. The cadmium solution for titration should, however, only be slightly acid. Assume that the solution so standardized has been suitably diluted so that 1 c.c. = 0·01 gm. Cd.

Alternatively—

Since 112 gm. Cd. ≡ 422 gm. $K_4Fe(CN)_6 . 3H_2O$
10 gm. Cd. ≡ 37·67 ,, ,,

Hence by dissolving 37·67 gm. of pure potassium ferrocyanide and making up to 1000 c.c. the resulting solution will have a value of ·01 gm. Cd per c.c. This may be sufficiently accurate for many purposes.

Take 10 c.c. of the cadmium solution. Destroy the carbonate and cyanide compounds by treating with strong H_2SO_4 with the addition of a little strong HNO_3 to simultaneously oxidize the iron to the ferric condition. Cool, dilute, and add excess of ammonia to precipitate the iron as ferric hydroxide which is filtered off and washed, and may be dried and weighed if required. Iron in the cadmium solution is usually in the form of sodium ferrocyanide. The solution is slightly acidified, warmed, and titrated with the ferrocyanide solution using uranium acetate as a spot indicator on a tile. If 1 c.c. of the ferrocyanide solution = 0·01 gm. Cd. then c.c. of ferrocyanide solution for 10 c.c. of the cadmium solution represent the grammes of cadmium per litre, a figure which by calculation can be converted into the equivalent quantity of cadmium oxide, as this material is used in making up the solution.

Other methods are available but require more chemical work and are not as a rule justified for the usual routine determination of the metal.

Estimation of Caustic Soda and Sodium Carbonate. Caustic soda will be a common constituent of the solution when cadmium oxide is dissolved in sodium cyanide (see page 337).

Carbonates result from the exposure of the alkaline solution. Of these the caustic soda content is the more important. Take 5 c.c. of the solution. Dilute to about 100 c.c. with water. Add a saturated solution of barium nitrate to precipitate the carbonate as $BaCO_3$—

$$Na_2CO_3 + Ba(NO_3)_2 = BaCO_3 + 2NaNO_3$$

The ppt. is allowed to settle and filtered off. After washing, the ppt. may be treated in the same manner as described for the estimation of carbonates in the silver solution (see page 260). After cooling the filtrate, N/10 $AgNO_3$ is run in to produce a faint turbidity thus neutralizing free cyanide. A few drops of phenolphthalein solution are added, producing with the alkali a violet colour. Deci-normal hydrochloric acid is now run in until the violet colour disappears.

Now N/10 HCl = 0·0040 gm. NaOH per c.c., from which the NaOH content is readily calculated. Thus

$$1 \text{ c.c. N/10 HCl} = 0{\cdot}004 \text{ gm. NaOH}$$

Assume X c.c. N/10 HCl used. Then—

$$\frac{X \times 0{\cdot}004 \times 1{,}000}{5} = \text{gm. NaOH per litre}$$

or

$$\frac{X \times 0{\cdot}004 \times 1{,}000}{5 \times 6{\cdot}25} = \text{oz. per gal.}$$

That is c.c. N/10 HCl $\div$ 7·8 = oz. NaOH per gal.

(2) A more approximate method is that of direct titration with N/2 acid.

Take 10 c.c. of solution and add a few drops of phenolphthalein solution. Titrate with N/2 H_2SO_4 until the violet colour just disappears. Call this reading "A." Add a few drops of methyl orange solution and continue the titration until the solution first assumes a pale pink colour. Call the additional acid added "B."

Then—

"A" represents the NaOH + half the carbonate, and "B" represents half the carbonate.

$$\text{Hence} \quad \text{NaOH} = \frac{(A - B) \times {\cdot}02 \times 1000}{10} = \text{gm./litre}$$

$$\text{and} \quad Na_2CO_3 = \frac{2B \times {\cdot}0265 \times 1000}{10} = \text{gm./litre}$$

Note. Should reading "B" be nearly equal to "A," add the two readings together counting the whole as due to carbonates.

CHAPTER XIX

DEPOSITION OF CHROMIUM

INTRODUCTION—Composition of the solution—Purity of the chromic acid—Chemistry of the solution—Density of the solution—Properties of the solution—Maintenance of the solution—Removal of excess sulphate—Rectification of trivalent chromium—Removal of iron by drag-out—Throwing power—Test for throwing power—The cavity method—Vats—Temperature—Anodes—Current density—Current efficiency and weight of deposits—Application of the current—Types of deposit—Some points in chromium plating—Manipulating the work—Plating die castings—Deposition of sheet chromium—Black chromium—Stripping chromium deposits—Recovery of chromium compounds—Health hazards—Applications of chromium plating—Hard chrome deposition—Deposition of chromium from trivalent solutions—Analysis of the solution

Introduction. No phase of electrodeposition has created so great interest, nor found such immediate and wide application, as that of chromium plating. Twenty years ago, it is safe to say, there was no commercial deposition of this metal on any scale.

The work of Sargent, in America, opened the eyes of electroplaters with vision of the possibilities of the metal. To-day, after this brief interval, the deposited metal is everywhere in demand.

During this period there have been many anxious times for those who were courageous enough to undertake the pioneer work in this direction, while those who at first wished to wait for the process to attain some state of stabilization, soon found it necessary to be up and doing, and to make some contribution to the progress, even though experiencing repeated failures, in order to attain the success which had been foreshadowed for the process.

To-day the chromium solution is to be found in almost every workshop, and the large current demanded for the operation has opened up a new order of things in electroplating, by far the most important in recent years.

Composition of Solution. Chromium plating solutions, while containing the minimum of added constituents, are nevertheless of varying compositions and concentrations. That recommended by Sargent and serving many purposes was as follows—

Chromic acid (CrO_3) . . .	40 oz.	250 gm.
Chromic sulphate ($Cr_2(SO_4)_3$) .	½ oz.	3 ,,
Water	1 Imp. gal.	1 litre

The chromic sulphate was originally recommended to supply what is called *trivalent* chromium. The substance, however, is of uncertain composition unless very carefully prepared, and is, therefore, frequently substituted by sulphuric acid as follows—

Chromic acid	40 oz.	250 gm.
Sulphuric acid	0·4 oz.	2·5 ,,
Water	1 Imp. gal.	1 litre

Sulphuric acid is a well-known chemical which can be easily purchased in a pure form, and is therefore more reliable. The proportion of chromic acid to sulphuric acid is all-important. When the ratio begins to vary the range of conditions for successful plating is decreased. We may not know exactly the reason, but the fact is attested by wide experience. The proportion of these two constituents is an essential in the specification of the solution.

While this solution is suggested as a good starting solution it may be said that many operators prefer a more concentrated solution, increasing the chromic acid content up to 50 and even 60 oz. per gallon, and the sulphuric acid proportionately. Others contend that no great advantage is to be gained by the additional cost involved in the stronger solution, with its correspondingly high "drag out" losses. Before embarking upon a stronger solution the plater is recommended to make preliminary experiments with a small bulk of solution. The solution recommended above can easily be strengthened if this course has, by experience, been found to be desirable.

Chromium plating solutions have undergone little if any change of composition during the past few years. Numerous solutions of the type shown above have given eminently satisfactory service over long periods, leaving any advantage of the stronger solution as of a doubtful nature.

Purity of Chromic Acid. The chromic acid should be pure. The commercial product prepared by the use of sulphuric acid may easily contain detrimental amounts of this acid. It may happen that the necessary additions of chromic acid to make good the loss of chromium may increase the proportion of sulphuric acid beyond that which is most efficient. The quality of the chromic acid must, therefore, be watched. Excellent qualities of the compound can, and must, be obtained.

Not many years ago commercial samples of chromic acid frequently contained as much as 1 per cent of sulphuric acid. Such chromic acid, if sufficiently pure from other points of view, would require no addition of sulphuric acid.

More recently, however, there has been a definite trend towards specifications for chemicals used in electro-plating. For chromic acid there is a demand for a material which contains not less than 99·5 per cent of chromium trioxide and not more than 0·20 per cent of sulphates calculated as H_2SO_4 together with limitations of other possible impurities, these in each case being determined by methods which must be specified.

Chemistry of the Solution. As regards the original substances from which the solution is produced, no solution could be more simple, containing only two constituents, chromic and sulphuric acids. The solution, however, well illustrates the general principle that while simple in original constituents, it may, and inevitably does, undergo changes of composition within a short period of operation.

The two original constituents are well known. They need little or no further comment. Originally the chromium in the chromic acid is in what the chemist calls the *hexavalent* form. Soon, some of this is reduced at the cathode to the trivalent form either as chromium sulphate or chromium dichromate $Cr_2(Cr_2O_7)_3$. The former compound is green in colour, and if present in any large quantity would produce a brown colour in the solution. Chromium dichromate, or chromium chromate as it is commonly called, is soluble and brown in colour, and is mainly responsible for the brown colour acquired by the solution after use. Either or both of these compounds are required in small amounts in the solution. Neither of them is exactly stable under the conditions of operation of the solution. They are primarily formed by the reduction of the chromic acid at the cathode, this action always accompanying the deposition of the metal and even going on without it, while at the anode these two compounds are reoxidized to chromic acid. Anode and cathode reactions are therefore of an opposite character, but in this case they are not necessarily equal. It may later be possible to define and maintain the required conditions for exactly balancing these opposite reactions. At present, however, there is a tendency to get too much of the trivalent chromium in the solution and therefore, also, the need to re-convert it to chromic acid by cutting out the cathodic reduction and allowing the anodic oxidation to proceed. This can be effected by the use of an inert cathode in a porous pot and passing the current.

In addition, the solution takes up iron from several sources. This iron exists in the form of ferric dichromate $Fe_2(Cr_2O_7)_3$. Small quantities are no disadvantage. When the iron is in the solution there is no easy method of removing it. In both of these dichromates there is a considerable proportion of combined chromic acid which is not available for conducting purposes and is therefore out of action.

The following analysis of a working bath illustrates this important point—

Total CrO_3	414	gm. per litre
Cr_2O_3	5·9	,, ,, ,,
Fe_2O_3	31·9	,, ,, ,,
H_2SO_4	3·14	,, ,, ,,
Free CrO_3 (by calculation)	271	,, ,, ,,

The free CrO_3 is deduced in the following manner—

	Cr_2O_3 combined with	$6CrO_3$	
	153 ,, ,,	$6 \times 100{\cdot}5$	
∴	5·9 grm ,, ,,	$\frac{5{\cdot}9}{153} \times 603$	= 23 gm.
	Fe_2O_3 ,, ,,	$6CrO_3$	
	160 ,, ,,	603	
	31·9 grm.	$\frac{31{\cdot}9}{160} \times 603$	= 120 ..
		Total combined CrO_3	= 143 gm

∴ Free $CrO_3 = 414 - 143 = 271$ gm.

Density of the Solution. The specific gravity of a wide range of solutions of pure chromic acid is given in Table No. LXIV.

The figures deduced from this table by the observed density of the plating solution can, however, only be regarded as approximate, and generally serve to indicate the total amount of solids in the solution. In a new solution this will be almost entirely chromic acid. After working, however, considerable quantities of iron and some amount of trivalent chromium are bound to occur. Analysis is important to indicate their amounts. They first influence the density, but more important still, their combination with chromic acid removes considerable quantities of the acid from the free and conducting form to the combined and practically non-conducting form. Examples have been noted in which poor operation of the bath was found by analysis to be due to undue amounts of iron and trivalent chromium with which was combined practically the whole of the chromic acid present in the bath. Consequently, the free chromic acid is an important factor which requires periodical determination.

TABLE LXIV

STRENGTH OF CHROMIC ACID SOLUTIONS

Hydrometer Reading		Sp. Gr.	CrO_3	
Beaumè	Twaddel		Gm. per litre	Oz. per Imp. gal.
10	14	1·07	100	16
11	16	1·08	114	18·2
14	20	1·10	143	22·9
16	24	1·12	171	27·4
18	28	1·14	200	32
20	32	1·16	229	36·6
21	34	1·17	243	38·9
22	36	1·18	257	41·1
23	38	1·19	272	43·4
24	40	1·20	288	46·1
25	42	1·21	301	48
26	44	1·22	316	50·6
27	46	1·23	330	52·8
28	48	1·24	345	55·2
29	50	1·25	360	57·9
30	52	1·26	375	60
31	55	1·275	400	64
34	62	1·31	450	72
36·5	68	1·34	500	80
39	74	1·37	550	88
41	80	1·40	600	96

In a case of a works solution analysis gave—

Total CrO_3 . . . . . . 262 gm. per litre
„ H_2SO_4 . . . . . 4·64 „ „ „
Sp. Gr. = 1·184.

Corresponding content of CrO_3 from Table = 263 gm. per litre.

Here there is good agreement. The small amount of H_2SO_4 present cannot seriously affect the density of the solution. The solution was comparatively new and contained only 8·7 grm. of mixed Cr_2O_3 and Fe_2O_3 per litre, combined with approximately 35 grm. CrO_3.

In another case, however, the density of the bath gave, not by the hydrometer, but by direct weighing, which is more accurate, the figure of 1·308.

From Table LXIV the total content of CrO_3 (omitting the sulphuric acid present) would be of the order of 450 grm. per litre.

Analysis showed the following composition—

Total CrO_3	335 gm. per litre
Cr_2O_3	25 ,, ,, ,,
Fe_2O_3	32 ,, ,, ,,
H_2SO_4	5 ,, ,, ,,

From which—

CrO_3 combined with Fe_2O_3	= 121 gm. per litre
CrO_3 ,, ,, Cr_2O_3	= 99 ,, ,, ,,
Total combined CrO_3	220 ,, ,, ,,
∴ Free CrO_3	115 ,, ,, ,,

Specific gravity methods are here of little value. They apply only in cases of simple salt solutions with very few exceptions. The existence of complex compounds effects unexpected variations in specific gravity, and the density of a used chromium solution has therefore little or no value as an expression of the properties of the solution.

Properties of the Solution. The application of the bent strip test readily shows the effect of a number of constituents, and varying proportions of even essential constituents. For this test, small volumes can easily be made up and "doctored" with various reagents to study possible effects.

A pure chromic acid solution will be found to yield little or no metal on the cathode at even a current density of 150 amperes per sq. ft. The addition of sulphuric acid to the extent suggested in the usual formula at once rectifies this defect. A further addition of a like amount of acid at once produces a marked reduction of throwing power. The proportion between the chromic acid and the sulphuric acid is of vital importance. Chromic acid (CrO_3) and sulphuric acid (H_2SO_4)

are compared thus: The molecular (molar) weight of chromic acid is 100·5, while the comparative weight of SO_4 is 96, and its equivalent weight is 48. The usual comparison in the case of the Sargent solution is—

$$\frac{CrO_3}{SO_4} = \frac{250 \div 100{\cdot}5}{2{\cdot}5 \div 48} = \frac{50}{1} \text{ approx.}$$

This is commonly called the *sulphate ratio.* Perhaps a more easily understandable ratio for the practical plater is that of—

$$\frac{CrO_3}{H_2SO_4} = \frac{250}{2{\cdot}5} = \frac{100}{1}$$

This sulphate ratio is of importance. Too often there is the tendency for it to become too low, due in part to the use of insufficiently pure chromic acid. Another source of added sulphate is that due to imperfect rinsing of the nickel plated work. This is seen in the fact that small amounts of nickel are often found in chromium solutions. The point calls for the most thorough rinsing after nickelling.

Altering the sulphuric acid content one way or the other, producing a difference in either of these ratios, makes a profound difference in the behaviour of the bath, for there is a limited range within which this ratio may be allowed to vary. The wider the range the better, for it allows of greater variation of composition without serious effect on the working of the bath. The throwing power of a stronger solution is definitely poorer than with one more dilute, and as this property is of the greatest importance to the electro-plater the solution containing 250 gm. per litre finds extensive application, following the recommendation of the Washington Bureau of Standards.

Trivalent chromium and iron compounds also vary the amount of chromium deposited. Their approximate amounts in the solution should be known. Trivalent chromium is usually in the form of chromium dichromate. Its presence in any quantity is seen by the brown colour of the solution. A good red colour is indicative of its absence to any extent. The substance dissociates but slightly, producing trivalent chromium ions which, though essential, are not required to any large extent. By bad manipulation the solution may acquire large amounts of this material, but it may be reconverted to chromic acid by anodic oxidation, as has already been indicated.

Iron is a frequent constituent of the bath. To a limited extent its presence is not harmful. In fact, even up to the extent of 6 gm. per litre, it is said to increase considerably the range of the sulphate ratio, and this, in itself, must, therefore, be regarded as an advantage. An excess over this amount, however, diminishes the range of the sulphate ratio. This range is also slightly increased by the presence of trivalent chromium, but not sufficiently to warrant a large proportion of this constituent in the bath.

The possibility of increasing the throwing power of the solution by additions to its composition appears to be extremely doubtful, and this difficulty is, therefore, usually surmounted by the application of a high current density.

Solutions having a low chromic acid content, say down to 150 gm. per litre (1½ lb. per gallon), have a high resistance, and a narrow range within which the bright deposit can be obtained.

Low throwing power can be to some extent compensated for by the use of subsidiary anodes. It is considered that tests on throwing power obtained with the bent strip give information which is quite comparable with that obtained under the strictest conditions of scientific tests.

Maintenance of Solution. A constant check on the composition of the solution must be kept. This is necessitated by the insoluble anodes used, and also the small variation of the proportion of chromic to sulphuric acids allowable. As far as analysis is concerned this is outside the simple type of test which can be undertaken in the workshop. It demands the skilled work of the chemist, and necessitates the determination of the free chromic acid, the combined chromic acid (which is not available for conducting purposes), the trivalent chromium, the iron, and the sulphuric acid.

Of these estimations that of the free chromic acid is the easiest and possibly the most important, as this material is almost solely responsible for the conductance of the solution. With the guidance of Table LXIV of densities of chromic acid solutions some idea of the requisite amount of chromic acid to be added from time to time will soon be gathered. The periodical chemical testing and the electrical conductance determination will be advisable.

Removal of Excess Sulphate. Occasional analysis of the solution may show an increase in the sulphuric acid content. This can be corrected by the addition, with stirring, of freshly precipitated lead chromate, when—

Lead chromate+sulphuric acid=lead sulphate+chromic acid

$$PbCrO_4 + H_2SO_4 = PbSO_4 + H_2CrO_4$$

The lead sulphate is insoluble and separates out. The operation, however, should only be conducted by one with some chemical knowledge of the quantities necessary.

An alternative method involves the use of barium hydrate. As a commercial salt this has the formula $Ba(OH)_2.8H_2O$, this being equivalent to H_2SO_4. From a review of these equivalent quantities it can readily be calculated that 3·2 oz. of the barium compound will be required for the removal of 1 oz. of sulphuric acid. From one and a half to twice this quantity must, however, be used, as there is also some precipitation of barium chromate. The loss of the chromic acid is not important, and can readily be made good. In application it is a simple plan to remove the whole of the acid from a portion of the chromic acid bath rather than attempt to remove a portion of the sulphuric acid from the whole of the bath. Thus if the solution contains 5 gm. H_2SO_4 and this is required to be reduced to 3 gm. per litre, the elimination of the acid from two-fifths of the solution will serve the required end.

Rectification of Trivalent Chromium. The reconversion of trivalent to hexavalent chromium is a process which naturally takes place at the anode and may be used for the reduction of trivalent chromium by enclosing a cathode in a porous pot and putting through the bath a considerable number of ampere-hours.

In a test on these lines, the volume of solution treated was 16 litres. A current of 100 ampere-hours was passed for one hour and continued for a second hour. Samples of the solution were tested at the beginning of the test and after each hour's running.

The results (grammes per litre) were as follows—

	initial	after 100 amp. hrs.	after 200 amp. hrs.
Fe_2O_3	34·4	36·8	35
Cr_2O_3	15·5	13·9	11·5

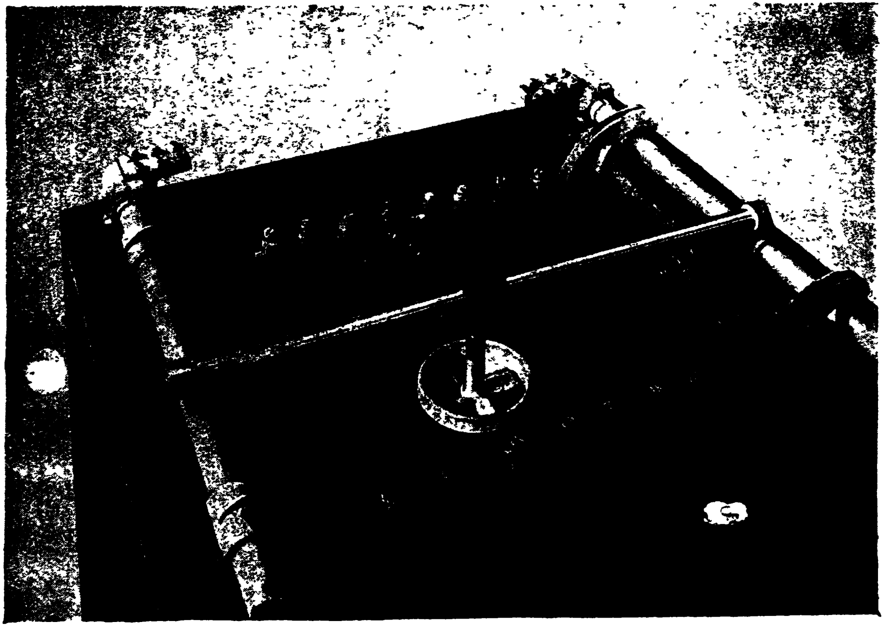

FIG. 86. "REDOX" DECHROMATOR

While, therefore, the iron content gave reasonably constant figures, the Cr_2O_3 was reduced in quantity according to expectation. Further the current efficiency of the transformation is calculated as follows—

$$Cr_2O_3 + 3O = 2CrO_3$$

The chemical equivalent of

$$Cr_2O_3 \text{ is } 153 \div 6 = 25{\cdot}5$$

and the E.C.E. = 0·0000104 × 25·5. One ampere-hour should therefore oxidize $0{\cdot}0000104 \times 25{\cdot}5 \times 3{,}600 = 0{\cdot}955$ gm. Cr_2O_3.

Over the period covered by 200 ampere-hour the production of Cr_2O_3 amounted to

$$16 \times (15{\cdot}5 - 11{\cdot}5) = 64 \text{ gm.}$$

from which the efficiency of the reduction is—

$$\frac{64 \times 100}{0{\cdot}955 \times 200} = 33{\cdot}5 \text{ per cent.}$$

This rectification is effected in the "Redox" Dechromator (Figs. 86 and 87) which comprises four iron cathodes suitably disposed in a porous cell, which is nearly filled with the solution and hung on to the cathode bar by means of an automatic tightening hook. This can be put into operation either when the bath is working or not in use, the usual type of cell being capable of taking a current of 200 amperes.

Fig. 87. "Redox" Dechromator

The presence of iron in the chromium solution constitutes a problem for which there is no immediate answer. In small amounts it cannot be regarded as harmful, rather the reverse, but the same avenues for its introduction into the solution will, by continuous operation, sooner or later give rise to considerable quantities. The presence of iron leads to the production of deposits which are not capable of satisfactory finishing. Reckoned as a percentage of the chromic acid content, when the iron is of the order of 10 per cent, it constitutes a real trouble and no method of removal can be satisfactorily applied to large volumes of solution. These therefore may have to be scrapped. The only remedy therefore is the complete exclusion of contact iron with the solution and also that the work treated should be instantaneously struck so that exposed iron may be as little acted upon as possible. Even when nickel-plated, much iron and steel work of a tubular character must of necessity expose some of the base metal.

Removal of Iron by Drag-out. Considerable quantities of iron are, however, removed by drag-out, but this involves a corresponding loss of chromic acid unless a wash water is used for make up purposes. The following example of a large bath in which the chromic acid content was kept up to about 400 gm. per litre may be quoted. The solution was originally contained in an unlined steel tank. During the course of 14 months the iron content expressed as grammes Fe_2O_3 per litre increased by fairly uniform increments from 3·0 to 23·0. This latter figure represents a large amount of combined chromic acid apart from that already combined with trivalent chromium.

The tank was then lined with lead, and glass plates installed. In the nine months following, the iron content fell uniformly from 23·0 to 5·7 gm. Fe_2O_3 per litre, the reduction being entirely due to drag-out. When it is remembered that this same degree of drag-out was taking place even during the period when with the bare steel tank the iron content was building up, some idea of the more rapid growth of iron content can be obtained. On the same basis there was during the first fourteen months a reduction by drag-out of

$$\frac{(23 - 5{\cdot}7) \times 14}{9} = 27 \text{ gm. } Fe_2O_3 \text{ per litre.}$$

Without this concomitant reduction the total increase in iron content would have been $23 - 3 + 27 = 47$, giving a total iron content of 50 gm. per litre.

Throwing Power. This is an all-important point in connection with chromium plating. The ordinary types of solution do not throw well. With a low C.D. on irregular work the recesses may receive no appreciable deposit. The first requirement is an increase in C.D., and in computing this it must be remembered that some parts of the work not receiving a deposit may nevertheless be receiving current, thus lowering the C.D. on the more important parts requiring plating. While it is not intended to refer to the throwing power of the solution quantitatively, it may at least be said that modern developments indicate the possibility of markedly increasing it. A number of factors militate against good throwing power. Some choice must be exercised in the metal to be plated. The nature of the cathode is critical. Copper, for example, is more easily chromium plated than iron and steel, and nickel less easily than copper. Iron and steel are difficult to chromium plate, and the desirability of coating these metals with an intermediate layer of comparatively non-corrosive metal leads to the selection of nickel rather than copper.

Test for Throwing Power. As has already been indicated, the method of the chemical analysis of the chromium solution is not one that can be completed in a short time. The estimation of the chromic acid is comparatively simple and quick. That of the sulphate content is, however, more difficult and tedious. Some rapid method of testing the solution is, therefore, desirable.

The *bent cathode* test, as it is called, gives some very useful information regarding the efficiency of the solution. This is a cathode of copper strip 1 in. wide and sufficiently long to allow 2½ in. to be immersed in the solution. The end inch of this cathode is bent at right angles so that the end projects towards the anode. Under ordinary circumstances, it is a more difficult proposition to deposit chromium into the recessed angle than on the projecting or flat portion. The throwing power of the solution is indicated by the extent to which the deposit, under standard conditions of temperature and current, is made towards this angle. Poor throwing power will be evidenced by inability to obtain a deposit easily in this remote portion of the cathode, while, conversely, with good throwing power it will be a simple matter to obtain a deposit in the angle of the bent strip.

The bent cathode test has been described and applied by Pinner and Baker* in the study of the control of the chromic sulphuric acid ratio of the bath. The test as applied, gives an approximate but rapid idea of this value and is capable, too, of interpretation in the study of the effects of the presence of

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* *Trans. Amer. Electrochem. Soc.*, lv, 315 (1929).

other constituents such as iron and trivalent chromium in varying the conditions for successful deposition.

An apparatus embodying this principle is shown in Fig. 88, in which will be seen the bent cathode test piece attached to

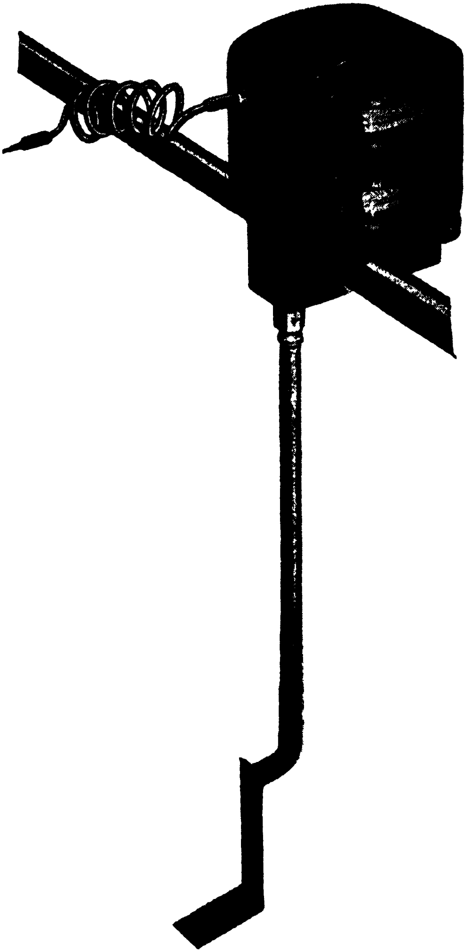

FIG. 88. BENT CATHODE TEST

an ebonite-covered support so that its current passes through an ammeter. A sensitive voltmeter with cable for ready attachment to the anode bar gives the bath voltage. A perfect deposit in the recessed portion is indicative of a correct proportion of the essential constituents. Lack of chromium in the angle bend indicates insufficient sulphuric acid in a new solution and/or excess of trivalent chromium in an old solution, while the appearance of a brown film on the edges or in the recessed position represents an excess of sulphuric acid which is, in small quantity, remedied by the addition of more chromic acid or, in larger quantity, by removal with barium hydroxide.

Cavity Method. This method is applicable for rough estimates of the throwing power of chromium plating solutions. A thick copper plate is drilled to carry ten circular depressions 1 cm. in diameter with depths of from 1 to 10 mm. These are numbered according to the depth in millimetres. This plate is made the cathode in the solution and the throwing power expressed as the number of the deepest depression into which chromium has penetrated. This appears to be a satisfactory method of ascertaining whether the solution is up to its required standard.

Vats. For small scale experimental work, vats of glass or stoneware will be found to be clean and useful. On the commercial scale the metallic tank will be required for its reduced cost and greater strength. Mild steel provides the best material.

Mild steel plates are welded together. They should be about ¼ in. thick. Riveting and bolting are quite unsatisfactory. If there are any connections to be made, such, for example, as the introduction of a pipe conveying either hot water or steam for heating purposes, the connections should also be welded. The solution has subsequently to be heated. The vat, therefore, requires to be mounted on either a steel frame or a minimum of brickwork. To maintain the temperature some type of covering should be supplied. This may take the form of a simple brickwork chamber built round the tank, or even an external asbestos lining. Neither will present any difficulty to the plant constructor. If the tank is to be heated, this may be done by the application of gas jets not directly impinging on the bottom of the tank, but on to plates leaving a space of about 1 in. between the plate and the bottom. This is to ensure that there is no local heating of the bottom of the tank as this, too, often leads to the attack of the chromic acid with thinning or even perforation of the plate.

These steel tanks are now, in many cases, lined with glass, this being simply effected by hanging on the sides plates of glass with steel clips, the plates covering most of the area of the sides. They need not, however, pass right to the bottom of the tank. Their purpose is to expose less steel area to the attack of the solution and, in addition, to prevent short circuiting of the current from the anodes to parts of the work which are adjacent to the sides of the tank. Steel is slightly attacked by warm chromic acid. The slight loss of metal from the tank may not matter so much so long as the attack is not local, although the accumulation of iron in the solution is to be avoided if possible. The greater trouble is the possibility of short circuiting, and this definitely leads to the anodic attack on the sides of the tank at points at which the short-circuited current leaves the tank on its way to the work.

Lead linings are sometimes used, but in this case the lead should at least be of chemical quality and as thick as the 6 lb. type. Even then some protection against corrosion from stray currents should be guarded against by the addition of glass plates behind the anodes where the current is most likely to short circuit on to the lining.

Practice now employs a water-jacketed tank. The advantages of this system are: (1) Uniform heating and therefore greater control over temperature, (2) elimination of risk of damage to tank which usually arises from direct contact with a flame, (3) the use of an uncovered steam coil in the water replacing a lead-covered coil in the chrome solution with the absence of any chance of corrosion of the hot steam coil.

Mounted on the steel tank, a substantial hardwood frame-provides a base upon which to mount the insulators carrying the anode and cathode bars. With the very heavy currents required for chromium plating these connections must be of a very substantial character; otherwise loss of power will occur with over-heating of the connections. Good contacts between the anodes and bars must be assured, the suspensions being by flat strips rather than by even thick wires of circular sections which only make very small contacts with the cathode bars. Hooks should be riveted to the anodes. All these contacts should be regularly inspected, overhauled, and cleaned, as the unavoidable splashing of the chromic acid solution leads to the attack of all lead with the production of insulating lead chromate. Too particular attention cannot be given to this matter in view of the heavy currents involved in the usual chromium plating process. Similar remarks apply also to the cathode connections.

Temperature. The temperature of operation of the solution is important. Cold solutions give dull and hard deposits, requiring excessive labour in finishing. These may, however, be required for special purposes not within the province of the work of the electro-plater. Warm solutions give much brighter and softer deposits sometimes requiring very little finishing after deposition. There are, therefore, limits of temperature between which the solution must be kept to produce the required deposit. With a rise in temperature there is a falling off in the amount of metal deposited per ampere hour.

From the plater's point of view it may be said that a temperature of 40° to 45° C. (104° to 113° F.) will be found to give good results. The watchful plater may find some variation from this range desirable for his particular purpose, especially with stronger solutions. Research is to be encouraged and its results applied to the production of more specialized and more satisfactory work.

Again, if 40° C. is recognized as a suitable temperature and with it current densities of about 100 amperes per sq. ft. can be used, an increase of temperature of 10° C. will almost if not entirely prevent the deposition of the metal at this C.D., and as high as 200 amperes per sq. ft. may have to be used.

When a solution is used at a temperature such as that recommended for chromium deposition, there is bound to be some evaporation. This can be readily made good. Again, the use of a solution as heavy as that for chromium is necessarily attended by heavy drag-out losses, and it is therefore good practice to keep a small volume of rinsing water for the first rinse, which can be used from time to time for make-up water.

Anodes. The decision as to the best type of anode has not been either a simple or a quick one. Anything in the nature of sheet chromium is out of the question. Metallic chromium is not available in this form, nor is it likely to be. Its properties preclude this. Even in the lump form, in which it may be procured, there are two serious objections to it. First, there is the cost. Metallic chromium is obtained with difficulty from chromic oxide. As an anode the chromium is at once converted to chromic acid. It would, therefore, seem reasonable to supply the deposited metal by the addition of easily dealt with chromic acid, thus avoiding, for one thing, the high cost of extracting the chromium. Secondly, chromium as an anode is highly efficient. It dissolves quantitatively. Assuming, therefore, a current efficiency of 12·5 per cent at the cathode, eight parts of the metal by weight would be dissolved at the anode for one part deposited at the cathode. The solution would soon become saturated and unworkable.

Lead anodes were therefore tried. These proved tolerably successful, except that they were prone to collect an insoluble and insulating film of lead chromate on the surface, this offering a high resistance, necessitating frequent cleaning. Otherwise they would have proved acceptable. The difficulty was then got over by taking out the anodes when the solution was not in use. This, again, was not ideal. The anode contacts must be substantial, and, therefore, once made, cannot readily be interfered with.

Finally, the difficulty has been got over by the use of chemically pure lead which has first been peroxidized by making it the anode in a solution of sulphuric acid. A lead cathode may be used. In a short time the lead anode is covered with a uniform brown and conducting layer of lead dioxide (PbO_2) which prevents attack by the chromic acid, so that the anodes need not be removed from the solution except only occasionally.

Steel anodes have also been tried. They suffer the disadvantage of being attacked by the solution, the iron becoming soluble in the form of ferric dichromate. This locks up chromic acid in a combined form which is then not available for conducting purposes, and, moreover, may introduce undesirably large amounts of iron into the solution.

With regard to the size of the anodes, the old suggestion of having as large anodes as possible again does not hold here. Large anode surface is productive of edge burning, while a more uniform distribution of current on the cathode results from a smaller anode surface. In addition, the smaller anode has the effect of encouraging deposition in the centre of the work, which is particularly desirable with large flat surfaces.

Several other suggestions for anode materials have also been made. Stainless steel is one. With this it might be arranged to dissolve chromium as fast as it is deposited, but there would also be the undesirable solution of the iron. Lead containing about 8 per cent of antimony makes a good anode, and is in successful commercial use. This might be anticipated from the use of this alloy in the lead accumulator. Whatever lead chromate forms on its surface is readily removed by brushing, the layer of antimony oxide preventing its firm adhesion.

Experience has, however, brought to light a number of mysterious and unaccountable breakdowns in the use of antimonial lead both for the purposes of anodes and linings for tanks. Severe local pitting occurred suggesting irregularity of composition of the alloy, though no trace of this could be proved by analysis.

Experience here goes to confirm the general resistance of this material to corrosion, though occasional lapses have been recorded. In addition it appears that precipitated lead chromate is much less adhesive to tellurium lead than to ordinary chemical lead.

Within recent years an alloy of lead with 0·2 per cent of tellurium has come into prominence owing to its good mechanical properties and also resistance to chemical corrosion.

Its possibilities as a new anode material for chromium deposition are under investigation and there appear good prospects of this material meeting, very satisfactorily, the requirements of this very corrosive solution. From the limited experience so far available, it has been observed that the material quickly assumes a rich brown adherent coating of the di-oxide with very little evidence of the formation of lead chromate. The present results are promising.

In order to keep down the anode surface the use of metal strip is resorted to. Such anodes can be conveniently placed to produce the required distribution of the current, and may well have about two-thirds of the area of the cathode.

Current Density. Chromium deposition is unique in the very high current densities usually employed to obtain commercial deposits. Sargent at first recommended a C.D. of 92 amperes per sq. ft., and while good deposits may be obtained with this or an even lower figure on flat work, experience has determined that for more irregular work with which the plater will come into contact a higher C.D. will be found desirable. The more usual figure, therefore, is of the order of 100 to 200 amperes per sq. ft., dependent upon a number of conditions such as concentration of the solution and its temperature. For general work in the solution recommended, a C.D. of 100 to 150 amperes per sq. ft. will be found to suffice. From this simple starting figure the experienced plater will soon find if any variation is necessary. Depending on the nature of the work, temperature and inter-electrode distance, it may be stated that on an average this C.D. will be obtained with from 5 to 6 volts, and this figure, once determined for work, the surface of which can be approximately computed, can then be adhered to, and somewhat increased upon work of an irregular type to guarantee getting down into the more remote parts.

In this connection, reference may be made to the variation of conditions necessary with a stronger solution. Such a solution is more conductive. The required bright deposit is obtained with a lower current density, and this results from a lower P.D. In fact, in a solution containing as much as 500 gm. of chromic acid per litre it may be necessary to use a current density as low as 80 amperes per sq. ft., with a P.D. of 4 to 5 volts and a temperature of 35° to 40° C. (95° to 104° F.).

Current Efficiency and Weight of Deposits. Again, a further feature of the chromium solution is the surprisingly low current efficiency. With a cold solution it may go up to 30 to 40 per cent—not more—while the deposit is dull and hard. With warmer solutions the efficiency falls appreciably, until, at temperatures in common practical use, it is probably not more than 12 to 15 per cent, this again depending upon the nature of the cathode metal. At 15 per cent 1 ampere-hour deposits 0·05 gm. of chromium, but the low current efficiency is largely compensated for by the high current density, so that deposits of commercial thickness are obtained in reasonable times.

At the time of writing, no definite thicknesses of deposits have been adopted as recognized standards to withstand the usual service of wear and tear and atmospheric corrosive conditions. The matter has, however, been under the consideration of the United States Bureau of Standards, who have tentatively adopted the following figures for plumbing fittings, assuming a current efficiency of 12·5 per cent.

(*a*) FOR DIRECT PLATING ON BRASS. A thickness of 0·0002 in. (0·005 mm.) equivalent to 0·112 oz. per sq. ft. (0·340 grm. per sq. dm.). This would require about 80 ampere-hours per sq. ft., equal to 48 minutes plating at 100 amperes per sq. ft., or 24 minutes plating at 200 amperes per sq. ft.

(*b*) CHROMIUM PLATING ON NICKEL OR BRASS. The nickel deposit is to be 0·0002 in. (0·005 mm.) and the subsequent chromium deposit 0·00002 in. (0·0005 mm.). The following table shows the relevant data for the production of such deposits—

TABLE LXV

THICKNESS OF CHROMIUM DEPOSITS

Deposit	Thickness	Current Ah per sq. ft.	Weight oz. per sq. ft.	Obtained by
Nickel	0·0002 in.	5	0·143	5 A per sq. ft. for 1 hr. or 10 A per sq. ft. for ½ hr.
Chromium	0·00002 in.	8	0·011	100 A per sq. ft. for 5 min. or 200 A per sq ft. for 2½ min.

The nickel deposit allows for 20 per cent loss by buffing.

The chromium deposit allows for a current efficiency of 12½ per cent.

Other American* specifications for the thicknesses of chromium deposits and their undercoats are as follows—

	Copper and Nickel	Final Nickel	Chromium	Salt Spray
General Service .	·00075 in.	·0004 in.	·00002 in.	48 hours
Mild Service . .	·0004 in.	·0002 in.	·000012 in.	12 hours

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* Dr. Blum; the American Electroplaters' Society; and the American Society for Testing Materials.

Considerable importance attaches to the final coat of nickel, while copper as an undercoat should not be in contact with the steel but serves merely as a thickener of the nickel undercoat. In any case the chromium deposit can only act as a protection against tarnish and not against corrosion.

It must, however, again be pointed out that mere thickness is not the sole criterion of good plating.

Application of the Current. Chromium plating demands. as has already been seen, a very high current density, and the design of the whole plant, including the generator, must be of the most ample proportions.

In almost every case striking the work must be resorted to. Few metals withstand the corrosive action of chromic acid, the usual run of metals rapidly dissolving in it. They may not, therefore, be left standing in the solution, and the connections must be arranged so that current is applied as the work enters the bath. Machines are called upon to supply heavy currents, and must have plenty of reserve power to enable them to do so without undue shock. Machines of 1000 amperes are common, while much larger types are occasionally employed. The introduction of a large piece of work at once demands the consumption of a considerable bulk of energy.

Cathode connections, too, must be amply proportioned. Even half a square foot will require nearly 100 amperes, calling for substantial connections, slinging wires and contacts with the work. In the absence of the latter, considerable heat will be developed at the imperfect contact, with possible melting of the wire. If the slinging wire protects a small portion of the work from receiving the deposit the wire must be shifted during the operation.

Types of Deposit. Three well defined types of deposit are produced in chromium plating, differing more markedly than with most electro-deposited metals. These depend upon the sum of the conditions. Dealing first with current density, a low C.D. produces a bright matt deposit, sometimes referred to as *milky*. This deposit is extremely thin, and of no commercial value. Increasing the C.D. changes this deposit to one which is bright, hard, and lustrous, requiring little finishing after removal from the bath. With further increased current the deposit changes to a matt which, while dull, is capable of being polished, with some labour. With the same current density at varying temperatures it is possible to produce the dull, hard deposit in the cold solution, this changing, too, with elevation of temperature to the bright, lustrous deposit, and at still higher temperature to the thin, milky deposit. Combining these two factors, it will be seen that there is a range within which the required lustrous deposit can be obtained, and this again varies with the composition of the solution. It is advisable, therefore, to start with the solution recommended, and explore the conditions for obtaining the required deposit. This experience is of far greater value than a mere statement of the conditions for many types of solutions. A full appreciation of these principles will go a long way towards fixing the conditions for successful work. They will show that while a temperature of 50° C. (122° F.) is desirable when working at 200 amperes per sq. ft., about 45° C. (113° F.) will be more useful at 100 amperes per sq. ft.

Similar tests should now be made with the different metals which are likely to constitute the cathode material. There can be no better method of tackling the problems which must come up before the chromium plater than that of acquiring his knowledge from some systematic experience.

Some Points in Chromium Plating. It is recognized that it is difficult to deposit other metals on chromium. The reason is much the same as that for aluminium. There is, on the chromium surface, an infinitesimally thin film of oxide, difficult to remove by any method other than that of treatment with HCl. This oxide is not dissolved by other metals, though soluble in chromium. To plate chromium on to chromium is, therefore, an easier proposition than that of putting nickel directly on to old nickel.

The deposition of chromium was at first attended by a number of difficulties which experience has now surmounted.*

One of the early troubles with chromium plating on brass was a very pronounced flaking of the deposit. This was at first suggested to be due to what the metallurgist calls *dezincification*, the solution of the zinc from the brass. It has been shown, however, that many chromium deposits, other than those put on to brass, exhibit a like phenomenon. Hair-like lines appear in the deposit. These are more probably due

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* *J. Electrodepos. Tech. Soc.*, 1935, x, 167.

to the crystalline structure of the underlying metals. All metals are more or less crystalline. Cast metals have larger crystals than worked metals. The fine metal between these crystals is invariably more susceptible to attack than that of the crystals themselves. This is where the trouble originates, leading to the flaking of the deposit. Nickel-plating covers all the defects in the basis metal, but the nickel deposit must be of the right type. No ordinary nickel deposit will withstand the corrosive action of the chromic acid and the strong currents used in putting the chromium on. The fact that a nickel deposit can be satisfactorily buffed constitutes no guide as to its suitability for this purpose. These deposits must, in addition to being thick, show no sign of internal stress, and must have been produced under conditions under which the minimum amount of hydrogen is deposited. They must be of a softer type than those usually required to withstand ordinary wear and tear of service.

Another important feature of the process is that of racking the work. Substantial connections, often soldered, must be made, and those engaged in chromium plating on a large scale are bound to give attention to this matter if their work is to be turned out quickly and satisfactorily.

Manipulating the Work. As has been stated, the process calls for special methods of handling the work usually requiring plating. This is occasioned by (1) the high C.D. employed; (2) the poor throwing power; and (3) the large volume of gas generated.

The high C.D. demands special care in the size of suspension wires and their manner of contact. Wherever possible, these should be screwed or soldered. For lamp reflectors, rings and radiator shells, special racks or frames should be constructed, and arranged to give large contacts up to 75 or 80 per cent of the circumference of circular parts, to guarantee uniformity of deposition. If the article cannot be racked, it will be necessary to move the suspension wire to avoid the marks due to the protective effect of the suspension wires. These wires should be of sufficient thickness, to enable them to carry the currents without undue heating. If heating occurs there is obvious waste of energy, and the current is being unnecessarily reduced.

The poor throwing power will call for the extended use of subsidiary anodes opposite recessed parts, and many difficulties of plating will thus be overcome. In other cases shaped work can be best dealt with by the use of similarly shaped anodes, and the usual lead anode readily lends itself to this adaptation. Bent lead strips are very serviceable for this purpose. These can be introduced into the bath by auxiliary bars resting across the usual anode bars, but covered with insulating tape at points near possible contact with the cathode bars. For radiator shells the anodes can be thus conveniently made to follow the contour of the shell.

Again, holes in the work cause some trouble by reason of the gas deposited within them escaping, and thus curtailing deposition over a small area around them. It is convenient to fill up such holes with cork or wood bungs. For other purposes of insulation, materials like plasticine and a paste made from red lead and glycerine are useful, while the points of first contact of slinging wires with the work may be advantageously covered with insulating tape to prevent undue deposition at these points, with burning and loss of metal on other parts. Inside surfaces may be dealt with in much the same way as in silver-plating, by the use of auxiliary anodes either of shaped lead or even iron wire, due care being taken to prevent short circuiting at possible points of contact.

Where a small portion of the surface has failed to receive a deposit the usual process of "doctoring" may subsequently be resorted to. The "doctor" may be made of iron wire covered with asbestos cotton, and connected to the positive or anode rod. The chromium solution is comparatively rich in metal, and can therefore safely be used in this manner. In subsequent buffing, however, care must be taken to deal more gently with these parts, as the doctored deposits will be thin.

Plating Die Castings. Much work of this description is now required. There are several precautions which should be observed. Nickel-plating will precede the chromium deposition. In originally cleaning the articles, care should be taken that, if an electro cleaner is used, the alkali content should be kept low. Otherwise zinc will be dissolved and will be redeposited on the work. This leads to stripping of the nickel deposit, especially under the rigid test of the chromium-plating. Furthermore, the acidity of the nickel bath should be kept down to avoid the deposition of hydrogen, which produces stresses in the deposit, with the tendency to peeling.

Deposition of Sheet Chromium. It is possible that many new applications of chromium deposition have yet to be explored and exploited. The production of the deposited metal in the sheet form has already been investigated. Thus, Roberts* produced deposits on a rotating cylindrical brass cathode with a hemispherical end to a thickness of about one millimetre. Depositing conditions were those obtaining in normal practice and deposition continued for 168 hours. The efficiency of deposition was 13·4 per cent under the usual reckoning. Subsequently, the deposits were removed by slitting the deposit with a sharp, high-speed rotating carborundum wheel, and dissolving away the brass cylinder with nitric acid. The deposits were hard and brittle, and were softened by heating in hydrogen to a temperature of 1600° to 1700° C., afterwards removing the hydrogen absorbed by evacuation at 900° C.

Black Chromium. Another variation of chromium deposition is that of the production of a black deposit, after the style of the platinum black deposited upon many electrodes used in electro-chemical work. Ollard† describes the deposit as one which is "burnt." It was obtained from a solution of normal composition, from which, however, the sulphate content had been removed by the usual method of the addition of barium chromate. A high current density was necessary and was produced by a voltage of from 12 to 16 volts. For this purpose the solution is kept cold, and with so high a C.D. artificial cooling may be necessary. While the result was at first not particularly promising from the point of view of a black finish, there may be possibilities in other directions such, for example, as the grids of thermionic valves. Further, adhesion presented a problem, in addition to which, resistance to wear seemed not too promising.

Stripping Chromium Deposits. Again both electrolytic and dip methods are used.

Electrolytic.

Solution. An ordinary alkaline cleaner may be used for this

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* *J. Electrodepos. Tech. Soc.*, 1937, xii, p. 111.

† *J. Electrodepos. Tech. Soc.*, 1937, xii, 33.

purpose, provided that it is not too alkaline. The chromium deposit is made anode in the hot (180° to 200° F.) solution, when the deposit passes off into the solution as yellow sodium chromate.

Dipping is much more frequently resorted to. For this purpose hydrochloric acid composed of equal volumes of the strong acid and water will be found readily to remove the chromium deposit with little or no attack on the basis metal. This method is quick and convenient.

Recovery of Chromium Compounds. With a large plant there may be a considerable loss of chromium in waste liquors. Its recovery may prove a commercial proposition. In a recent example Hoover and Masselle* endeavoured to avoid a loss of 100 lb. of chromium per day by reduction of the chromic acid in the waste liquor with scrap iron. Alternatively sulphur dioxide could be used or even barium sulphide, after which the liquor, made alkaline, precipitates chromium hydroxide. The method is being tried out on from 40,000 to 100,000 gallons of liquor per day.

Health Hazards. Chromium deposition is unique in yet another way. The anodes are insoluble, and therefore all the current is there expended in producing and evolving gas, viz. oxygen. At the cathode the current efficiency is of the order of 12½ per cent, meaning that some seven-eighths of the cathode current also produces gas, hydrogen. Thus it may be said that fifteen-sixteenths of the current is engaged in producing these gases. When pure the gases are harmless. From the strong chromium-plating solution, however, they produce considerable quantities of spray, which, passing into the atmosphere, renders it quite unfit for inhalation. Some steps to protect the worker are not only necessary, but are enforced by the health authorities. No plant should be installed without being submitted to competent advice prior to inspection by the authorities.

The dangers attending the use of chromium compounds arise from the handling of the material, both in the solid and solution form, and also from the inhalation of the spray arising from the bath.

Both the skin and mucous membranes are severely affected. On the skin chromic acid gives rise to dermatitis, which usually

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* Amer. Chem. Soc., 1941.

takes the vesicular form. The hands are usually affected as being more exposed. Another form of attack is that of chrome holes, which arise at cracks or injuries to the skin. In its initial stage the attack is without pain, but the sores are long in healing.

By inhalation the nasal septum may be perforated following irritation. The perforation is permanent, though there is seldom appreciable loss of blood.

The whole problem has been carefully explored by the thorough examination of large numbers of workers engaged in the chromium industry, and a number of preventive measures are available.

In the first place it is desirable that chrome plating be kept apart from other parts of the works, and other workers not admitted to it unless necessary. (It is equally desirable that, from other points of view, the chromium-plating solution should be kept quite away from other plating solutions.)

Further, cleanliness should be carried out to the last degree, all spillage being cleaned up as soon as possible. Some protection can be gained by the use of several types of protective clothing, but rubber gloves and boots must be prevented from picking up small quantities of the solution, otherwise they are even worse than useless. We are past the day when goggles find application, as prevention is now carried out in most cases to a satisfactory degree. Protective ointments such as lanoline may be used by well rubbing into the skin prior to engaging on the work of the day.

Ventilation, however, constitutes the main source of protection.

This chromic acid spray is particularly irritating to the mucous membrane. Adequate ventilation, both of the vat and the room, is essential. Many schemes have been put into operation to maintain a sufficient purity of the atmosphere. In the early days it was thought sufficient to cover the tank by means of a hood provided with an exhaust fan. The hood, however, was a serious obstacle to handling work. Other suggestions included slotting the tubes which formed the electrode "bars" underneath, connecting these tubes to a fan and dispersing the fumes in this way, catching, as it were, the fumes immediately they rise from the anode and cathode liquids.

Yet another scheme provides for an exhaust system, which comprises slots in the sides of the tanks above the level of the liquid, and leading into channels which are ventilated by suction from a fan.

This equipment, illustrated in Fig. 89, comprises an exhaust duct running along each side of the plating tank and terminating in a solution recovery chamber situated at one end of the tank. This duct rests on the top of the angle iron framework of the tank, and presents a flat surface, giving the operator easy access to the work rods. The spray to be exhausted is drawn through a series of $\frac{1}{2}$ in. slots, and, passing through the solution recovery chamber, continues through a motor-driven fan to the air outlet. The collected spray is periodically removed from the solution recovery chamber and returned to the tank. The average air velocity at the duct mouth is of the order of 2000 ft. per minute. Low-speed

Fig. 89. Chromium Plating Tank with Exhaust Equipment

multi-blade fans are to be preferred on account of their comparative noiselessness, this easily compensating for their slightly increased power consumption.

Another difficulty attaching to the use of chromic acid is the development of sores where the acid comes into contact with the broken skin. It behoves the worker to exercise some care in the preservation of his hands, attending to any sores by means of a suitable dressing under a waterproof cover. In any case, the use of rubber gloves for this work is highly recommended.

On the smaller scale it has been found possible to eliminate the spray nuisance by covering the surface of the solution with a layer of paraffin oil about a quarter of an inch in depth. The spray is filtered out as the evolved gases pass through the oil, which should have a sufficiently high flash point to be free from danger of ignition by unavoidable sparking when making and breaking the current. Such oils are readily available. As far as we are aware, however, the method has not yet been applied on any scale.

The problem of medical supervision has engaged the attention of the Home Office authorities, and elaborate rules are now enforced. Action is taken to detect any troubles in their initial stages and then combat them, and the worker is prohibited from further work until the trouble has been to a large extent remedied. It has been suggested, however, that it is well for the worker not to stay away until the recovery is quite complete, as a lengthy absence from the work engenders susceptibility to a recurrence of the trouble.

Finally, methods have been developed for the estimation of the chromic acid content of the atmosphere, and definite limits set to ensure the maximum of security to those engaged in the industry.

Applications of Chromium Plating. No other deposited metal has, in the course of electro-metallurgical history found such an immediate and wide range of application as chromium.

Three properties of the deposit are mainly responsible for this—

1. Resistance to corrosion under most conditions, with the exception of the action of hydrochloric acid fumes. A wide field of use is thus at once opened.

2. Its high polish, adding the note of decorative effect.
3. Its extreme hardness, deposited chromium being one of the hardest metals yet produced.

All types of domestic metal work are thus submitted to the process, including mirror frames, and plumbing supplies. Automobile parts provide another wide application. Tarnishing does not occur. Some deposits of dirt may accrue due to splashing. These are readily removed by wiping with a soft duster. No abrasive is required, as with nickel, with which corrosion goes into the metal instead of residing on its highly polished surface. Taps, for example, when brightly finished, endure for an indefinite time, and show little signs of deterioration.

Service, in addition to appearance, is supplied by chromium deposits, and automobile parts thus treated include bumper bars, radiators and lamps. The chromium is readily recognized by its continuing bluish lustre in contrast with the quickly dulling and yellowish nickel.

Moulds used in the manufacture of rubber goods are, when chromium-plated, stable against the action of the chemicals used in the process of vulcanization. Steel moulds used in the mass production of bottles endure much longer without cleaning when previously chromium-plated, and the life of chromium-plated printing plates is increased manifold. As a mirror surface, chromium is stated to be not quite so good as silver, but very much more permanent.

These examples suffice to show the extraordinary range of applications at once served by successful chromium deposition. The metal has undoubtedly extended the lease of the industry of electro-deposition.

The throwing power of the chromium-plating solution, with the very low current efficiency, is necessarily very poor and quantitatively always has a negative value. Practically the only improvement which can be effected is that which relates to the disposition of the anodes. As far as possible, then, these should be parallel and far apart. Subsidiary anodes should be used for deeply-recessed parts, while the more prominent parts can be shielded from excessive current by interposing insulating shields. In addition, the work can be so wired as to bring the current more readily to the recessed parts, any resistance of the work being used to minimize the current passing to the conspicuous parts. By these or similar methods there will be some prospect of getting the same type of deposit all over the work.

There is, however, evidence that, ere long, the composition of the chromium solution will be modified to admit of cold working, with lower current densities and a much improved throwing power.

Hard Chrome Deposition. Of all the industrial applications of chromium deposition none can compare with that associated with engineering—a somewhat wide term. It is commonplace knowledge that the deposit is exceedingly hard, and therefore able to make a valuable contribution to the construction of parts which, in the course of use, undergo abrasion and yet are required to maintain their dimensions. The, at first decorative, claim of chromium deposition has more recently given place to that for engineering, and bids fair to hold the field long after the exigencies which gave it birth. The long-felt need for harder surfaces for all manner of tools including dies, punches, gauges, etc., is now supplied by this hardest of metals applied by electrodeposition.

The solution commonly used for this purpose contains from 250 to 300 gm. of chronic acid per litre, with 2½ to 3 per cent of sulphuric acid. Trivalent chromium needs control as, in the plating of some tools, it tends to increase sufficiently to an extent which decreases the efficiency of chromium deposition and also its rate. The solution temperature is of the order of 120° to 150° F. with a C.D. of 150 to 250 amps. per sq. ft. Numerous points come up for consideration in this class of work. One of these is the jigging of the tools, which calls for some ingenuity in order to achieve the maximum amount of work in a limited vat space, with the best exposure towards the anode surface of those portions to be plated. Thickness of the deposit is not always important, as it has been found that all the necessary hardness and wearing qualities can be produced with very thin deposits, which can be of use only in the case of screw gauges on which it is difficult to obtain any uniformity of deposition.

In some cases, the work is etched by anodic treatment in the chrome bath, with a quick reversal of the current for deposition. There is some building up of the iron content by this method, but experience goes to show that this increase in iron soon attains a maximum which is not detrimental to the deposition.

Current efficiency runs up to about 16 per cent. Thinner deposits of the order of 0·003 in. are subsequently lapped before going into service, while thicker coatings up to 0·012 in. are both ground and lapped. It is natural that differing methods will be applied to different classes of work and also to special requirements.

The effectiveness of the process is readily appreciated when it is claimed that the life of tools may be increased up to twenty-five times, and most commonly up to ten times or more. This more economical use of special tool steels and the speed with which tools may be restored for service, provide ample incentive for the use and further development of the application of chromium plating as an important adjunct to the toolmakers' art.

Continued use of a chromium solution in this, as in other examples, necessitates a watch on the sulphate content as well as, in some cases, the iron content. The removal of the latter impurity on a large scale is not at present a practical proposition, but in order to avoid the need for scrapping the solution, portions of it can be removed from time to time and, after the removal of the sulphate content, the solution can be passed on for use in the usual process of anodizing thereby minimizing waste.

Much more appears to be on hand in this important development of electro-plating as applied to so important an industry as engineering. Time and more convenient opportunities will, however, be required to make these developments more widely known.

Deposition of Chromium from Trivalent Chromium Solutions. This is a problem which has not been left unexplored.* There are some admitted disadvantages in the strong chromic acid solution which has attained such wide application. Many attempts have therefore been made to substitute solutions of chromic compounds in which the chromium is trivalent. It has to be admitted, however, that any success in this direction has been small, but at least one advantage would be that of the

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* Schlötter Proc. 1st I.E.C., *E.T.S.*, March, 1937.
Britton and Westcott: *J. Electrodepos. Tech. Soc.*, 1932, vii, 33; *ibid.*, 1933, viii, 5·1.

larger electro-chemical equivalent and thus, with the same current efficiency, double the rate of deposition of chromium from trivalent compound solutions.

ANALYSIS OF THE SOLUTION

The chromium solution has originally two chief constituents —chromic and sulphuric acids. After use, a number of new compounds are developed, these including those containing trivalent chromium and also iron, this being introduced either by the tank, anodes or work. Their influence has already been referred to. Generally, the relevant analysis will include determinations of chromic acid, sulphuric acid, trivalent chromium and iron, and from these the free chromic acid can be approximately calculated.

Total Chromic Acid. To bring it into line with the usual type of standard solution, the chromium solution has to be diluted about 25 times. Take 10 c.c. of the bath and dilute to 250 c.c. This constitutes a stock solution for all the analyses. For the chromic acid test two standard solutions are required. They are—

N/10 $FeSO_4.(NH_4)_2SO_4.6H_2O$ containing 39·2 gm. of the salt per litre.

N/10 $KMnO_4$ containing 3·16 gm. per litre.

The ferrous solution is an accurate standard. The permanganate is made up approximately and standardized by reference to the ferrous solution.

Standardization of $KMnO_4$. Take 10 c.c. of the ferrous solution into a conical flask, dilute, and add dilute H_2SO_4. Run in the $KMnO_4$ solution from the burette till, after shaking, there persists the faintest trace of the violet permanganate colour. The reaction is as follows—

$$2KMnO_4 + 10FeSO_4 + 9H_2SO_4 = 5Fe_2(SO_4)_3 + 2KHSO_4 + 2MnSO_4 + 8H_2O$$

The permanganate oxidizes the ferrous to a ferric salt. While the double sulphate is the most convenient for the purpose, the ammonium sulphate remains indifferent to the reaction.

Assume that 10 c.c.Fe solution require 9·5 c.c. $KMnO_4$. The $KMnO_4$ is obviously stronger than N/10 and requires dilution to the extent of 0·5 c.c. water to 9·5 c.c. $KMnO_4$. The two solutions then exactly balance.

Estimation of Total CrO_3. Take 10 c.c. of the stock solution. Add dilute H_2SO_4. Add N/10 ferrous solution 10 c.c. at a time until the original red colour has completely changed to green without any trace of brown in it. A portion of the ferrous compound has been oxidized by the chromic acid and the remainder is now estimated by $KMnO_4$ which is run in from the burette until there is a distinct change of colour from green to puce. The oxidation of ferrous by chromic acid takes the following course—

$$2CrO_3 + 6FeSO_4 + 6H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6H_2O$$

Hence $\underset{201}{2CrO_3} \equiv 6FeSO_4 \equiv \underset{6 \times 392}{6FeSO_4.(NH_4)_2SO_4.6H_2O}$

from which

1 c.c. standard ferrous solution

$$= \frac{201 \times 39{\cdot}2}{6 \times 392 \times 1{,}000} = 0{\cdot}00335 \text{ gm. } CrO_3$$

The following figures are taken from a worked example—

10 c.c. stock solution
30 c.c. standard ferrous solution
2 c.c. standard $KMnO_4$

therefore c.c. ferrous solution oxidized by the CrO_3

$$= 30 - 2 = 28$$

from which

Gm. CrO_3 per litre original chromium solution

$$= \frac{0{\cdot}00335 \times 28}{10} \times \frac{250}{10} \times \frac{1000}{1} = 235$$

This test is readily carried out.

Estimation of Trivalent Chromium and Iron. 50 c.c. of the stock solution are treated with excess of ammonia solution. This ppts. the trivalent chromium and iron as their hydroxides [$Cr(OH)_3$ and $Fe(OH)_3$]. Excess of ammonia is boiled off to ensure complete pptn. of the trivalent chromium, as $Cr(OH)_3$ is appreciably soluble in excess of ammonia, giving a violet solution. Filter. The filtrate contains the whole of the chromic acid in the form of ammonium chromate which gives the yellow colour to the filtrate. This may be neglected.

The ppt. is transferred to a beaker by pouring through the filter a small amount of warm HCl which readily dissolves the ppt., the green-brown solution formed being washed through the filter with hot water. From this acid solution the iron is obtained by the addition of NaOH solution till there is evidence of precipitation, after which the addition of sodium peroxide redissolves the chromium hydroxide by oxidizing it to sodium chromate which is soluble, the ferric hydroxide remaining insoluble. The mixture is warmed to get rid of excess of oxygen and diluted before filtering. The reactions taking place are—

$$Na_2O_2 + H_2O = O + 2NaOH$$

and

$$2Cr(OH)_3 + 3O + 4NaOH = 2Na_2CrO_4 + 5H_2O$$

There is now a yellow solution with suspended brown ppt. of $Fe(OH)_3$. This is filtered through a paper of known and preferably little ash, and thoroughly washed to get rid of all caustic soda from the ppt. The iron ppt. is now dried and burned to ash in a weighed porcelain crucible the residue being Fe_2O_3, the weight of which is now taken. For this purpose good filter papers containing negligible ash are best used. They are also less liable to attack by the relatively strong caustic soda solution.

Assume weight of Fe_2O_3 to be 0·02 gm.

Hence—Gm. Fe_2O_3 per litre of the strong chromium solution

$$= \frac{0{\cdot}02}{50} \times \frac{250}{10} \times \frac{1000}{1} = 10$$

The filtrate contains the trivalent chromium as sodium chromate. This is made slightly acid with H_2SO_4 when the yellow colour changes to pink due to the formation of sodium dichromate, thus—

$$2Na_2CrO_4 + 2H_2SO_4 = Na_2Cr_2O_7 + 2NaHSO_4 + H_2O$$

The chromium content of the solution could now be obtained by titration with ferrous solution and permanganate as in the estimation of the total CrO_3. An alternative and better method, however, follows gravimetric lines. The acid solution of dichromate is treated with sulphur dioxide gas (conveniently obtained from a syphon of the liquid) when the red colour changes to green due to the formation of chromium sulphate. thus—

$$Na_2Cr_20_7 + 3SO_2 + 2H_2SO_4 = Cr_2(SO_4)_3 + 2NaHSO_4 + H_2O$$

Excess of SO_2 is boiled off and the chromium obtained by precipitation with ammonia boiling off the excess of ammonia. The green ppt. is filtered, washed, dried, and burned to Cr_2O_3 in a weighed porcelain crucible

Assume the weight of Cr_2O_3 obtained to be 0·024 gm. Then—

Gm. Cr_2O_3 per litre strong chromium solution

$$= \frac{0{\cdot}024}{50} \times \frac{250}{10} \times \frac{1{,}000}{1} = 12$$

From the figures for the iron and trivalent chromium content the amount of chromic acid combined with them is obtained by the method shown on page 349, and deducting the combined CrO_3 from the total chromic acid gives the amount of free CrO_3 per litre.

Estimation of H_2SO_4. In whatever form the acid may have been added it is, after working, in the form of sulphates, chiefly chromium sulphate. The estimation involves no variation because of this, the method being equally applicable for free or combined H_2SO_4, and the result is invariably expressed as gm. H_2SO_4 per litre.

The gravimetric estimation of sulphuric acid is made by its conversion into insoluble barium sulphate by the addition of barium chloride ($BaCl_2$) solution, but in the presence of chromic acid a large amount of insoluble barium chromate will be formed. It becomes necessary therefore to reduce the chromic acid to a trivalent chromium compound in order to obtain uncontaminated barium sulphate. Sulphur dioxide is quite out of the question for this purpose owing to its oxidation to H_2SO_4 free or combined. The reducing agent commonly used is alcohol in the presence of acid which again for this purpose cannot be sulphuric. Take 100 c.c. of the stock solution. Add 10 c.c. pure, strong HCl and 10 c.c. pure alcohol.

Both of these reagents should be free from H_2SO_4. Unless they are, a similar test must be made with separate and like amounts of these reagents to determine their combined content of H_2SO_4. This, with access to normally pure materials, is not usually necessary.

Warm the mixture. The red colour slowly changes, first to brown (a mixture of green and red) and then to a deep green, the alcohol being oxidized to aldehyde, which is a volatile liquid of low boiling-point and therefore readily expelled. The reaction is—

$$2CrO_3 + \underset{\text{alcohol}}{3C_2H_5OH} + 6HCl = 2CrCl_3 + \underset{\text{acetaldehyde}}{3C_2H_4O} + 6H_2O$$

While the solution is still boiling, add a boiling solution of barium chloride. Owing to the small quantity of sulphuric acid usually present, the volume of barium chloride necessary is not large, but safety demands an appreciable excess of $BaCl_2$. Boil the mixture for some time. This yields a granular and more easily filterable ppt. Allow to stand, preferably overnight. Filtering the ppt. is a simple matter, as the bulk of the solution can be put through the filter while the ppt. remains undisturbed at the bottom of the beaker.

The small quantity of barium sulphate ppt. must be thoroughly washed to free it from the excess of chromium sulphate, and this washing with hot water is more conveniently done before transferring the ppt. to the filter paper. Washing should be continued, after the ppt. has been transferred to the paper, until the washings show no trace of turbidity by the addition of $AgNO_3$ solution (HCl was used in the reducing stage). The ppt. is now dried and burned in the usual manner in a weighed porcelain crucible to get the weight of $BaSO_4$.

Assume this to be 0·025 gm.

Now $$\underset{233}{BaSO_4} \equiv \underset{98}{H_2SO_4}$$

and the amount of H_2SO_4 per litre of the original chromium solution is given by the following expression, the several factors of which will now be easily identified—

$$0{\cdot}025 \times \frac{98}{233} \times \frac{250}{100} \times \frac{1000}{10} = 2{\cdot}63 \text{ gm.}$$

Rapid Estimation. Where a centrifuge is available, a more rapid method of estimating the sulphuric acid is possible. The principle is applied in other examples of analysis in which rapid results with approximation are desirable, without the delay of the more tedious and accurate method of weighing up the barium sulphate. In this method a determined quantity of solution is treated in the usual way and transferred to a tube with a lower part which is narrow and graduated. In a centrifuge the ppt. readily settles and its bulk is compared with that of a standard test from which the result is easily deduced.

CHAPTER XX

DEPOSITION OF VARIOUS METALS

THE deposition of iron—Steel facing solution—Modern methods of iron deposition—Typical solutions—Notes on iron deposition—Deposition of tin—Solutions for simple immersion tinning—Electro-deposition of tin—Tinning of steel strip—Bright tin deposition—Deposition of lead—Analysis of lead solutions—Deposition of aluminium Cobalt—Manganese—Deposition of rarer metals—Tellurium—Platinum—Palladium—Rhodium—Indium

DEPOSITION OF IRON

FOR many years the deposition of iron or "steel," as it was incorrectly called, has been practised for the production of a smooth, hard facing for printing plates, thereby considerably increasing their life by the prevention of attack by the chemicals constituting the inks used, and also increasing the sharpness of the impression. These deposits were thin. When worn they were readily removed by dilute acid and the plate re-faced. The production of considerably thicker deposits, the mechanical properties of which were applicable in engineering, was a war-time innovation, and this application has, with some modifications, become standard practice, in addition also to the production of electro-types in the deposited metal.

Steel Facing Solution. For steel facing, a simple solution was invariably used such as—

Ferrous ammonium sulphate	1 lb.	100 gm.
Water	1 gal.	1 litre

The solution was worked as neutral as possible, any acid formed by inefficient anode corrosion being neutralized by the addition of ferrous carbonate, made by the addition of sodium carbonate to any ferrous salt. A slight acidity such as that obtained by the presence of a small amount of acetic acid was permissible. To-day we know better than we did then what this acidity means.

Alternatively a solution could be prepared by using an iron anode in a solution of ammonium chloride (sal ammoniac) with an iron cathode in a porous cell, allowing the anode to dissolve with current until the resulting solution gave a satisfactory deposit.

The process of deposition was simple. The copper plate, which obviously could not endure rough treatment, was cleaned in hot potash and, after rinsing, passed through weak acid or cyanide to remove tarnish. About 10 minutes' deposition at a few amperes per square foot sufficed. Subsequent to use, and when the deposit showed signs of wear, it became necessary to remove the deposit by immersion in a 10 per cent sulphuric acid solution, the deposit easily dissolving from the copper and, after rinsing, a further coat of iron could be imparted. The number of impressions possible from such a steel-faced plate very largely exceeded that from a similar but untreated plate, and the process had a large vogue and is still used.

Modern Conditions of Iron Deposition. Since that time a flood of light has been thrown on the process through the work which found its origin during the war, and we now know at last exactly the conditions required for the deposition of the metal to any thickness. So successful has the work been that it is even possible to deposit the metal on a scale of sufficient magnitude for it to be regarded as a commercial refining process.

In general the conditions of this deposition are comparable with those of nickel, with, however, the disadvantage that while ferric salts are useless for the purpose, and, therefore, ferrous salts only serviceable, these are always tending to become oxidized to the ferric compounds, and this change is accompanied by a change of other conditions, such as acidity, the regulation of which is very important.

The older terms of " slightly acid " and " neutral " have now given way to precise pH values, which, for successful iron deposition range between 5·5 and 6·0. With this degree of acidity it is possible to precipitate the ferric salts by the addition of ferrous carbonate. Again, it was once thought that the extreme hardness of deposited iron. justifying the appellation "steel," was due to the presence of organic matter. In modern practice few suggest the addition of organic reagents. The intense hardness of the deposited metal is the product of the crystalline formation and the presence of some co-deposited hydrogen.

Typical Solutions. Three solutions are now in use for the production of appreciable thicknesses of iron.

These are—

1. THE CHLORIDE SOLUTION

Ferrous chloride	6 lb.	450 gm.
Calcium chloride	6·6 „	500 „
Water	1 gal.	750 cc.

According to T. Johnson,* the solution gives good deposits over a wide range of C.D., and working conditions. At 60° to 70° C. (140° to 160° F.) C.D.'s up to 120 amperes per sq. ft. can be used, this figure being still further increased at higher temperatures.

2. THE SULPHATE SOLUTION

Ferrous ammonium sulphate	2¾ lb.	275 gm.
Water	1 gal.	1 litre

This solution is of the same type as that formerly used for steel facing but considerably stronger. It has been used for the production of pure iron for scientific testing purposes and also for the production of thicker deposits for building up the dimensions of worn machine parts. Used cold, only a comparatively low C.D. of 6 to 10 amperes per sq. ft. can be used, but this can be considerably increased up to 50 amperes per sq. ft. at 60° C. (140° F.).

3. THE SULPHATE CHLORIDE SOLUTION

A combination of both sulphates and chlorides has been made in the following solution—

Ferrous sulphate	1½ lb.	150 gm.
Ferrous chloride	¾ „	75 „
Ammonium sulphate	1¼ „	125 „
Water	1 gal.	1 litre

This solution gives smooth deposits, especially with addition agents at low current densities, and is of a type employed for the production of pure iron for experimental purposes.

Notes on Iron Deposition. As iron deposition is not practised in the usual run of plating shops, it will suffice to give in a short space a few remarks on the general subject of the operation. Experience soon shows that the deposit is particularly susceptible to changes of properties due to even slight change in composition and conditions. In order, therefore, to obtain satisfactory results, some general conditions

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* *J. Electrodepos. Tech. Soc.*, 1929, ii.

are aimed at. These include high ferrous ion concentration at the cathode, obtainable by circulation of strong solutions, and low acidity, this being kept down by the addition of ferrous carbonate, high temperature, the presence of some chlorides, and the freedom from organic matter. In some cases, however, the presence of an addition agent is suggested, though not strongly recommended, and glue has been mentioned in this connection.

Another expedient which is resorted to is the addition of powdered charcoal as a suspension in the solution, this, it is said, minimizing troubles connected with the deposition of hydrogen. The presence of hydrogen absorbed or occluded in the deposit gives rise to hardness and brittleness, and this is removed by subsequent annealing, though the last traces of the gas are not expelled until nearly the melting point of the metal is reached. The whole subject is one of great interest, though not usually within the scope of the work of the plater, who is usually more concerned with deposition from the protective and decorative point of view.

Deposition of Tin

The deposition of tin is now being largely practised, as from the first it was thought that the metal offered great possibilities. Tin is certainly one of the best metals to put upon iron and steel to withstand corrosion. The magnitude of the tinplate industry is the best evidence of this.

In view of the enormous amount of tinned iron or steel used in industry, and especially in the canning trade, there would seem to be great possibilities for any electrolytic process which will yield a satisfactory coating with a smaller consumption of tin than is possible by the usual dipping process. An attractive feature of such a process would be the more economic use of a metal which is none too abundant and definitely costly. Already plants are in operation in the U.S.A. which turn out 450,000 tons per annum of this product, with the consumption of only one-third of the tin which the hot dipping process involves. These processes cater both for large sheets, and also by continuous operation for strip up to 30 in. to 36 in. wide. The electrolytic process admits of building up a deposit of any thickness with the curtailment of this to a minimum necessary for each application of the metal. Moreover, it is possible to obtain different finishes by variations in the procedure, thus adding variety to the process and product.

It may be safely taken for granted that, ere long, similar processes will be in operation in this country for the production of tinned sheet and strip on some considerable scale.

In some industries, however, tinned copper and brass have a wide use. These metals were also prepared by a method not unlike the hot dipping process, but it is in this direction that, first in America, electro-tinning has to some extent superseded the older process, and the electro process has now a considerable vogue.

In this country, the production of munition parts in iron and steel necessitated some type of satisfactory coating to preclude corrosion prior to assembly, and in this direction tinning was largely resorted to. One great advantage offered by the process was the great depth to which the tin could be made to penetrate; in other words, the throwing power of the solution was excellent. The metal, however, is soft and not calculated to withstand much wear.

A disadvantage of tinning in the earlier days of electrodeposition was the difficulty in obtaining smooth deposits. Treeing was pronounced. The use of addition agents has, however, overcome this trouble.

Solutions for Simple Immersion Tinning. The metal tin is readily displaced from its solutions by the process of simple immersion. Large quantities of brass and copper articles of the smaller type are still thus treated. The methods comprise both immersion and contact processes. In the latter, the articles are boiled in a tin-free solution with the metal tin which, in contact with the articles, functions as a soluble anode. In other methods, zinc is used in place of tin, and the solution contains tin. Again the zinc acts as an anode, though of the more active type.

Solutions contain a tin salt dissolved in a convenient solvent. For this purpose cream of tartar ($KHC_4H_4O_6$) is largely used. One recipe is—

Tin chloride (stannous chloride) .	4 oz.	25 gm.
Cream of tartar	2 ,,	12·5 ,,
Water	1 gal.	1 litre

The solution is used at a temperature of 80° C. (176° F.) and the cleaned brass articles are rotated in a barrel with pieces of zinc. These act as anodes, and the tin is really electrodeposited by locally developed currents.

Alternatively, a solution may be used in which there is no tin at all. The solution is one containing some solvents, such as cream of tartar and common salt, possibly only half an ounce of each per gallon. The cleaned brass articles are placed in trays of iron wire and are interlayered with perforated sheets of tin. On nearly boiling, the tin dissolves, and is subsequently deposited out on the brass. The process occupies some time. After each operation the solution is scrapped, there being no appreciable amount of tin in it.

Electrodeposition of Tin. For any assured thickness of tin or for the production of a deposit which has a real protective value rather than a merely decorative one, electrodeposition must be resorted to, and the operation is being increasingly applied. One of the first solutions recommended for this purpose was that of Roseleur. This was as follows—

Stannous chloride ($SnCl_2 2H_2O$) . . .	1½ oz.	9·4 gm.
Sodium pyrophosphate ($Na_4P_2O_7 10H_2O$) .	12 ,,	75 ,,
Dextrine	1 ,,	6·25 ,,
Water	1 gal.	1 litre

This solution was used at a temperature of 60° C. (140° F.) with a current density of about 5 amperes per sq. ft. More recently, however, there has been a decided change over to

THE ALKALINE STANNATE BATH, which now commands a wide application. The essential constituent of this solution is sodium stannate, made by dissolving tin oxide (SnO_2) in caustic soda. The material can be purchased, and to it is added a number of other materials found beneficial in the deposition. A formula published by Oplinger* for this solution is as follows—

Sodium stannate .	12 oz.	75 gm.
Sodium acetate . .	2 ,,	12½ ,,
Caustic soda . .	1 ,,	6¼ ,,
Sodium perborate .	¼ ,,	1½ ,,
Water . . .	1 gal.	1 litre

This solution yields excellent results at a temperature of 70° C. (158° F.) and a C.D. of 20 to 60 amperes per sq. ft., P.D. 4–6 volts. For barrel work the strength of the solution is increased, and the P.D. also raised at the same temperature.

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* *Met. Ind.* (N.Y.), 1931, 29, 529.

In this type of solution sodium stannate provides the source of tin for deposition while oxidizing agents such as sodium perborate and hydrogen peroxide serve to convert stannous ions into stannic ions, the former conducing to the formation of spongy deposits. Caustic soda is necessary to keep the anodes clean as free cyanide is for cyanide solutions.

It has recently been found that perfectly smooth and sound deposits up to one-quarter of an inch in thickness may be made from a simple solution of sodium stannate containing merely a slight excess of caustic soda.

Thus Hothersall, Clarke, and Macnaughtan* in a subsequent paper have shown that the formation of spongy deposits in the stannate bath is due to the presence in the solution of small concentrations of stannite and that, provided the solution is maintained in an oxidized condition, sound deposits up to the thickness mentioned may readily be obtained.

They therefore recommend the use of insoluble anodes, preferably of nickel sheet or foil, as an alternative to the peroxide additions used by Oplinger, and suggest various methods of replenishing the tin content of the solution. The following conditions are recommended—

SOLUTION.

$$\left.\begin{array}{l}\text{85 gm. Tin (as sodium stannate)}\\ \text{15–20 gm. NaOH}\end{array}\right\}\text{per litre}$$

TEMPERATURE 70–75° C.

C.D. up to 60 A per sq. ft. but preferably 15–20 A per sq. ft.

Owing to the variable composition of commercial sodium stannate it is not desirable to specify merely stannate. The chemical should be free from chloride.

The throwing power of the solution is exceptionally good.

More recently, practice has been improved by the use of tin anodes, but these require careful preparation by the production of a greenish yellow film of SnO_2. This "filming" is produced by an initial high current density of from 1½ times to twice that for normal deposition. A minute or so of this treatment shows the production of the film by an increased voltmeter and a decreased ammeter reading. The operation can be achieved by loading the bath with work and lowering

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* *J. Electrodepos. Tech. Soc.*, 1934, ix, 101.

the anodes—in contact with the bar—into the solution thereby obtaining the higher C.D. on the partially immersed anodes. On unloading the bath the anodes are first removed before cutting off the current and not allowed to stand in the solution. Carbonates accumulating in the solution are periodically removed by cooling and crystallization.

For deposition, anode C.D. is one-half of that at the cathode. Further a substantial degree of purity is essential in the sodium stannate ($Na_2SnO_3 . 3H_2O$) used. Nitrates appreciably lower the cathode efficiency.

The Acid Bath. The following acid solution has also yielded good results—

Sulphuric acid	85 gm. per litre
Tin	30 ,,
Cresol sulphonic acid	100 ,,
Gelatine	2 ,,
B. naphthol	1 ,,

From this solution 10 amp./sq. ft. at 20° C. yields a good deposit not requiring agitation and giving ·001 inch in 50 minutes.

Oxalate Bath.

Stannous oxalate	50 gm. per litre
Ammonium oxalate	60 ,,
Oxalic acid	15 ,,
Gelatine or peptone	2·5 ,,

This solution at 20° C. yields satisfactory deposits at 5 amp./sq. ft.

A comprehensive survey of the applications of tin deposition has been given by Baier and Tait.*

Tinning of Steel Strip. As a protection for steel, electrodeposited tin has been explored as a competitive process to hot tinning. For this purpose an acid bath composed of stannous sulphate, sulphuric acid, cresol-sulphonic acid with addition agents has been found more satisfactory than the usual alkaline solutions. The method has been described by Macnaughtan, Tait and Baier.† The solution is worked at room temperature with a relatively low bath voltage and yields twice the weight of metal with the same current density in comparison with alkaline solutions. Subsequent tests‡ on

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* *J. Electrodepos. Tech. Soc.*, 1940, xvi, 45.

† *Ibid.*, 1937, 12. ‡ *Ibid.*, xii, 1937.

the mechanical properties of the deposit proved satisfactory, showing a ductility which admitted of the usual deformation in manufacturing processes. It remained, however, to be determined whether the process could be worked with the required economy, in view of the possible improvements in hot dipping process and its application to steel strip.

Bright Tin Deposition. Tin provides another metal the production of bright deposits of which has attracted attention with a considerable degree of success. For this purpose Schlötter proposes compositions of which the two following may be regarded as representative—

Example 1.

Tin (as a stannous salt)	25	gm.
Sulphuric acid 66° B.	75	,,
Glue	1	,,
Resins obtained by the sulphurizing of phenol	1·5	,,
Naphthol	·5	,,
Water	1000	,,

Example 2.

Tin in the form of tin benzene disulphonate	30	gm.
Benzene disulphonic acid	90	,,
Gelatine	·8	,,
Beech wood tar	20	c.c.
Water	1000	gm.

From such electrolytes tin is obtained with very satisfactory bright surfaces using a C.D. of 3 to 6 amp. per dm.^{2} or about 28 to 56 amp. per sq. ft. Usually no subsequent polishing treatment is required, but after rinsing and drying, deposits may be rubbed with a cloth or silk pad with the application of a little french chalk.

Here, again, we may assume that the presence and co-deposition of these colloidal substances effects the extremely fine crystal structure in the deposit which is responsible for the mirror-like surface.

DEPOSITION OF LEAD

The deposition of lead is being increasingly practised. Originally, from such a simple solution as the acetate, unpromising results were obtained. Treeing was unavoidable, but more recently Mathers and Schwartzkopf* have been more successful with the following solution—

Lead acetate ($Pb(C_2H_3O_2)_2 . 3H_2O$)	100 gm.
Sodium acetate ($NaC_2H_3O_2 . 3H_2O$)	120–160 ,,
Glue	4–6 ,,
Cresol	30–40 drops
Water	to 1 litre

A C.D. of 10 amp./sq. ft. gave quite satisfactory deposits. The solution has the advantages of simplicity, cheapness and no action on ceramics. Its conductance, however, is low and the deposits somewhat brittle.

It has for some time been known that a solution of lead fluosilicate, with an addition agent—usually glue—gave good deposits, and the process is extensively used in the electrolytic refining of the metal. The solution used for this purpose is made up as follows—

Lead (as fluosilicate)	8 oz.	50 gm.
Hydrofluosilicic acid	16 ,,	100 ,,
Water	1 gal.	1 litre

The lead as oxide (PbO) is dissolved in the acid, which then leaves a proportion of the acid in the free form for conductance purposes. The addition of glue is of the order of ·5 gm. per litre. It is absorbed by the deposited lead, and hence requires renewal. The C.D. permissible is of the order of 10 to 20 amperes per sq. ft., and very satisfactory deposits from the point of view of refining are obtained. The solution, however, is not exactly suitable for the more ordinary process of electro-plating.

A later solution proposed by Mather† contains lead perchlorate as its chief constituent. It is compounded as follows—

Lead (as perchlorate)	8 oz.	50 gm.
Perchloric acid (free)	8 ,,	50 ,,
Peptone	$\frac{1}{12}$,,	·5 ,,
Water	1 gal.	1 litre

Lead requires practically its own weight of perchloric acid to convert it into perchlorate and, therefore, the amount of pure acid ($HClO_4$) required will be 1 lb. per gallon of solution (100 grm. per litre). The lead as oxide (207 of lead are contained in 223 of oxide) is readily dissolved in the acid, which is purchased, allowance being made for the strength of the

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* *J. Electrodepos. Tech. Soc.*, 1940, xvi, 45.

† *Trans. Amer. Electrochem. Soc.*, 1920, xvii, 261.

acid as received. Alternatively, the total amount of acid is divided into two equal parts, one of which is saturated with lead oxide and the solution mixed with the unused acid. Such variations in making the solution will be appreciated with a slight knowledge of chemistry.

Without the addition of peptone the deposition can only proceed very slowly, and even then is not sufficiently good to be serviceable for many purposes. The addition of the peptone makes a remarkable improvement in the nature of the deposit, permitting the use of a current density up to 20 amperes per sq. ft. The addition agent is absorbed in the deposit and again, therefore, requires renewal. Peptone is a somewhat expensive material, and its place may be taken, though less effectively, by clove oil.

Still another solution is of the fluoborate type. This is composed as follows—

Basic lead carbonate .	20 oz.	125 gm.
Hydrofluoric acid (50%)	36 „	225 „
Boric acid . . .	16 „	100 „
Glue	$\frac{1}{32}$ „	·2 „
Water	1 gal.	1 litre

The preparation of the solution is simple, once it is borne in mind that the hydrofluoric acid should be used not in stoneware or glass vessels, but in a lead-lined wood tank. The hydrofluoric acid is put into the tank and the boric acid added. This forms the fluo-boric acid. Lead carbonate is now added, slowly, to prevent too rapid effervescence. Some lead sulphate will settle out owing to the presence of sulphuric acid in the hydrofluoric acid. The solution can be poured off and the glue, first dissolved in water, added. This solution works satisfactorily at 20 amperes per sq. ft., but more rapid deposition can be effected in a stronger solution.

An innovation in lead deposition is that proposed by Mathers and Forney[*] starting with sulphamic acid ($HSO_3 . NH_2$). This acid is purchasable. A 5 per cent solution (5 gm. per 100 c.c.) is treated with an excess of basic lead carbonate. The excess of lead compound is filtered off and a further 5 gm. of acid added. The solution then contains 5·4 gm. Pb per 100 c.c. and its pH is of the order of 1–1·5. From this solution the deposits "tree." A good variety of

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[*] *Trans. Amer. Electrochem. Soc.*, 1939. lxxvi, 373.

addition agents serve to produce smooth, tough and crystalline deposits, with C.D.'s to 20 amp./sq. ft. and a current efficiency of 95–96 per cent. The throwing power is given as 18·2 on the Haring and Blum scale, and 22·7 on the Hartley scale.

Finally, reference may be made to the alkaline solution. This is prepared by dissolving litharge in potash in the following quantities—

Lead oxide (litharge) .	1 oz.	6·25 gm.
Caustic soda. . .	6 ,,	37·5 ,,
Water	1 gal.	1 litre

The caustic soda is dissolved in a quarter of the water and the lead oxide dissolves readily in this fairly strong solution, which can then be made up to the final bulk with water.

The solution may be contained in an iron tank and warmed. In coating steel it is advantageous to coat the work quickly, afterwards reducing the current. Only a slow rate of deposition can be permitted if smooth deposits are to be ensured.

The deposition of lead finds application for coating metals which are required to come into contact with sulphuric acid, as in accumulator work.

Analysis of Lead Solutions. The following brief method is applicable to all the usual lead depositing solutions. Take 10 c.c. of the solution, dilute to 150 c.c. and heat nearly to boiling. Now add a slight excess of dilute sulphuric acid. This precipitates heavy lead sulphate which, quickly settling, provides an opportunity of judging when sufficient acid has been added. A large excess is very inconvenient. Allow the ppt. of lead sulphate to settle and filter on to a weighed Gooch crucible washing the ppt. first with very dilute H_2SO_4 and finally with water. Dry and weigh the $PbSO_4$ from which the weight of lead or lead fluosilicate, fluoborate or perchlorate can be calculated.

Free Acid. Free fluosilicic acid can be approximately determined by titrating with potassium hydroxide using phenolphthalein as indicator. Free perchloric acid can be determined by direct titration, or, more accurately, by precipitating the lead with a known excess of sulphuric acid and titrating the total acid in the filtrate. From this the free perchloric acid can be calculated.

For free fluoboric acid there appears to be no very simple method to yield satisfactory results.

Deposition of Aluminium. This may sound unusual in view of the repeated references to this metal in the earlier portions of this book. Its extremely electronegative character at once suggests the improbability of this being achieved from aqueous solutions, but we are still left with a range of organic solvents from which the deposition of the metal might be possible. Thus Blue and Mathers* have shown that the deposition of the metal is possible from solutions of aluminium bromide in a mixture of ethyl bromide and benzene. While the earlier experiments were purely of an investigatory character to test the possibility, a measure of success was attained in the production of deposits of a bright and crystalline character with a C.D. of 8 amps./sq. ft. with a cathode efficiency of 60 to 70 per cent.

An alternative method was that of the production of an alloy of copper and aluminium which again showed signs of even commercial success.

Cobalt. While the deposition of this metal has not attained much commercial importance the process seems to hold out possibilities by reason of the whiteness, lustre and hardness of the finished deposit. Militating against its use is the high cost of the metal and its compounds. On the other hand, the metal can be deposited at a very much more rapid rate than nickel. The solutions employed are on the lines of those of nickel as follows—

Cobalt ammonium sulphate	2 lb.	200 gm.
Water	1 gal.	1 litre

This solution, which requires less care with regard to acidity than nickel solutions, can be worked with current densities up to and exceeding 30 amperes per sq. ft.

The single sulphate solution, however, far exceeds this rate of deposition. It is as follows—

Cobalt sulphate . .	4·5 lb.	450 gm.
Boric acid . .	5 oz.	31 ,,
Sodium chloride .	2 ,,	12·5 ,,
Water . . .	1 gal.	1 litre

Used at 35° C. (95° F.) the solution gives good deposits with current densities up to 150 amperes per sq. ft., and even much higher rates of deposition have been used over short periods.

So far, however, its applications are few. The metal is

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* *Trans. Electrochem. Soc.*, 1934 lxv, 339,

seriously affected by some of the acids occurring in foodstuffs, and this is likely to limit its applications. The deposit is, however, hard and durable. The metal may easily be obtained in the form of thicker deposits than are usual with nickel, and may be deposited directly upon nearly all the usual metals, including tin, lead, and Britannia metal. The deposits, when required, can readily be removed by immersion in dilute sulphuric acid, care being taken when the base metal is also liable to attack by this acid.

Manganese. The deposition of this metal has attracted attention, and recent work by Oaks and Bradt* and by Fink and Kolodney† has shown that the metal can be deposited in a pure, coherent, smooth and silver-white form from both the sulphate and chloride solutions.

With the sulphate solution, the anodes were of both graphite and manganese, an anode entirely of the metal resulting in a much larger solution than deposition, thereby considerably enriching the bath in metal. With the chloride solution, platinum anodes gave rise to the formation of precipitates of black manganic hydroxide, while with manganese anodes the ppt. formed was of the manganous type. More success was therefore obtained by the use of some type of diaphragm. With both types of solutions, the optimum conditions for deposition were determined and these details may be found in the original papers to which references are given.

DEPOSITION OF RARER METALS

Tellurium. Ordinarily tellurium is regarded as a non-metal but physically it possesses marked metallic properties. Further, its deposition has so far only been carried out on a relatively small scale for the purpose of obtaining the pure from the available crude element. The "metal" is grey in colour and very brittle, but possesses a marked degree of resistance to chemical and atmospheric corrosion.

Its deposition has been explored by Mathers and Turner‡ who used a number of solutions, the best of which constituted a solution of the dioxide in a mixture of sulphuric and hydrofluoric acids.

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* *Trans. Amer. Electrochem. Soc.*, 1936, lxix, 567.

† *Ibid.*, Preprint, lxxi, 3 (1937).

‡ *Trans. Amer. Electrochem. Soc.*, 1928, liv, 293.

The dioxide is an article of commerce; alternatively it may be made from the metal by treatment with sulphuric and nitric acids, yielding the hydrated dioxide which can be dehydrated by evaporation to dryness and gently igniting.

The use of hydrofluoric acid involves the use of a containing vessel of some material not attacked by this corrosive acid, and in following out the method, a wood box lined with wax was found convenient.

The composition of the solution is as follows—

Tellurium dioxide	250 gm. per litre
Hydrofluoric acid (48%) . . .	500 ,,
Sulphuric acid (96%)	200 ,,

The oxide readily dissolves in the acids and there is perhaps some slight disadvantage in this solution in that it gives off some hydrofluoric acid fumes. The solution is worked at ordinary temperature with a tellurium anode and platinum cathode. With a current density of 10 to 20 amperes per sq. ft., very compact deposits are obtained which are almost entirely free from selenium, which is usually associated with tellurium. Anodes of tellurium are very poor conductors and this leads to rapid solution of the anode just below the level of the liquid. It was found convenient to introduce the anodes only to a small depth at first, gradually lowering them as the action continued. The solution is an excellent conductor and this involves the use of only a small P.D., usually not exceeding one volt.

The fact that the element can be deposited in a substantial, compact and crystalline form is a matter of interest, paving the way for possible applications in the near future.

Platinum. This was one of the earliest of this group of metals to be electro-deposited though the applications were necessarily limited on account of the high cost. A general survey of the history of the process with modern developments has been given by Atkinson, Davies, and Powell and Schumpelt,* to which reference will be found instructive.

Palladium. Palladium also offers advantages for the production of a non-tarnishable deposit, and has been applied in this direction for certain examples of marine practice. The properties of the metal are similar to those of platinum,

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* *Proc. 1st I.E.C., E.T.S.*, **March, 1937.**

and it is recorded that one of the earliest examples of this deposition goes as far back as 1855.

A detailed account of the processes which have been proposed and applied is given by Atkinson and Raper.[*] In earlier examples the process was worked with an insoluble anode, but it was later found possible to design a soluble anode process. The electrolyte for this purpose is as follows—

10 gm. palladium as $Na_2Pd(NO_3)_4$ per litre.
30 gm. NaCl per litre.

The usual conditions comprise a current density of about 1 ampere per sq. ft. at a temperature of 40° to 50° C. This current density is obtained, with an interelectrode distance of 15 cm., with 1·5 volts. The anode is of hard rolled palladium sheet, both anode and cathode efficiencies being of the order of 95 to 98 per cent.

Rhodium. This further example of the precious metals was discovered as far back as 1804, and among the platinum group has some distinctive properties. Its nobility exceeds that of platinum and its melting point is approximately 1900° C., again exceeding that of platinum. The metal is very hard and tough, but its lack of ductility prevents its use in some of the well-known forms such as wire. It is very white and exhibits high reflectivity. But it is very costly. Some compensation is found in the extremely thin deposits necessary to impart its desirable properties. Urgency of modern requirements has, however, established its practice so that after the war we may hope to find it in extended use. It is capable of successful deposition from a solution containing 2 gm. of rhodium and 33 c.c. sulphuric acid per litre. The process has been described by Atkinson and Raper,[†] who indicated a number of methods by which the solution can be prepared from the metal. With this solution satisfactory deposits were obtained in from 5 to 15 minutes, equivalent to 1·5 to 4·5 mg. per sq. in.

The latter figure corresponds to a thickness of 0·0001 in.

The deposited rhodium is characterized by its unique permanence under corrosive conditions. It is on record that a deposit of this thickness withstood the action of hot aqua regia

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[*] *J. Electrodepos. Tech. Soc.*, 1933, viii, 10.

[†] *J. Electrodepos. Tech. Soc.*, 1934, ix, 77.

for 30 minutes without showing any signs of discoloration. Further, its hardness is considerably greater than might be ordinarily imagined.

In colour the metal approximates to that of silver and the deposition of the metal enhances the value of the article plated.

Possibly the high cost might seem a deterrent to the general application of the metal for domestic use, and would seem therefore to limit its range to the more expensive forms of jewellery and, possibly, for reflectors. These were among the first applications of the deposit.

For general table ware, however, it would seem possible to apply the deposit to the prongs of forks—as one example—which in use receive the more drastic abrasion and are moreover much more difficult to keep clean. These are indications of an extending range of usefulness in spite of the high cost of the metal.

Deposition of Indium. This process provides another recent adaptation of a relatively unusual metal into the realm of electro-deposition.[*] It has been placed on record that small additions—from ·2 to 4·0 per cent—of this metal in silver, lead, copper, etc., increase their anticorrosive properties. According to Linford[†] the solution is prepared by dissolving the metal in sulphuric acid and adding sodium sulphate to the following composition—

Indium (as sulphate)	21 gm.
$Na_2SO_4 . 10 H_2O$	10 gm.
Water to	1 litre
pH	2·2
Temperature	20° C.
C.D.	20 amp. (sq. ft.)
C. Efficiency up to	80%

An indium rod serves as anode. A cyanide solution is also available.

The method of alloying with lead is that of making the requisite deposit of indium within the lead deposit and subsequently effecting the distribution through the lead by heat treatment. A commercial development of the process is anticipated.

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[*] *Mon. Rev. Amer. E.P. Soc.*, March, 1941.

[†] *Trans. Amer. Electrochem. Soc.*, 1941.

CHAPTER XXI

DEPOSITION OF ALLOYS

INTRODUCTION—Special features: scope for alloy deposition—Comparison of zinc and copper cyanides—Deposition of brass—Function of constituents—Composition of brass deposits—Throwing power of brassing solutions—Points about electro-brassing—Analysis of brassing solutions—"Bronze" plating—Lead-tin alloys—Lead-silver alloys—Aluminium alloys—Zinc-cadmium alloys—Cadmium-silver alloys—Possibilities of alloy deposition

Introduction. One of the features of the deposit of copper obtained from the sulphate solution is its purity. Many impurities may be present in the solution without passing into the deposit. Upon this fact is based the very largely applied process of the electrolytic refining of copper. With the exception of a few metals, it is difficult to persuade impurities to pass into the deposited copper. This has its advantages and also its disadvantages.

Of all the common metals zinc would be one of the last to be deposited with copper in the acid bath, and the possibility of depositing an alloy of the type of brass is, therefore, very remote. The two metals are altogether too dissimilar electrochemically. This is seen in the ease with which zinc turns out copper from so many of its solutions. A further example is found in the manner in which the different behaviour of the two metals enables them to be employed as the essential constituents of the Daniell cell. The difficulty of the co-deposition of these metals is further turned to account in the process of electrolytic analysis, in which complete separation of the two metals is essential and easily achieved.

The production of electro-deposited alloys, therefore, involves the use of metals the electro-chemical properties of which are somewhat alike. This condition can be met with copper and zinc by the use of compounds other than the sulphates.

Special Features. The deposition of alloys raises a number of interesting problems such as are not met in the case of single metals. Among them are the composition of the solutions, the choice of anodes and the conditions of operation in order to secure the required composition in the deposited alloy. In the first place the solution will not necessarily contain the alloy constituents in the same proportion as that of the required alloy deposit, and the two constituents will have different chemical equivalents which largely influence their proportion in the deposit. The case of brass will be dealt with in greater detail later.

Further, anode and cathode efficiencies are not likely to balance and this inequality occasions a variation in the composition of the solution. A brass anode, for example, dissolves with greater efficiency than that of the cathode process. This leads to an increase in the metal content of the solution with corresponding decrease in the free cyanide content. Correction for this defect may be made by the partial substitution of insoluble anodes, for example iron, following the example in cadmium plating, and also at times in the cyanide coppering solution.

Coming next to the composition of the anode, it is obvious that this must be that of the required deposit, whatever may be that of the solution, so that the metal passing out from the solution is exactly made good by that entering at the anode. Usually anodes of the same alloy are used as in the case of brass. If one of the two main constituents—zinc for example—shows any greater tendency to solution over the other—copper—this leads to the exposure of a larger proportion of copper, and with it, greater solution, the defect thus correcting itself.

Again, brass is an alloy which is readily workable over a wide range of composition. It is, however, possible to conceive of alloys which, in the thin form of a deposit, show all the required strength, but which, in the more massive anode form, are either brittle or otherwise unworkable. Here the use of the two metals in the form of separate anodes becomes possible, each of which will dissolve in the proportion of the chemical equivalent and the current passing from it. There is the possibility of one of these anodes becoming passive by the production of insoluble compounds upon it, thus throwing an undue proportion of the current through the other metal. Again, one of the two metals may have a natural tendency to dissolve more freely than the other. These are irregularities which can be guarded against by the use of separate anode circuits, each being independently controlled by its own rheostat with the introduction of an ammeter, so that the exact current passing through may be known. This condition is readily attainable. It will then be a matter of determining the exact proportion of current to be passed through the individual anodes and thereafter maintaining it.

There are many other matters of more theoretical interest which need not be entered upon here.

Scope for Alloy Deposition. Many advantages would seem to accrue to the deposition of alloys. Hepburn* has enumerated these as follows—

1. Reduction of metal cost (e.g. nickel-iron instead of nickel).
2. Special and variable colour effects for decorative purposes (e.g. brass and gold alloys).
3. Production of bright deposits (e.g. nickel-cobalt and zinc-cadmium).
4. Possibility of the deposition of rare metals in useful alloy forms, while such metals are not capable of satisfactory deposition alone.
5. Special properties (e.g. brass for rubber adhesion and silver-cadmium for resisting tarnish).

Further the general aim in such solutions will be—

1. The reproductibility of colour or composition.
2. Constant metal ratio in the bath.
3. Anode and cathode control to maintain constant metal ratio in the bath.
4. Wide plating range.
5. Easy analytical control.

In the case of some well-known examples these conditions are being met after extensive experiment and practice. Other examples must be explored along these lines.

These conditions provide wide scope for research in the cases of many binary alloys (those containing two metals). The difficulties of achieving them are likely considerably to increase in the case of ternary alloys (those containing three metals), and it is quite probable that, with the impetus

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* Presidential address; Electrodepos. Tech. Soc., 1943.

provided by existing exigencies, the problems of alloy deposition will receive considerable attention in the future.

Comparison of Zinc and Copper Cyanides. The double cyanides of the two metals have at least this one common feature. In solutions of each there is an almost complete absence of zinc and copper ions which usually impart the characteristic properties to the solutions of these metals. The ions in each case are $2K^+$ and $Zn(CN)_4^{--}$, and $2K^+$ and $Cu(CN)_3^{--}$. It must, however, be clearly understood that very small quantities of zinc and copper ions do exist in these solutions, but they are not sufficient to impart the usual properties of zinc and copper compounds. This small proportion of ions is the result of the further ionization of the complexions $Zn(CN)_4^{--}$ and $Cu(CN)_3^{--}$. In the case of the former the dissociation is as follows—

$$Zn(CN)_4^{--} \rightarrow Zn^{++} + 4CN^-$$

In the double cyanides we have compounds which are electrochemically very much alike, and which offer, therefore, the possibilities of the co-deposition of the two metals in the form of an alloy.

These remarks, while referring specially to copper and zinc, have a general application to all other components of alloys.

Deposition of Brass. Brass is the alloy which has been most widely deposited.

For very many years it provided a coating both decorative and protective for iron and steel, and large amounts of such work found their way into domestic and other uses. More recently a deposit of brass has been found most effective as a base upon which to obtain a firm adhesion of the various rubber compositions which now so widely constitute the linings of metal tanks containing corrosive-solutions. This latter application will doubtless extend the scope of brass deposition. In recent years, too, the brass plating solution, comprising a number of constituents, each with its determining influence on the process, has been subjected to a more thorough chemical investigation, with the result that these factors in deposition have been evaluated with some precision, leaving less room for the recourse to the more original rule-of-thumb methods.

Little need be said with reference to the preparation of the solutions. In a few words it may be stated that the process is identical with that of the preparation of cyanide copper solutions, with the exception that a proportion of the copper compound is replaced by the similar zinc compound, for usually the proportions of zinc and copper in their compounds are sufficiently alike to be taken as the same. One point may require some further explanation, and that is why we may employ equal amounts of the two metals in the solution when we expect to obtain a deposit containing roughly twice as much copper as zinc.

This is accounted for as follows: If the two compounds are present in equal quantities they may be roughly regarded as equally sharing the current. The two metals are then deposited out in the proportion of their chemical equivalents. That of copper in this cyanide solution is 63·6, and of zinc 32·5. The figure for copper is practically double that of zinc, and thus twice as much copper appears as zinc, giving a deposited alloy of the usual brass type, which may, however, be widely varied by changes in the electrical and chemical conditions.

Another important factor has then to be taken into consideration. It is the general experience that colours of deposited brass differ from those of cast brass of the same composition. For example, to obtain the same yellow colour of the cast metal having the composition 65 Cu to 35 Zn, will require a deposit containing as much as 75 per cent Cu. The deposited zinc has apparently a far greater whitening power on the colour of the copper. These two facts have to be taken into consideration in the selection of the relative proportions of the two metals in the solution. Thus it is that more copper is required in the solution than zinc.

Again, stronger solutions are invariably used for barrelling than for stationary deposition. For the former, a typical solution is as follows—

Copper cyanide (65%)	3¾ oz.	23·5 gm.
Zinc cyanide (54%)	1¼ ,,	7·8 ,,
Sodium cyanide (129%)	6 ,,	37·5 ,,
Sodium carbonate	¾ ,,	4·7 ,,
Sodium bisulphite	1½ ,,	9·4 ,,
Water to . .	1 gal.	1 litre

As has been explained in other parts of this book, these ultimate constituents may be obtained by starting with different compounds in different proportions. The above compounds are, however, easily procurable, and are standard materials with which to prepare a solution.

For stationary deposition, a weaker solution may be used even as dilute as one-half of the above strength.

Function of the Constituents. Each constituent should have its particular part to play in the process of deposition. That of the free cyanide is to keep the anodes free from the accumulation of insulating films of the single cyanides. It also supplies, to some extent, conducting ions. Of the soluble complex cyanides, that of zinc more freely supplies metal ions than that of copper, this to some extent assisting the co-deposition of the two metals. Further, the hydrolysis of the free cyanide supplies some proportion of OH ions required to maintain the high pH essential to good operation. The addition of ammonia serves a similar purpose, though the estimation and therefore the control of this constituent is a little difficult. Though by no means general, other small additions have from time to time been proposed and made.

CONDITIONS OF OPERATION. The solution is usually used warm—from 40° to 50° C. (104 °to 122° F.). The permissible P.D. and C.D. are not so readily and exactly stated. These may be determined by a little experience. In any case, considerable volumes of hydrogen are likely to be evolved, and the cathode efficiency is, therefore, low. Deposits of good uniform colour, rather than those which are quantitative, provide the chief aim in brass plating.

DEFECTS IN THE SOLUTION. A number of defects are likely to arise with this solution. Lack of free cyanide will be evidenced by the formation of insoluble products on the anodes, and decrease of current, a defect readily remedied. Difficulty in maintaining a uniform colour will be remedied by the addition of either of the metallic cyanides, or an alteration in the composition of the anodes. These should be of the same composition as that desired in the deposit, although the solution may not agree with this composition.

There are then a number of variations of depositing conditions which influence the proportion of the two metals deposited, and therefore the colour of the deposit. Generally speaking, those conditions which make for easier deposition facilitate the deposition of a larger proportion of copper with a redder deposit. Such conditions are an elevation of temperature, the addition of free cyanide, and low current density. Concentration of the solutions has a like effect. The reverse conditions tend to the production of lighter deposits which are, therefore, obtained with weaker and colder solutions, with increased C.D.

From the commercial point of view a good solution is one which, over a wide range of composition and conditions, will yield uniform shades of deposit. From another point of view, however, a good solution might be regarded as one so nicely balanced that a slight alteration of any of the conditions previously mentioned will at once yield the change of colour.

There is, however, one possible defect which will tend to the production of red deposits. This is the precipitation of the zinc compound owing to its inferior solubility. The zinc compounds are readily soluble in ammonium compounds, and the zinc precipitates are, therefore, readily dissolved by the addition of either liquid ammonia or solid ammonium carbonate. These produce, almost immediately, a change of colour, and need, therefore, to be added with some discretion.

Composition of Brass Deposits. An interesting feature in brass deposition and to some extent in other examples of alloy deposition is the fact that the weight of the deposit obtained by a definite number of ampere-hours is an indication of the composition of the deposit. This result is arrived at in the following manner. Assume for the moment that the whole of the current is occupied in depositing copper and zinc—that there is no co-deposition of hydrogen. Put the brassing solution in series with an acid copper bath which, with moderate current density, can be regarded as a coulometer. Compare the weights of brass and acid copper deposits. Call the ratio of the brass to the acid copper R.

Take the extreme case of the brass solution containing copper compound alone. The copper is in the cuprous form. Its equivalent is 63·6, that is, twice the value of that in the acid copper solution. In this extreme case, therefore, $R = 2$. At the other extreme, consider the brass solution to be composed wholly of zinc cyanide. The equivalent of zinc is 32·5 and R becomes $32{\cdot}5 \div 31{\cdot}8 = 1{\cdot}022$.

For all mixtures of deposited copper and zinc the value of R will lie between these extremes. The values may easily be calculated. Take the case of a 50/50 deposit and consider 100 gm. of the deposit. The equivalent amount of copper from the acid bath will be obtained as follows—

50 gm. "cyanide" copper = 25 gm. acid copper

50 ,, zinc $= \frac{31\cdot8 \times 50}{32\cdot5} = 48\cdot92$ gm. acid copper

100 gm. 50/50 alloy = 73·92 gm. acid copper

R in this case is therefore

$$\frac{100}{73\cdot92} = 1\cdot353$$

Other values for alloy deposits of different compositions are similarly calculated and are shown in Table LXVI.

TABLE LXVI

COMPOSITION OF BRASS DEPOSITS

% Cu	% Zn	$R = \frac{\text{Brass deposit}}{\text{Acid Cu}}$
100	0	2·000
90	10	1·825
80	20	1·678
70	30	1·558
60	40	1·446
50	50	1·353
40	60	1·271
30	70	1·198
20	80	1·133
10	90	1·074
0	100	1·022

The values may now be plotted in the form of a curve shown in Fig. 90.

From this curve any value of R can at once be expressed in terms of the composition of the alloy. More accurately the percentage of copper in the deposited alloy may be obtained from the following expression, which is the simple mathematical expression of the curve—

$$\text{Percentage Cu in alloy} = \frac{204}{R}(R - 1{\cdot}022)$$

This is no more than a simple mathematical exercise the details of which need not here be considered. The accuracy of the expression can, however, easily be checked with any of the values on the table. Thus with the ratio $R = 1{\cdot}5$ the percentage of copper becomes—

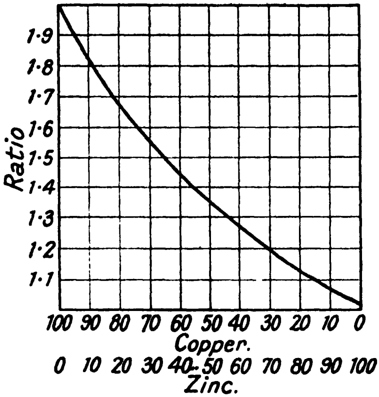

FIG. 90. COMPOSITION OF BRASS DEPOSITS

$$\frac{204}{1{\cdot}5}(1{\cdot}5 - 1{\cdot}022) = 64{\cdot}7 \text{ per cent}$$

The use of this relationship is now illustrated in the following table (No. LXVII), which is drawn up from actual experimental data. The percentage of copper is shown first by calculation and then by chemical analysis. The chemically determined amount of copper is deducted from the weight of the alloy to give the weight of zinc in the deposit. The weights of both copper and zinc are then converted into the percentages of total current (as measured in the acid copper bath) required to deposit them. These should theoretically add up to 100. Any deviations therefrom represent either the inaccuracies of the experimental work involved (and these are bound to be present, though they should be negligibly small) and/or the small proportion of the current which unavoidably deposits hydrogen.

The figures in the table are sufficiently indicative that good results are obtainable under conditions in which the deposition of hydrogen is preventable by the choice of sufficiently strong solutions and the method of operation, which, it must be recognized, may not be those of usual workshop practice.

TABLE LXVII

COMPOSITION OF BRASS DEPOSITS CALCULATED AND FOUND

	$\frac{\text{Brass}}{\text{Cu}^{++}}$	% Cu (Calc.)	% Cu Found	% current depositing		
				Cu	Zn	Diff. from 100
1	1·91	95·0	95·8	91·2	7·9	− 0·9
2	1·90	94·6	94·3	89·4	10·4	− 0·2
3	1·77	86·4	84·8	75·2	26·1	+ 1·3
4	1·60	73·5	72·8	58·4	42·0	+ 0·4
5	1·54	68·3	68·0	52·5	47·9	+ 0·4
6	1·52	66·5	65·5	50·0	50·8	+ 0·8

They do, however, well illustrate the principle, and in the case under consideration the figures for the copper percentages show values which are in close agreement with those obtained by analysis.

The same type of treatment can be followed with other alloys. The process is of use in experimental work in which the conditions of deposition can be kept in the region of those required for quantitative deposition, though these conditions are far from being realized in the practical deposition of metals from cyanide and some other solutions.

Throwing Power of Brassing Solutions. These solutions of the cyanide type are usually good throwers. "Good" is a relative term, and does not mean perfect. Both cyanide copper and cyanide zinc solutions show good throwing power, but whereas in these cases lack of throwing power does not produce a marked change of colour between the prominent and recessed parts, there may still be differences in the thickness. With the brassing solution, however, the case is somewhat different. Differences in C.D. on the different parts will be accompanied, not only by differences in thickness of deposits, but also there will be a difference in composition, and, therefore, colour. Prominent parts will, therefore, tend to be whiter than recessed parts. This difference of composition has been experimentally confirmed by quantitative analysis. It is something to be avoided, and this can only be done by maintaining a larger distance between the anodes and work than would usually be allowed in the cyanide copper solution.

On this matter, however, there appears to be some divergence of opinion. Thus, Coats,* in a general survey of the subject of brass plating, suggests that on the inside of a bowl there was found a redder deposit than on the outside, and that this contained 44 per cent of zinc. This is hardly in keeping with our experience nor with general deductions.

Points about Electro-brassing. The desirable control of the current and therefore colour can best be effected by the use of a rheostat in the circuit. The amount of free cyanide should be watched. With too much, there will be much evolution of hydrogen with accompanying loss of metal deposit and also the tendency to blistering. Excess of free cyanide can be corrected by the addition of both copper and zinc carbonates approximately in the same quantities. Insufficient free cyanide will be seen by the formation of insoluble single cyanides on the anodes.

The solution can conveniently be contained in an iron tank, heat being applied by one of the several methods already indicated.

The colour of the brass is enhanced by the addition of small quantities of aluminium compounds. These can be added in the form of alum to the extent of 6 to 10 gm. per litre or 1 to 1½ oz. per gallon.

Where comparatively thick deposits of brass are required, recourse must be had to occasional scratch-brushing, and the solution kept as clean as possible to avoid the deposition of dirt, with its tendency to roughness. Further, while the colour may still be good, an excessive current will give rise to burning. The treatment of iron castings occasions some difficulty, due almost entirely to the poor quality of the metal. Deposits are often of a grey colour. Where possible, the surface should

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* *Trans. Electrochem. Soc.*, 80, 1941, 445.

be well scratched with a steel brush to disengage the small particles of loose graphite which occur on the surface, and further, if the work justifies the trouble, a thin deposit of tin or nickel will considerably improve the appearance of the subsequently deposited brass.

Generally the cathode efficiency is low. Moreover, the usual C.D. is also low. These factors lead to the production of relatively thin deposits in comparison with those of other metals. Low cathode efficiency may call for some adjustment by the limitation of anode surface, or the introduction of a proportion of insoluble anode such as iron. It is generally agreed that the first deposit contains a larger proportion of zinc, which soon decreases to that which is more normal for the type of solution.

Additions of arsenic are sometimes made to lighten the colour of the deposit. If in excess, the deposit will be of a pasty white colour. Nickel makes another possible addition with a view to whitening the deposit, but the control of colour is best achieved by a constant solution with variations in the operating conditions. Some metals are more difficult to brass plate than others. A copper strike removes this difficulty, but interferes with the analysis of the deposit were this may be required. In this case a strike of cadmium will supply the need. For continuous work, solutions should be kept filtered, and successful deposition requires a clean cathode metal.

Routine analysis should be resorted to periodically, though this is not so simple as in other depositing solutions. A little experience soon leads to reliable and comparable results.

Analysis of Brassing Solutions. Two schemes of analysis are required according to the composition of the solution—

1. For solutions containing the two double cyanides of copper and zinc with free cyanide, but no addition of ammonia or ammonium compounds.

(*a*) Estimation of free cyanide. This is carried out in exactly the same manner as for the copper cyanide bath (page 240).

(*b*) Estimation of copper. This again follows the same course as in the cyanide copper bath (page 240).

(*c*) Estimation of zinc. Take 10 c.c. of the solution. Destroy cyanide compounds with H_2SO_4 and HNO_3 as in the estimation of copper in the cyanide bath. Dilute with water. Add sodium carbonate to neutralize excess of acid, that is, until there is a slight green precipitate of copper carbonate. Add 10 c.c. dil. HCl and make up to 100 to 150 c.c. Pass H_2S for five minutes to precipitate the whole of the copper as black cuprous sulphide (Cu_2S). Filter into a conical flask, washing the precipitate with water into which H_2S has been passed. A clear filtrate will indicate the complete precipitation of the copper. From the filtrate boil off H_2S (testing with filter paper moistened with lead acetate solution which should remain without discoloration). Cool the solution to about 50° C. and titrate with standard potassium ferrocyanide solution as in the case of the acid zinc bath (page 331). The necessary calculation need not here be repeated.

The three essential constituents are thus readily determined.

2. For solutions to which ammonia or ammonium salt have been added—

(*a*) Estimation of free cyanide. This follows on the same lines as with the zinc cyanide bath (page 333) in which the total cyanide is determined by titration with silver nitrate in the presence of NaOH. This estimation gives the cyanide which is free together with that originally combined in the soluble double zinc cyanide constituent. The cyanide combined with the zinc is then calculated from the zinc present and thus the free cyanide is obtained. The cyanide combined with the copper compound is unaffected by the action of NaOH.

(*b*) Copper and zinc are separately estimated as previously described.

(*c*) Ammonia is estimated by the distillation method already described for the nickel solution (page 308). To do this, take 25 c.c. of the solution. Acidify with acetic acid, testing with litmus. Then add silver nitrate solution until there is no further precipitation of silver cyanide. This brings down all the cyanides in the form of insoluble silver, copper and zinc single cyanides. Filter with necessary washing into a flask fitted with distillation as shown in Fig. 85. Add 10 gm. of solid NaOH and distil off into 50 c.c. N/10HCl. Excess HCl is then titrated back with N/10 NaOH, so that the volume of N/10 HCl used to absorb the distilled ammonia is obtained. Each cubic centimetre of this N/10 HCl represents 0·0017 gm. NH_3 from which the amount of NH_3 in either the free or combined form is calculated.

Deposition of Bronze. What is often erroneously misnamed bronze-plating, but which is really a light-coloured brass deposit, is practised by taking a good copper cyanide solution and adding to it just sufficient zinc solution to give the required shade. Anodes of copper may be used, in which case frequent additions of zinc solution will be necessary. If, on the other hand, anodes can be used corresponding to the composition of the deposit there will be little or no need to make these zinc cyanide additions. Usually, however, copper anodes are employed.

The deposition of true bronze, an alloy of copper and tin, is not largely practised. It is not altogether easy to find compatible solutions from which the co-deposition of the two metals can be effected. Mixtures of double oxalates were originally investigated by Curry* and Treadwell and Backl.† More recently they have been more thoroughly explored by Mathers and Sowder.‡ One solution which gives satisfactory results is compounded as follows—

Copper solution.

Copper sulphate	1 oz.	6·25 gm.
Ammonium oxalate	2½ ,,	15·5 ,,
Oxalic acid	¼ ,,	1·5 ,,
Water	1 gal.	1 litre

Tin solution.

Tin protochloride	1 oz.	6·25 gm.
Ammonium oxalate	2 ,,	12·5 ,,
Oxalic acid	¼ ,,	1·5 ,,
Water	1 gal.	1 litre

The two solutions are separately prepared by dissolving the metallic compound and the ammonium oxalate in small quantities of water. Add the ammonium oxalate solution to the metal salt solution. In each case a precipitate of the single oxalate is formed. These dissolve by further addition of the ammonium oxalate. To each add the oxalic acid, and make up with water to the required bulk. Both solutions have the same metal content. They are now mixed in the proportion of two volumes of the copper solution to one of the tin solution, and worked, preferably warm, with an anode of the

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* *J. Phys. Chem.*, 1906, x, 516.

† *Z. Electrochem.*, 1915, xxi, 314.

‡ *T. Amer. Electrochem. Soc.*, 1920, xxxvii, 525.

same composition as that required in the deposit. The exact shade can be adjusted by the addition of one solution or the other, and also by suitably varying the current and other conditions on similar lines as with brass.

The deposition of copper-tin alloys from mixed solutions of sodium cuprocyanide and sodium stannate has been investigated by Baier and Macnaughtan,* who obtained with bronze anodes very satisfactory deposits under perfect control up to approximately 1 mm. in thickness.

The two compounds were present in a proportion which gave a metallic ratio of tin: copper :: 3·5 : 1. A C.D. of up to 50 amp./sq. ft. could be used, the composition of the solution being maintained by the use of anodes of the same composition as that of the required deposit.

Lead-Tin Alloys. The deposition of lead-tin alloys is not a common operation in electro-plating. In attempting it, difficulty was at first experienced in finding a solution from which the co-deposition of the metals could be effected, as each metal displaces the other according to the concentration of the solutions. Solutions containing the fluoborates of the metals were eventually worked with success, but as no satisfactory method could be devised for preparing a suitable tin fluoborate, the solution of the mixed metals was made by taking the usual lead fluoborate solution (page 395) and using in it a tin anode until sufficient tin has passed into the solution to give an alloy deposit of the required composition, which might be of the order of 50 per cent of each metal.

The tin anodes are withdrawn and replaced by anodes having the composition required in the deposit.

A C.D. of 7 amperes per sq. ft. was employed with the solution agitated. Very satisfactory deposits were obtained of fine grain and close texture, and sufficiently elastic to withstand expansion when the steel base was subjected to pressure.

The current efficiency is high, approaching 100 per cent. Under these ideal conditions it becomes possible to obtain a very good idea of the composition of the alloy deposit by a comparison of the weight of deposited alloy with that of either copper or lead deposited in the same circuit. For this purpose the lead fluoborate solution provides a convenient coulometer. As an example, let *A* represent the weight of lead deposited in

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* *J. Electrodepos. Tech. Soc.*, 1936, xi.

the coulometer and B the weight of tin-lead alloy. Let x represent the faradays depositing tin in the alloy. Now the chemical equivalents of lead and tin are 103·5 and 59·5 respectively. The weight of tin deposited is therefore 59·5x gm. For each faraday depositing tin, there is a decrease in weight in the alloy from that of pure lead of 103·5 – 59·5 = 44 gm. Hence—

$$A - B = 44x$$

or

$$x = \frac{A - B}{44}$$

Now the weight of tin deposited is—

$$59{\cdot}5x = \frac{59{\cdot}5\,(A - B)}{44}$$

and the percentage of tin

$$= \frac{59{\cdot}5\,(A - B)}{44} \times \frac{100}{B}$$

$$= \frac{135\,(A - B)}{B}$$

Hence, if in two baths in series the weights of lead and alloy are 100 gm. and 80 gm. respectively, the percentage of tin

$$= \frac{135\,(100 - 80)}{80} = 33{\cdot}8$$

These results are of sufficient accuracy for most work where some idea of the composition of the alloy in relation to the composition of the solution is required. For more accurate work, however, an analysis of the deposit by chemical methods would be necessary.

Of the two metals lead is the more easily deposited and constitutes the sole deposit until the solution contains a large proportion of the tin compound, and it is only when the tin and lead contents are in the proportion of 0·81 N and 0·19 N respectively, corresponding to 47·8 and 19·66 gm. of the metals per litre, or 71 per cent of tin reckoned on the total metal content of the solution, that the deposit contains the two metals in the same proportion as that of the solution. To maintain this composition in the alloy would necessitate the use of an anode of identical composition with the assurance of its complete solution. More often, however, it is necessary to deposit alloys with a much smaller content of the costly tin.

To produce the required deposit, a lead fluoborate solution is worked with a tin anode until the deposit contains (as found by analysis or by comparison with a lead coulometer) approximately the percentage of tin required. Du ing this process the solution is kept stirred. The tin anode is then replaced by one containing a somewhat smaller proportion of tin than that required in the deposit. For example, for a 50 per cent tin deposit the anodes should contain approximately 45 per cent of tin.

The refining of lead from the silico fluoride solution (page 394) while extensively practised, showed the possibility of the undesirable co-deposition of tin. This has now been turned to commercial advantage for the deposition of lead–tin alloys. In the lead solution, impure anodes containing from 50–85 per cent lead, 13–48 per cent tin and up to 10 per cent of impurities may be used to yield a pure lead-tin alloy deposit. No control of the composition of the deposit is carried out, but, after analysis, the alloy deposit can be melted down and blended to meet any required specification.

Lead-tin alloys have recently been applied in the deposited form to provide a bearing metal. The metals are, however, deposited separately, a subsequent heating bringing the two metals into the alloy form. In this application the bearings are first degreased and then cleaned electrolytically with subsequent rinsing. Lead is then deposited from the usual fluoborate bath (page 395) at room temperature, using a centrally-disposed revolving lead anode to ensure uniformity of deposit. Tin is then deposited from an alkaline bath—after rinsing from the lead solution—to a thickness of about 0·0001 in. Rinsing follows, first in cold water and then hot water, drying being done in warm air. The tin deposit is then fused into the lead deposit by immersion of the plated bearing in a bath of oil at 350° F. for one hour, the deposit then having a dull grey appearance.

Lead-Silver Alloys. A reference to the table of the hardness of metals reveals the fact that silver must be definitely regarded as a hard metal, one which therefore might find some application as a bearing metal. Its high cost could at once be offset by the use of relatively thin coatings, and these might be effectively made by deposition. The value is increased by the addition of a few per cents of lead, and so it is that the deposition of lead-silver alloys containing up to about 4 per cent of lead has been investigated with a measure of success. Further, it will be recalled that deposited metals are usually distinctly harder than in the cast or mechanically-worked form. This is an added advantage in the production of bearing surfaces by electrodeposition.

A solution for this purpose is—

Potassium cyanide . . .	22	gm. per litre
Silver cyanide	30	,, ,,
Potassium tartrate . . .	47	,, ,,
Potassium hydroxide . .	0·5	,, ,,
Basic lead acetate . . .	4	,, ,,

The solution is prepared by dissolving the silver cyanide in the potassium cyanide, and the basic lead acetate in a solution of the mixed potassium tartrate and hydroxide. Both solutions should be clear and can then be mixed.

The solution is operated at a temperature of 74° to 90° F., when dense and ductile plates with comparative smoothness are obtained with a current density of 5 to 15 amps./sq. ft.

With anodes cast in graphite moulds, and of the required composition of the deposit, the anode efficiency is slightly higher than that at the cathode, but this possible increase in metal content of the bath somewhat offsets drag-out loss, thus minimizing the need for the periodic addition of salts. Anode composition is practically the same as that of the deposit and the solution works consistently over long periods.

Aluminium Alloys. The possibilities of the production of aluminium alloy deposits have been investigated by Blue and Mathers* by the addition of compounds of the several metals to the usual aluminium bath containing aluminium bromide and chloride in ethyl bromide, benzene, or xylene. (See page 397.) These tests were attended by some measure of success, though the second metal was more usually worked into the solution from an anode.

Zinc Cadmium Alloys. These metals are capable of simultaneous deposition from solutions of their double cyanides with excess free cyanide, caustic potash, and addition agents.†

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* *Trans. Amer. Electrochem. Soc.* 1936, lxix, 529.

† Wright and Riley: *J. Electrod os. Tech* Soc., 1935, x.1.

There is the greater tendency for the cadmium to plate out, but reasonable control can be exercised by the use of an alloy anode with small additions of cadmium to the bath. The presence of more than 2 per cent of cadmium in the deposit has a marked whitening effect and the alloys generally have properties intermediate between those of the two metals.

Cadmium-silver Alloys. These alloys are known to have a markedly less tendency to tarnishing than silver alone, cadmium adding, to some extent, its permanence to the silver. It is, therefore, not surprising that numerous attempts have been made to deposit nearly stainless alloys of these metals, especially as both are separately deposited from cyanide solutions of simple types. So far no real success has attended the effort. The metals are too far apart electro-chemically to make control of the deposition easy. This can soon be verified by suitably mixing the two solutions and preparing a series of deposits. Further, the deposited alloy lacks the finish of pure silver, and these and other difficulties leave the problem in the region of the unsolved.

Possibilities of Alloy Deposition. The extensive use of alloys in industry seems to suggest that more might yet be done in the deposition of these products. In engineering, for example, not many metals are used in the pure state, enhanced properties resulting from controlled mixture with other metals. So far, very little use has been made of electro-deposited alloys, and there would seem to be justification for much more experimentation in this direction. Doubtless an attraction is that of the deposition of stainless alloys. So far, however, no great success has attended efforts in this direction. The cadmium-silver alloys have been referred to. Of still greater interest would be the possibility of the co-deposition of iron and chromium with the production of a deposit of stainless steel. Present methods are, however, not very hopeful. Iron is at present deposited entirely from ferrous solutions, and chromium entirely from chromic acid solutions, and these might be described as incompatible in that they cannot co-exist in the same solution. There would appear to be no reason why other solutions of chromium compounds should not again be explored, this time more fully and with the larger experience which modern methods of deposition have given. We might then hope for the simultaneous deposition of the two metals from solutions compounded from ferrous and chromium salts, which are stable in the presence of each other.

Assuming this to be some time achieved, there will then be the problem whether any advantage accrues to the new method when compared with all the advantages which are already common experience with the present methods of chromium deposition.

CHAPTER XXII

THE TESTING OF ELECTRODEPOSITS

INTRODUCTION—General methods—Adhesion—Thickness—Determination of thickness—Stripping methods—The jet test—Mesle chord method—Brenner magnetic test—Knight permeability method—Hardness—Porosity—Special methods of testing porosity

Introduction. Recent developments in electrodeposition with ever increasing ranges of application have necessitated stricter control over the different types of deposit for, sometimes, very different purposes. Apart from mere appearance or decorative effect, electrodeposits are required to increase endurance against either corrosive influences or wear and tear. In previous chapters reference has been made to the imposition of specifications for these deposits. Considerable difficulty must arise with any attempt to reduce such specifications to a minimum, and many suggestions have been made for the desirable thicknesses of deposited coatings to meet particular needs. Doubtless in the course of time these requirements may be brought within narrower limits and suitable specifications then drawn up. In any case, specifications imply some means of checking that deposits shall conform to them. At the time of writing, methods of control of deposits are far more exacting than specifications, and it is to the testing of metallic deposits that we must now give a little attention.

General Methods. In any case much work is and will for a long time continue to be approved by the simple process of inspection, while samples from batches will be withdrawn for more exact treatment. Among the requirements will be those for testing adhesion, hardness, thickness and freedom from porosity. Some of these tests may be of a qualitative character while stricter supervision will at times call for quantitative methods of testing. In any case a large proportion of relatively thin deposits must be passed and accepted without anything in the nature of exact testing, but these more precise methods will find increasing application in industry and also when new methods of deposition are being investigated.

Adhesion. In by far the larger number of cases of deposition adhesion will definitely count, and this is a property in which there must be of necessity much room for individual assessment in the absence of more exact methods of measurement. The matter has, however, been successfully tackled from the quantitative point of view. A few of the methods available will be briefly reviewed.

(1) A simple yet effective method requires no more elaborate apparatus than the back of a penknife or similar piece of metal. An inconspicuous part of the deposit is rubbed backwards and forwards by the applied metal with a little pressure. No impression is made on a deposit which adheres well, but with one of poor adhesion small blisters will develop. Such rubbing accentuates poor adhesion to such an extent that soon the deposit and base metal part company. Personal judgment plays a large part in deciding the degree of adhesion.

(2) A more exact method devised by Hothersall* calls for a relatively thick deposit usually of nickel of the order of two to three hundredths of an inch, this being formed on a piece of brass about two inches square. The outer margins of relatively rough deposit are first sawn off, the edges being filed smooth. The plate is gripped in a vice and a chisel point inserted between the deposit and brass. The deposit is thus turned outwards and possibly flattened forming a tongue which can be gripped with pliers and thus pulled away from the basis metal. Alternatively, if there is difficulty in inserting a chisel, a cut is made on one side of the deposit and the sample bent through an angle of 90 degrees.

In either case poor adhesion is evidenced by the easy separation of the deposit, leaving the basis metal relatively smooth and free from deposit. Strong adhesion will be shown by a sharp fracture of deposit and basis metal, and where the deposit can be torn away it will bring with it some of the surface of the basis metal so that the brass is torn rather than the two metals separated.

(3) While such qualitative methods are of value in providing useful indication of the success of the plating process, more exact scientific testing is needed, if possible, of a quantitative character. Adhesion may then even be expressed in terms of the pull of tons per square inch to effect the separation. These requirements are met in the Ollard† method

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* *J. Electrodepo. Tech. Soc.*, **1932**, vii, **115**.

† *Trans. Far. Soc.*, **1926**, *21*, **81**.

(Fig. 91), in which a small cylinder of base metal is taken and stopped off so as to leave one circular end and a small distance along the length to receive the deposit. This stopping off can be done with wax. A minimum thickness of about one-tenth of an inch or more of electrodeposit is now made since the method is not applicable to thin deposits. A little of the deposit may grow over the edge of the wax, the general appearance being represented in (*b*). The wax is removed and the deposit machined to the form shown in (*c*). This is now placed in a support as shown in (*d*) and pressure applied to effect separation on the overhanging part of the deposit resting on the cylindrical support, and force applied to the cavity until the deposit is torn from the cylinder. The applied force is measurable and so also is the area of the end of the cylinder remaining after the machining. From these data, the force required to bring about separation may be expressed in lbs. or even tons per sq. in. Some surprisingly high figures have been revealed by this method and many examples showed that, by careful attention to the preparation of the surface before the application of the deposit, it frequently happened that basis metal was torn away with the deposit rather than the deposit being detached from the basis metal.

A more recent review* of the process has shown that with accurate machining of the test piece there is a closer approach to tensile separation, and that the sometimes very high figure (in one case of 60 tons per sq. in.) is due to the continuation of the crystal structure of the basis metal by the growth of the deposited nickel. In such cases the deposit is held to the basis metal by atomic forces.

Thickness. This is obviously an all-important property and for at least three reasons: (1) It has been definitely established that there is a relation between thickness and porosity, increasing thickness diminishing porosity, so that in order to obtain minimum porosity there must be some minimum thickness. (2) Naturally too, increasing wear will accrue to increased thickness other conditions being equal, while (3) on account of the very poor throwing power of a number of solutions there is, in consequence, very uneven distribution of current and wide variations of thickness. Some knowledge

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* *Metal Industry*, 13th June, 1941.

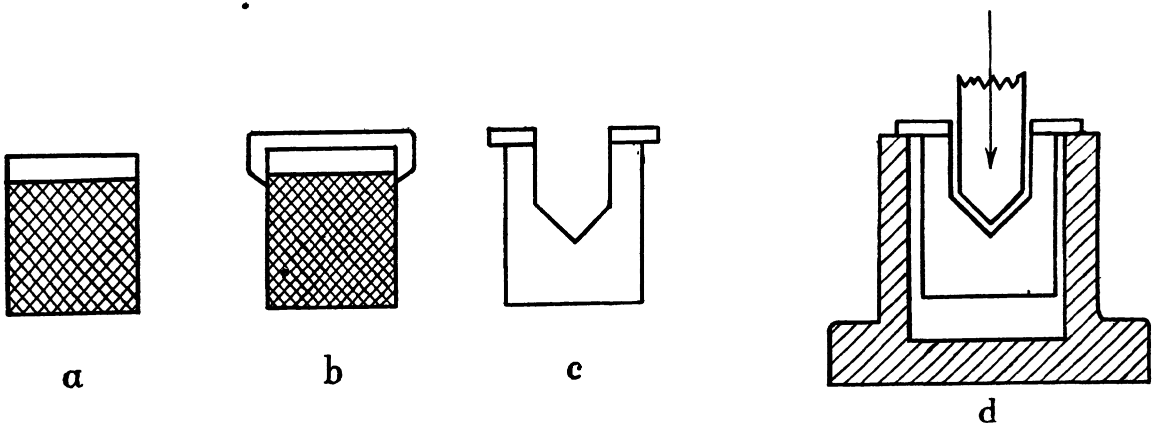

Fig. 91 Ollard Adhesion Test

of thickness thus becomes essential. Further, in the case of the precious metals an idea of thickness is useful.

In devising methods for this purpose it is desirable that (1) these should be as simple as possible and not involve expensive or complicated apparatus, (2) they should not damage the article more than is absolutely necessary, and (3) they should take into account variations of thickness.

DETERMINATION OF THICKNESS

(*a*) **Direct Measurement.** Such methods involve making sections of the deposits, mounting them in Wood's metal or Bakelite and measuring the thickness under a metallurgical microscope using a magnification which may need to go up to 250 diameters. The disadvantages of this method are that the article is damaged and also that relatively expensive apparatus is required with the application of considerable technique. Further, soft deposits flow during polishing, leading to indefinite boundaries. Against these must be set the great advantage that the method is absolute and is applicable to composite coatings.

(*b*) **Chemical Stripping Methods.** These methods involve taking a sample of given area and dissolving off the deposit by means of some reagent which does not attack the basis metal. The amount of metal removed can be ascertained either by loss of weight or, more tediously but more accurately, by the analysis of the solution formed. Accuracy in the measurement of the area thus treated is essential, and from the weight of metal removed the thickness can be easily calculated.

For the stripping process a number of reagents are available. For example, chromium may be removed by cold dilute HCl or hot dilute H_2SO_4. Tin, cadmium and zinc are readily removed by immersion in a strong HCl solution containing antimony chloride. This reagent is generally made by dissolving 20 gm. of antimony oxide in a little conc. HCl and adding the solution to a litre of the strong acid. Silver is removed by immersion in a mixture of conc. H_2SO_4 and conc. HNO_3 in the proportions of 19 to 1 by volume, the mixture being kept at 80° C. The application of these reagents together with some needful preparation of the specimen and the final rinsing and drying of the metal are points which should not require emphasis here.

A simple calculation then serves to show that—

0·0001 in. of chromium weighs 0·0113 gm. per sq. in.
0·0001 in. of zinc ,, 0·0113 ,, ,,
0·0001 in. of cadmium ,, 0·0142 ,, ,,
0·0001 in. of tin ,, 0·0118 ,, ,,

from which table, thicknesses of any deposit can be obtained from the weight of metal removed by a simple calculation.

Similarly, the following formulae may be used for calculating thickness from the weight of metal removed—

$$(1)\quad \frac{\text{Wt. coating (oz.)} \times K_1}{\text{Area (sq. in.)}} = \text{Thickness (inch)}$$

$$(2)\quad \frac{\text{Wt. coating (gm.)} \times K_2}{\text{Area (sq. cm.)}} = \text{Thickness (cm.)}$$

$$(3)\quad \frac{\text{Wt. coating (gm.)} \times K_3}{\text{Area (sq. cm.)}} = \text{Thickness (inch)}$$

the values of the constants K_1, K_2 and K_3 being given in Table LXVIII.

TABLE LXVIII

CONSTANTS FOR THICKNESS OF DEPOSITS

	K_1	K_2	K_3
Cadmium	0·201	0·116	0·0458
Chromium	0·243	0·141	0·0554
Copper	0·195	0·112	0·0443
Nickel	0·195	0·112	0·0443
Silver	0·165	0·095	0·0375
Tin	0·237	0·137	0·0539
Zinc	0·243	0·141	0·0554

These constants embody the relative weights of equal thicknesses of the various metals.

Variations on this principle are capable for individual metals. Thus in the case of—

(1) **Zinc** the deposit is readily removed by immersion in a solution of lead acetate which should be almost saturated, and the free acid removed by shaking with lead oxide and filtering. A measured sample of the plated metal is cleaned and weighed. The zinc dissolves, depositing an equivalent weight of lead. The completion of the process is shown by the

surface of the metal remaining unaffected. After rinsing and drying, the specimen can be reweighed to ascertain the loss in weight, and therefore the average thickness, by calculation.

Three pieces of hot galvanized steel were submitted to this process with the following results—

Weight before	20·765	20·904	20·302 gm.
,, after	19·621	19·690	19·099 ,,
Loss	1·144	1·214	1·203 ,,

The small plates were 2 in. by 1½ in. Adding these losses together and taking the area of the three pieces on both sides the weight per foot super becomes—

$$\frac{3\cdot561 \times 144}{2 \times 2 \times 1\frac{1}{2} \times 3 \times 28\cdot4} = 1 \text{ oz. approx.}$$

A further method for zinc is that of immersing the cleaned and weighed specimen in a solution containing—

Ammonium persulphate . .	5 gm.
Ammonia (·880) . .	10 c.c.
Water to	1 litre

With stirring, the deposit will be dissolved off in the course of 30 minutes after which the specimen is rinsed, dried and weighed. Then—

$$\text{thickness (inch)} = \frac{\text{loss in weight (gm.)}}{\text{area (sq. in.)} \times 113}$$

A simple calculation based on the examples on page 427 will show how the figure 113 is derived.

(2) **Cadmium.** A convenient method of testing the thickness of cadmium deposits is that of taking a small smooth steel rod of 2 in. length and half an inch in diameter. A fine hole is bored through at one end in order to allow of convenient wiring. This is cleaned and weighed and plated with a batch of work which is being tested. When deposition is finished the test piece is washed, dried and reweighed. From the increase in weight the thickness of the deposit is readily obtained thus—

The surface of the test piece can easily be calculated to be practically 3·5 sq. in. One mil of cadmium on this surface represents—

$$\frac{7}{2} \times \frac{1}{1000} \times \frac{16\cdot4}{1} \times \frac{8\cdot6}{1} = \cdot5 \text{ gram.}$$

In any test therefore each ·5 gram of cadmium on the test piece represents a deposit of one mil. The cadmium deposits are then easily removed by a few moments immersion in hydrochloric acid containing antimony chloride.

A further test for the thickness of cadmium deposits follows the same lines as that for zinc (page 427) when—

$$t\text{ in.} = \frac{\text{loss (gm.)}}{\text{area (sq. in.)} \times 142}$$

(*c*) **The Jet Test.** By far the most reliable method for quick determination of thickness of deposit is the so-called B.N.F. jet test due to S. G. Clarke,* in which a continuous stream of a liquid reagent is allowed to impinge upon the surface of the deposit and the time noted to produce perforation. This test necessitates calibration by the production of a series of curves relating the thickness of the deposit with the times of perforation at different temperatures.

The apparatus, now in a very standardized form, is shown in Fig. 92. The specimen to be tested is first freed from grease and mounted in an inclined platform. On to it the special reagent is allowed to flow as a continuous stream, the time required to eat through the deposit being noted. Quite obviously the rate will depend upon a number of conditions, including the nature and strength of the reagent, the rate of dropping, the temperature, etc. There is consequently the need for the calibration of the method against a number of deposits of accurately known thickness. This calibration is expressed as a number of curves from which thicknesses are readily computed from the times required for perforation of

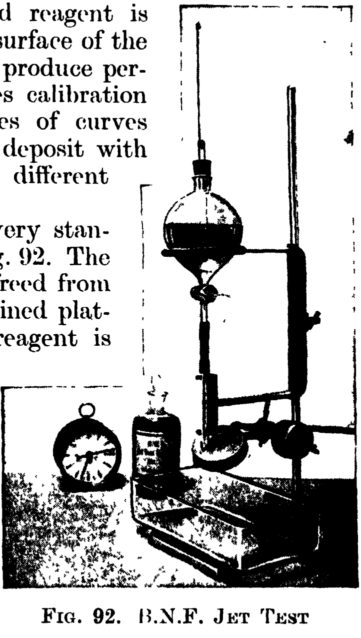

FIG. 92. B.N.F. JET TEST

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* *J. Electrodepos. Tech. Soc.*, 1937, xii, 1.

deposits under definite conditions. Details of the use of the apparatus are supplied with individual sets and given also in the original paper referred to. This jet-test marks an advance on a somewhat similar method of applying a stream of drops to the test piece.

Etching reagents are a matter of investigation, and some of these are given herewith—

(1) Cadmium—

Ammonium nitrate . . .	110 gm.
Hydrochloric acid . . .	10 c.c.
Water to	1 litre

(2) Zinc—

Ammonium nitrate . . .	100 gm.
Hydrochloric acid . . .	55 c.c.
Water to	1 litre

An alternative solution for zinc and cadmium deposits proposed by Brenner is as follows—

Chromic acid (CrO_3) . . .	200 gm.
Sulphuric acid	50 ,,
Water to	1 litre

To it is added a small amount of potassium ferricyanide. Results obtained with this reagent checked very closely with those obtained gravimetrically by the antimony chloride method.

In an example for zinc and cadmium, this reagent is applied at the rate of 100 drops per minute (1 drop = ·05 c.c.) on to the deposit until it is penetrated. The time for penetration is a measure of the thickness by the use of a factor derived from careful tests on deposits of known thickness. The thickness of coating in hundred thousandths of an inch is derived by multiplying the time for penetration in seconds by the following factors for different temperatures—

TABLE LXIX

° F.	Factors.	
	Zinc	Cadmium
70	0·97	1·31
75	1·01	1·37
80	1·06	1·43
85	1·11	1·50

(3) Silver—

The solution proposed by Hammond* for this purpose is as follows—

Iodine	7·5 gm.
Potassium iodide	250 ,,
Water to	1 litre

The solution is prepared and filtered through asbestos pulp in a Gooch filter and then by titration with a standard thiosulphate solution reduced to a strength of 14·65 ÷ 25 N/10.

(4) Nickel, cobalt, copper, bronze and composite nickel-copper-nickel coatings—the solution contains—

Ferric chloride ($FeCl_3 . 6 H_2O$)	300 gm.
Copper sulphate ($CuSO_4 . 5 H_2O$)	100 ,,
Distilled water to	1 litre

while a somewhat similar solution with an addition of antimony chloride is suitable for the special case of copper deposits on steel.

In all cases special attention must be paid to the form of the tube from which the drops of reagent are produced and exact specifications have been drawn up and must be adhered to. Details will be found in the relevant literature to which references are made.

The method is now applicable to deposits of most metals including nickel, copper, zinc, cadmium and silver. Generally the conditions of the test are adjusted so that one second of dropping is equivalent to one hundred-thousandth of an inch of deposit.

There are also variants of this dropping method. In one, the thickness of chromium deposits is determined by dropping conc. HCl and noting the time from the commencement of gassing to the removal of the deposit each second corresponding to one millionth of an inch of deposit.

The thickness of alloy deposits can be determined with a fair degree of approximation by the loss of weight method. Thus in the case of brass the specific gravity may be taken as roughly 8·3. By chemical stripping the loss of weight and area are known. Then—

$$\underset{\text{(sq. in.)}}{\text{Area}} \times \underset{\text{(in.)}}{\text{thickness}} \times \underset{\text{(cc. per cub. i .)}}{16{\cdot}4 \times 8{\cdot}3} = \underset{\text{(gm.)}}{\text{Wt.}}$$

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* *J. Electrodepos. Tech. Soc.*, 1940 xvi 9

from which

$$t\ (\text{in.}) = \frac{\text{Wt. (gm.)}}{\text{area} \times 16{\cdot}4 \times 8{\cdot}3}$$

and

$$t\ (\text{mils}) = \frac{1000 \times \text{Wt.}}{\text{area} \times 136}$$

$$= \frac{7{\cdot}35\ \text{Wt. (gm.)}}{\text{area (sq. in.)}}$$

The only difficulty is that of knowing the specific gravity of the particular composition of the alloy deposit under test.

(*d*) **The Mesle Chord Method.** This consists of just grinding through the deposit with (1) a flat grinder such as a file on on a curved surface or (2) a curved grinder such for example as a precision wheel of known radius on a flat surface. This serves the purpose of first magnifying the thickness of the deposit. Where a file is used, it must be kept flat and not allowed to rock. The method is not applicable to concave surfaces. Without discussing the geometrical properties of the surface produced it may be simply stated that as in Fig. 93 the thickness in the case of a circular grinding wheel is deduced from the following formula—

$$T = \frac{C^2}{8R}$$

where R = radius of the wheel and C the distance across the ground surface. The accuracy is of the order of 10 per cent but the method is not suitable for thin deposits of less than ·0002 inch.

(*e*) **The Brenner Magnetic Test.** This is designed for magnetic deposits such as nickel on non-magnetic base metals such as brass. A magnet is suspended and supports the deposited test piece. The magnetic pull is proportional to the mass of the nickel and therefore to the thickness of the deposit. It is necessary therefore to determine the pull required to effect separation and compare this with standard pulls previously determined against deposits of accurately known thickness. It will be noted that many of these calibrated methods provide rapidity combined with an accuracy which has previously been assured in the carefully conducted calibration tests.

There is, however, some variation in the magnetic properties of nickel deposited under different conditions, but these properties are made much more uniform by annealing them at 400° C. before testing.

The Knight Magnetic Permeability Test. This to some extent reverses the previous process, determining the thickness of non-magnetic coatings on magnetic base metals by the reduction of the magnetic flux due to the coating. This "flow" of magnetic current is produced between pole pieces and the magnetic base metal. The principle is developed in the form of an instrument which by calibration yields easily interpretable figures. The method has been successfully applied to the determination of coatings of enamel and of tin.

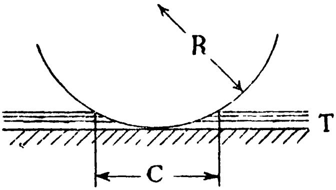

FIG. 93. MESLE CHORD TEST

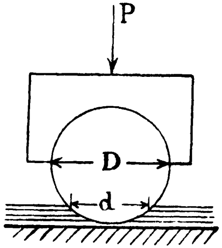

FIG. 94. BRINELL TEST

Hardness. Quite a lot of useful work has been done on the hardness of electrodeposits. In the early days quick and rough reliance was placed on such simple qualitative tests as scratching the deposit with, in the case of very soft deposits, the finger nail, or for harder deposits, a file. Such a method was obviously deceptive as a very thin deposit of a hard metal on a soft base such as lead might easily show an apparent scratch with the finger nail due to the yielding of the soft metal underneath the deposit.

Metallurgical practice has called for much quantitative work on hardness, a property not easily definable but nevertheless all-important. In general, hardness may be defined as resistance to deformation, yet that shown in the production of a scratch by a diamond point under some pressure may be markedly different from that of the resistance to the indentation of a hard steel ball of known diameter again under pressure. The diamond scratch method was first employed by Prof. T. Turner in his sclerometer, while the ball method was devised by Brinell.

The Brinell method will be appreciated from Fig. 94 in which is shown a hard steel ball which may be either one centimetre or one millimetre in diameter being pressed into the relatively thick deposit. Under similar conditions there is little indentation with hard deposits and larger "dents" in softer deposits. The method has been very thoroughly tested out, the two chief items required for the expression of the hardness being the surface of the indentation and the pressure producing it, together with the diameter of the ball. A hardness number is thus obtained representing the load per unit surface of the spherical indentation. This is referred to as the Brinell number (B.N.) and is obtained thus—

$$\text{B.N.} = \frac{\text{load}}{\text{spherical area of depression}}$$

$$= \frac{P}{\frac{\pi D}{2}(D - \sqrt{(D^2 - d^2)})} \text{ Kg./mm}^2$$

where—

P = Load in kilograms
D = Diameter of ball (mm.)
d = Diameter of depression (mm.)

More recently a difficulty arose from the fact that a steel ball does not produce a desirably sharp outline of indentation with heavy loads, some of the metal being pushed upwards and producing a curved edge, adding to the difficulty of measuring an exact diameter of the depression. The ball has therefore, in another instrument, been substituted by a carefully shaped diamond which gives a sharp outline. Results obtained by this method are referred to diamond point numbers (D.P.N.) and the method is finding increasing adoption in the field of research on the hardness of electrodeposits.

While no great difference is observed between the values obtained by the two methods in the smaller values, some divergence is observed with the larger values. The generally accepted values of a number of metals and deposits are shown in Table LXX.

TABLE LXX

HARDNESS OF METALS AND DEPOSITS

Metal	Annealed B.N.	Hard Rolled B.N.	Cast B.N.	Electro-deposited
Soft brass .	60			
Mild steel .	130			
Silver . .	25	68	30	61–79 matt B.N. 130 bright B.N.
Platinum .	47	97	50	606–642 D.P.N.
Palladium .	48	109	52	387–435 hard 190–196 soft D.P.N.
Rhodium .	101		101	594–641 D.P.N.
Nickel . .	70-90	90–300	70–90	155–429 B.N.
Chromium .			91	500–900 B.N.

B.N. = Brinell number.

D.P.N. = Diamond point number.

At least one comment must be made on the high values obtained for electrodeposits, these in some cases considerably exceeding the values for the same metals in the cast or wrought condition. This would appear to be due to the method of building up the deposit from an infinite number of atomic starting points with the production of very fine crystal structures with accompanying hardness.

Porosity. This is an all-important property in view of the fact that the degree of protection from corrosive influences depends to a large extent upon the lack of pores. It is, moreover, obvious that such metals as iron and steel which corrode easily will require more effective protection than non-ferrous metals such as copper and brass.

The methods of protection have already been discussed briefly on page 66. Here we have to deal only with the effect of porosity, and for this some definite and if possible quantitative tests will be required.

Such tests should—

(1) Clearly reveal porous sites,
(2) Not attack the coating itself,
(3) Be simple, rapid and cheap,
(4) Suitable for flat or curved surfaces,
(5) Be non-destructive,
(6) Be capable of easy recording and interpretation, and
(7) Be applicable to composite coatings.

Preliminary operations involve the removal of all grease films and this can most effectively be done by means of some liquid or vapour solvent as trichlorethylene or carbon tetrachloride, as grease most usually collects in pores. (It will be recalled that the application of lanoline in the anodic oxidation of aluminium (page 444) is designed to fill up such pores, if any, in the oxide coating.) This may appropriately be followed by cathodic cleaning in a weak alkaline solution such as a 1 per cent sodium carbonate, followed by thorough rinsing. Subsequent to these operations a number of tests are then available such as—

(*a*) *The Salt Spray Test.* This test is in extensive use, particularly for zinc coatings.

Specimens for examination are submitted to an atmosphere simulating marine conditions by the continuous or intermittent fine spraying of an enclosed atmosphere with a 20 per cent salt solution, the comparative endurance of the specimen being measured by the period of exposure without revealing weak spots and also the general type of the weakness thus revealed. As an accelerated test this apparatus might well be much more extensively employed in works in which continuous and intelligent use would yield comparative results with a good degree of trustworthiness, even though the system may not attain the status of scientific investigation. The simple type of apparatus is shown in Fig. 95, in which the specimens are conveniently mounted on glass supports.

The 20 per cent salt solution has a Sp. Gr. of 1·15 and is sprayed to form a dense fog, but not directly on to the specimen. A constant temperature of 95° F. ± 5° F. is maintained and the solution drained away and not used continuously.

(*b*) *Rusting or Exposure Test.* This consists of submitting the sample to atmospheric exposure. It thus shows the behaviour of the specimen under actual conditions of service, but involves long time and is therefore not suited to rapid testing. It is available for most coatings but especially for zinc, cadmium and tin.

(c) *The Hot Water Test.* This has been designed more particularly for tin coatings. It consists in immersing the sample in distilled water with a slight acidity of pH 4 to pH 7 at a temperature of 95° to 100° C. but not actually boiling, for about 6 hours. The water should contain practically no solids and should be contained in a tinned copper vessel. From this treatment some qualitative idea of the degree of rusting can be obtained.

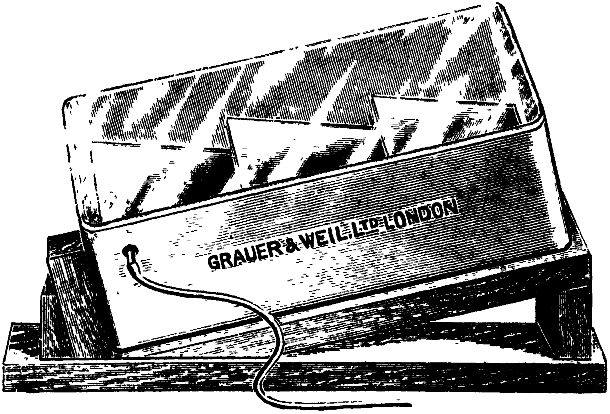

FIG. 95. SALT SPRAY BOX

(d) *The use of Test Papers.* This is more generally known as the "ferroxyl" test and consists in applying a piece of porous paper soaked in a potassium ferricyanide solution to the article to be tested and allowing contact for about 10 minutes. The presence of iron through, for example, a defective nickel deposit is detected by the formation of blue spots on the test paper. It will be realized that this provides some quantitative idea of the porosity in that on a given area it may be possible to actually count the spots and thus derive some knowledge of their number and location.

For this purpose the following mixtures have been used.

	NaCl	$K_3Fe(CN)_6$	Gelatine	Agar-agar
1907 Walker's jolly	10	1	20	
1927 Pitchers paper	60	6		30
1933 Macnaughtan	10	5		
1934 U.S.A. Bureau of Standards—				
(A)	60	0·5		
(B)	60	0·5		10

A large number of photographs of these papers after application in various tests have appeared in publications dealing with corrosion.

Some sort of quantitative expression can then be made by taking the reciprocal of the number of spots on a given unit area or, alternatively, of dividing this number into 100 so that

$$\text{Resistance to corrosion} = \frac{100}{\text{No. spots per unit area}}$$

Special Methods for Testing for Porosity. With so large a variety of deposits on different base metals special porosity tests become necessary and are available. They are not altogether capable of simple classification. Among them are—

(*a*) *For Zinc on Steel.* A test may be made by immersing the zinc plated steel in a 10 per cent solution of caustic soda at 70° C. and noting where bubbles of hydrogen appear. The test can only be a rough one.

(*b*) *For Cadmium on Steel.* This may be done by immersing the cadmium plated steel in a 1 per cent HCl solution for 10 minutes when bubbles of hydrogen will appear at the pores. The test is non-destructive as the test piece may then be washed, rinsed and dried.

(*c*) *Deposits on a Copper or Brass Base.* For this purpose use is made of the ferroxyl test substituting potassium ferrocyanide in place of the ferricyanide. Any attack on the copper is attended by the formation of brown copper ferrocyanide spots but the test cannot be regarded as so sensitive as in the case of iron and steel.

(*d*) *Zinc Base Die-castings.* Pores in the coatings on these metals will be revealed by immersion in a 10 per cent solution of caustic soda at 70° C. when bubbles of hydrogen will appear at points where the zinc base metal is exposed. Alternatively the specimen is immersed in a slightly acid solution of copper sulphate for 10 minutes. It is rinsed and exposed to H_2S, when dark spots of copper sulphide appearing will indicate the exposed points on the zinc base metal.

(*e*) *Porosity of Chromium Deposits.* Chromium deposits are well known to be very thin and porosity takes the form of very fine cracks. These may be revealed by—

(1) Copper plating. Chromium deposits are covered with thin films of oxide which, while not visible, are not capable of receiving a coat of copper from the sulphate bath. Any attempt to plate such a porous deposit will result in the deposition of copper on the exposed nickel base between the cracks of the chromium deposit. These fine lines of copper deposit can usually be seen with the naked eye, but a quantitative test involves the use of a standard acid copper sulphate solution with known electrical conditions, when the current passing will be a measure of the exposed surface through the cracks.

(2) A di-methylglyoxime test, in which the article is pickled in a very weak nitric acid and after rinsing a "ferroxyl" paper impregnated with dimethylglyoxime solution is applied, and will show up the exposed nickel as pink spots or cracks.

CHAPTER XXIII

ALLIED PROCESSES

ALUMINIUM—Deposition on aluminium—Anodic oxidation—Chromic acid process—Sulphuric acid process—Dyeing of anodic deposits—Protection of magnesium alloys—Electrolytic polishing—Production of detachable deposits—Silvering non-metallic surfaces—Stopping off—Parkerizing—Bonderizing

CLOSELY allied to the general processes of electro-deposition are a number of operations of interest and importance. It will be convenient to refer to several having close association with the work which has been touched upon in the previous chapters.

Aluminium. The metal aluminium has occasioned considerable trouble to the electro-plater, and it is only recently that this metal and its several important alloys can be regarded as having been successfully plated. Prior lack of success was not the mere result of lack of effort. Many and varied have been the methods attempted to overcome what at first appeared to be insuperable difficulties attaching to the task. A keener appreciation of these difficulties and persistent effort to overcome them has now resulted in the successful plating of this metal on lines not at first considered as most promising of success.

Aluminium is, to some extent, a unique metal. It has presented difficulties in other departments of industry, difficulties which were only overcome by unstinted attention to fundamental principles and details of manipulation. The main stumbling-block is the presence, on the surface, of the very thin adherent film of oxide tenaciously clinging to the surface, and powerfully resisting the contact of two surfaces of the metal. This trouble long endured in the attempt to weld the metal, and the same cause is responsible for the difficulty in producing adherent deposits upon the metal.

Deposition on Aluminium. This is an interesting problem which merits some attention. Numerous have been the attempts to plate successfully aluminium and its alloys. Almost as numerous have been the failures to achieve the desired end. There are inherent difficulties attaching to the problem. These have to be systematically tackled. Haphazard methods can never be expected to solve difficult problems. The difficulties have been stated by H. K. Work* to be as follows: (1) Presence of an oxide coating on the metal; (2) high position of aluminium in the electromotive series; (3) presence of gas either in the metal or the plating on the metal; (4) failure of the aluminium to alloy with the plating; (5) attack of the aluminium by the constituents of solutions; (6) presence of impurities in the aluminium; (7) presence of pinholes in the deposit which allow subsequent corrosion; (8) difference of expansion of the aluminium and subsequent coating; (9) presence of solution retained in the pores of the metal; and (10) tension in the coating metal. Truly a formidable list!

A number of these difficulties will now be fully appreciated. They are not uncommon in other examples of electro-plating. Added to these are the very adherent nature of the oxide coating, the unusual rapidity with which the cleaned metal invisibly re-oxidizes, and the great reactivity of the metal in the electro-plating solutions, and also in contact with even microscopic proportions of solution retained after deposition. Yet another difficulty arises in the many different types of alloys which may be passed on to the electro-plater, who has no knowledge of their composition, and, therefore, the special treatment required. Some more than simple metallurgical knowledge is necessary to appreciate these differences.

Numerous and lengthy articles have, from time to time, been written explanatory of the several methods which are claimed as having given excellent results. Here it is intended to give but a few indications of methods by means of which there would appear to be some chance of overcoming these troubles. For this purpose mere laboratory experiments do not go far. Whatever success may appear to attend such experimental work must be subjected to the test of service, either chemical or mechanical, or both. Tests of corrosion are not everything. Mechanical tests, subjecting the plated metal to those distortions which accompany service, must necessarily be made, often with disastrous results. Finally, it should even be necessary to combine the two sets of conditions.

Among the earlier methods proposed for plating aluminium

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* *Trans. Amer. Electrochem. Soc.*, **1928, 53, 361.**

was that of subjecting the ordinary cleaned metal to the action of cathode hydrogen in a weak sulphuric acid solution; from this followed the obvious step of adding the metal to be deposited, and so catching the aluminium ere it had time to further corrode. The success of this method may be judged by its lack of application and the trend towards other methods, which do not make for large evolution of gas which may be retained by the metal. More recently, there has been the growing recognition that the composition of the metal is all-important. The different constituents require different methods of treatment prior to the metal finding its way into the plating solution. One of these elements, often unintentional, but sometimes definitely added, is silicon, which is not removed by ordinary pickling acids. The use of hydrofluoric acid here seems very desirable. Again, the extreme liability to reoxidation after cleaning and previous to plating, brief though the period may be, involves the use of some protective medium absolutely free from oxygen. The lower salts of some metals, such as manganese and iron—for example, ferrous chloride—have been proposed and used with some success. Ferrous chloride, however, must be strong, and moreover, it undergoes rapid oxidation itself by exposure. The liquid is, therefore, not altogether convenient. It is possible that the solution might be kept in the ferrous form by passing a current through it with iron electrodes. Further, at the plating stage a more active metal deposit, like zinc or nickel, would seem to be preferable to a less active one like copper. More success has attended the deposition of nickel in the absence of copper than in its presence. Further, deposits should be made in the absence of gas rather than in its presence. These are, at the best, only hints as to possible methods of attacking the problem.

An indication of a method which has been found satisfactory may be given. This consists in removing the grease by scouring with slaked lime, followed by pickling in hydrofluoric acid. With some alloys this may suffice for the cleaning, while, with others it may be necessary to scour lightly to remove loosened dirt or oxides of metals. In any case the metal is quickly plunged into a solution of ferrous chloride, which may be treated, from time to time, with sulphur dioxide to maintain it in the ferrous condition. Previous to plating in a nickel solution of the type recommended for the preliminary coat for chromium, the work is quickly rinsed in clean water, always retaining water upon its surface to prevent the free access of air. By this method very satisfactory deposits have been made which have also been satisfactorily chromium-plated.

From another point of view, however, the deposition of metals on aluminium and its alloys for protective purposes provides an attractive proposition. Zinc and cadmium deposits are recognized as satisfactory for this purpose. Moreover, where applied to this end, there is usually no occasion for the deposit to be smooth. Matt deposits from the bath are adequate. This at once admits of the preliminary sand-blasting of the base metals, a very satisfactory method of getting rid of the troublesome oxide coatings. In this application the grease is first removed, and, after sand-blasting, the work is immediately rinsed and transferred to the plating bath. The deposition of zinc and cadmium is accompanied by the advantage that in such solutions the very considerable electrochemical activity of aluminium is less conspicuous, and successful deposits are, therefore, more easily obtained than in the case of copper. The solutions for this purpose, however, should contain markedly less alkali than is usually permissible and desired. (See page 325.)

In this connection the following extract* may be of interest: "The main difficulty in the nickel-plating of aluminium is to obtain satisfactory adherence of the nickel to the aluminium. This has been solved by two methods: (1) A French process in which the article is cleaned with organic solvents, washed in a soda solution and then in pure water, and immersed in a nearly boiling solution containing 3·5 per cent ferric chloride solution (density 1·4) and 2½ per cent of 22° Bè hydrochloric acid. This covers the aluminium with a very adherent film of iron, and nickel-plating can then be easily effected electrolytically with baths containing nickel sulphate or chloride and another salt such as ammonium or magnesium sulphate. (2) An American process in which the article is treated with hydrofluoric and/or nitric acid, washed and nickel-plated in the usual manner. The best results are obtained by (1)."

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* From *Institute of Metals Abstracts*, July, 1936, vol. III, Pt. 7, p. 262.

Anodic Oxidation. The thin films of oxide which form on the surface of aluminium have at least one great advantage. They prevent further access of air, and thus inhibit corrosion, thereby maintaining the lustre of the metal. This advantage, however, is offset by the difficulty in its removal where this is required in order to get down to the actual metal to effect welding or adhesive plating. So successful is the oxide film in resisting further corrosion of the metal that it is not surprising that attempts—very successful, too—have been made definitely to produce such films, with their protective properties, by electro-chemical means. The process has come to be known as *anodic oxidation.*

Chromic Acid Process. Such a method was explored by Dr. Guy Bengough and Mr. Stuart, and attained large scale adoption, especially in all examples in which this metal and its alloys are used in aeronautical work.

The principle of the process is simple. Suitably cleaned aluminium, or its alloys, are made the anode in a 3 per cent solution of chromic acid at a temperature of about 40° C. The anode suspension must be by means of aluminium wire. Carbon provides a suitable cathode. The arrangement is put in a circuit with an available voltage of 60 or more. By suitable resistances a current is first passed through the bath, the aluminium being the anode as previously suggested. A P.D. of about 4 volts will be observed, but this immediately begins to increase slowly up to about 40 volts, at which pressure the current has automatically been reduced. The 40 volts is maintained over a period of 40 to 45 minutes. It is then increased to, say, 50 volts for a few minutes, after which the work is withdrawn, well rinsed, and dried. A dull deposit of aluminium oxide then covers the surface. It is adherent and protective. Its insulating properties have already been evidenced by the increase in P.D. to maintain a normal C.D. of about 3·6 amperes per sq. ft. For further protection the deposit is sometimes rubbed over with a soft duster smeared with lanoline.

For this process the metal does not seem to require special care in cleaning. A striking feature of the process, and one that might be anticipated from its nature, is the almost perfect covering power of the operation. With the usual plating processes, weak spots do not naturally tend to mend themselves, else there would be little use for the "doctor." In the anodic oxidation process, however, the film-covered portions of the metal are insulating, while exposed metal is conducting, and, therefore, there is naturally a concentration of current on the untreated portions of the surface. By reason of this, very remote and deeply recessed parts are completely covered. In fact the solution becomes a perfect "thrower" in the sense that the treatment gets down into the most minute crevices. Long tubes of narrow diameter are, therefore, easily anodically treated throughout their interiors. Would that we had such remarkable throwing power with the deposition of some of the common metals!

The method is largely used for all aluminium and alloys of this metal used in aircraft construction, and while it may not constitute the last word in the protection of aluminium it nevertheless goes further than any method previously devised for this purpose.

Alloys are similarly treated, among them duralumin. For this purpose it is necessary that there shall be some limit to the amount of the metallic addition, possibly of the order of 6 per cent, as most other metals are readily dissolved out under this treatment. If the metalic impurities or additions have dark oxides the film will be correspondingly darkened, but this need occasion no concern. The amenability of an alloy to the treatment is evidenced by the voltmeter reading. If this rises normally, as has been indicated, the process is proceeding. If, on the other hand, the voltage refuses to increase, it may be taken that constituents from the alloy are being dissolved out. Protracted treatment might then give rise to more normal behaviour, but the result can hardly be regarded as satisfactory.

These films are of appreciable thickness. By the use of hot hydrochloric acid vapour it is possible to remove the metal from them, as aluminium chloride is volatile, and so to obtain the oxide film free from the metal.

Sulphuric Acid Process. Alternatively, sulphuric acid varying in strength from 5 to 80 per cent may be used either with or without the addition of other compounds. These may comprise either active acids which are themselves capable of acting as electrolytes for anodic oxidation, for example oxalic acid, or alternatively, neutral salts of metals, for example aluminium sulphate. It should be noted, however, that this compound is bound to accumulate in the process owing to solvent action.

The C.D. employed may vary from 5 to 40 amperes per sq. ft. although the latter figure is seldom used in practice, the C.D. generally used being of the order of 20 amperes per sq. ft. Bus-bar voltages of 10 to 20 volts are necessary for this purpose. Although the current remains remarkably constant during the process, there is immediately an initial current "surge" which is much higher than the stable current which follows when the first layer of oxide is formed on the anode surface.

The oxide as it is formed increases the internal resistance, and the bath gradually warms up in consequence. It is therefore necessary to employ means of cooling the electrolyte to keep it at a comparatively low temperature.

There are very distinct differences in the operation of this bath from the chromic acid process. It has already been noted that the power operates at constant voltage while the chromic acid process necessitates continuous voltage increase. The latter is therefore a "batch" type of process while the sulphuric acid process is not, and the bath may be loaded at any time, irrespective of the presence of other work in the bath, while the time of treatment in the sulphuric acid bath is of the order of 20 to 30 minutes against not less than 60 minutes in the chromic acid process.

Further, the chromic acid process is unable to anodize aluminium alloys containing metals other than aluminium in excess of about 6 per cent, while the sulphuric acid electrolyte is not so sensitive to "impurities" in the alloy and can successfully anodize materials containing as much as 12 to 14 per cent of alloying metals.

Again, the type of oxide film differs in the two processes. The chromic acid film is characteristically opaque while that from the sulphuric acid process is translucent, and the hardness may vary considerably with the conditions employed in its production. The film may be so ductile that mild forming and pressing operations are possible with the treated sheet and it may also be so hard as to scratch glass.

A comparison of the several processes has been made by Willstrop and Sutton.* These investigators find that although

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* *J. Electrodepos. Tech. Soc.*, 1939, xv, 53.

some claim is made for the use of A.C. when used either alone or superposed upon D.C. for the sulphuric acid process, there appears to be no advantage in this method in the case of the chromic acid process. When applied in the sulphuric acid process there is less solution of the aluminium than with D.C. alone, while with the acid of 16 per cent concentration by volume, effective film formation occurs at lower voltages than those of the chromic acid or oxalic acid processes. In sulphuric acid, loss of metal is greater than with chromic acid, and amounts to 0·13 gm./dm.^{2} with aluminium and 0·033 gm./dm.^{2} for duralumin, while with the Bengough-Stuart process the corresponding figures are 0·004 to 0·007 and 0·010 to 0·023 gm./dm.^{2}.

A quick test for the efficiency of such anode films is that of putting the part as an anode in a circuit containing a flash-amp as source of current with a small lamp in circuit. An adequate coating will prevent sufficient current passing to light up the lamp, while, on the other hand, if the lamp lights up, it shows that there is an appreciable part of the surface inadequately oxidized and therefore functioning as an anode.

During steaming there is a definite absorption of water in a combined form, the bulk of which is retained in combination after heating to a temperature of 170° C. for several hours. Generally, however, no great advantage seems to accrue to the general properties of the chromic acid film by the process, though the protective properties of the oxalic acid film are enhanced by steaming.

Again, in the chromic acid process it has been shown that only 5 per cent of the film is produced during the first 15 minutes while the voltage is rising to 40, although 12 to 15 per cent of the total energy was consumed in this initial stage, an expensive one from the point of view of energy consumption.

Phosphoric acid solution of 3 per cent by volume of the 1·75 specific gravity acid also gives good films, but there is the serious risk of the solution of the metal.

Chemical examination of the oxide films gives them a water content varying from 1 to 6 per cent, much less than that required by the formula of the monohydrate ($Al_2O_3 . H_2O$). The forming process is attended by a loss of aluminium, part of which is directly converted into oxide while an appreciable amount passes into the solution. That some aluminium also passes into the solution by chemical action is shown by the presence of hydrogen in the oxygen evolved. The oxide film has a lower density than that of the metal and while only 60–80 per cent of the missing metal is converted into oxide, it may even be possible that some allowance must be made in the case of fine tolerances. Again, it is known that porosity of the film is diminished by treatment in boiling water with the formation of a larger proportion of the monohydrate the increased volume accounting for the closing of the pores. Finally, it may be stated that a similar oxidation can be effected in an oxalic acid solution of 3 per cent or thereabouts.

Dyeing of Anodic Deposits. Inasmuch as aluminium compounds are frequently employed as mordants in the dyeing of fabrics, there at once arose the possibility of decorative effects upon these oxide films produced electrolytically. It was soon seen that such deposits of aluminium oxide lent themselves admirably for this decorative work, and by immersion in suitable dyes very pleasing colour effects are readily attainable. Numerous dyes are available for this purpose, these being of the water-soluble type, in some cases, too, undergoing a change of colour in combination with the oxide film. Generally, it may be said that such colouring effects are best obtained on the newly formed films rather than after drying off, and in some cases the dyeing process can be carried out simultaneously with the production of the oxide film.

Such coloured films considerably increase the range, hitherto very limited, of colour effects on aluminium and aluminium alloy products. Where, however, dyeing is to be applied, there is greater need for preliminary cleaning to secure greater uniformity of colour.

Protection of Magnesium Alloys. Recently, the metal magnesium, on account of its extreme lightness (specific gravity 1·74), has come, in the alloy form, into extensive use in aircraft construction. The alloys most commonly used—and they are many—are those containing, in addition to the magnesium, aluminium and zinc, together with small additions of other metals. The range of these additions is extensive, and reference should be made to the literature* on the subject for details. These alloys, in common with those of aluminium, require some surface treatment to enable them to stand up against corrosive influences. A number of methods are now being applied to achieve this end.

Generally, the surface to be treated requires preliminary treatment in order to eliminate grease. Both acid and alkali solutions are used for this purpose. A 10 per cent cold nitric acid serves the purpose by repeated dipping and rinsing, though it occasions some etching, and this may be a disadvantage with accurately machined work, in which case a hot 2 per cent solution of caustic soda is to be preferred, but this again cannot be used if the component under treatment contains aluminium parts. The protective treatment is then affected in one or other of a number of solutions—

The chromate bath

Potassium dichromate	15 per cent
Nitric acid (1·42)	22 ,, ,,
Water	63 ,, ,,

The solution is used cold with a dipping period of from ¼ to 3 minutes.

This bath is capable of a number of variations.

The selenium bath

Selenious acid	10 per cent
Sodium chloride	0·3 ,, ,,
Water	89·7 ,, ,,

The solution is used cold with an immersion period of up to 15 minutes.

Electrolytic Polishing. The subject of electrolytic polishing has already been referred to in the cases of silver (page 254) and nickel (page 299). It is of comparatively recent origin and bids fair to justify further exploration. A survey of the subject has been made by Wernick,† who points out the pioneering work which came to be undertaken as a result of the more or less chance observation of the improved appearance of a number of metals by anodic etching. The fundamental principle as explained in the connection with silver seems to be that of the masking of depressed portions of the anode

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* *Magnesium: Its Production and Use.* Pannell. (Pitman.)

† *J. Electrodepos. Tech. Soc.*, 1943, *18*, 103-120.

surface, probably by the temporary formation of less soluble films, thus diverting the current to the more elevated, and therefore exposed, portions of the surface. Two immediate applications are possible. In the first, metallographic specimens have now for quite a long time been prepared for examination by this method. Obvious advantages are the less laborious process, together with the fact that the surface is not deformed, and the crystalline structure interfered with by the mechanical work involved in the usual polishing process. Once the apparatus is set up, the process is simple, and the time involved independent of the area of the surface required to be treated.

But the process has big possibilities in industry. Stainless steel, for example, is not readily amenable to the ordinary polishing processes, some limits being set by the available polishing compositions. The electrolytic process overcomes many of these inherent difficulties. Variations have been developed both in America and in this country. They employ fairly strong solutions of phosphoric or sulphuric acids to which the addition of some organic addition agent seems to be advantageous.

One such solution proposed by Uhlig[*] is—

Phosphoric acid	42% by weight
Glycerine	47% ,, ,,
Water . .	11% ,, ,,

The solution is used at a temperature approaching 100° C. with a C.D. of up to 80 amperes per sq. ft. Lower C.D's lead to a more anodic solution which is quite low at high C.D's, amounting to not more than 0·0005 in., so that dimensional tolerance limits may be adhered to. The temperature is a little against the process on account of the high rate of evaporation. The action of the glycerine is probably to form complex compounds with the acid of higher resistance in addition to some inhibitive effect.

Aluminium is another metal amenable to the electrolytic polishing process. Processes have been described by Pullen[†] and Ensor.[‡] They usually employ an alkaline electrolyte, this difference from other metals being probably due to the

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[*] *Trans. Electrochem. Soc.*, 1940, *72*.

[†] *J. Inst. Metals*, vol. 59.

[‡] *J. Electrodepos. Tech. Soc.*, 1942, *18*, 19.

amphoteric character of the metal. Sodium carbonate and sodium phosphate provide the chief constituents with a temperature of 150° F. or over, and C.D.'s of 50 to 60 amperes per sq. ft., for from 5 to 8 minutes. The film produced requires some protection, which is afforded by a further anodic treatment in a solution of sodium bisulphate, finally rinsing the product in hot water.

Production of Detachable Deposits. Some branches of electrodeposition necessitate the removal of the deposit from the surface upon which it is made, and a number of methods are available to effect this detachment.

1. GRAPHITE FILM. In electrotyping with wax the removal is readily effected by reason of the graphite conducting film.

2. CHROMATE METHOD. In lead moulding, immersion of the lead mould in a weak solution of potassium dichromate (1 gm./litre) produces a thin film of lead chromate which serves the same purpose. The dichromate method is available also for other metals.

3. SULPHIDE METHOD. In the production of copper sheets on rotating brass mandrels, separation is usually effected by wiping over the surface of the brass cathode with a solution of a sulphide, for which purpose the sulphides of potassium, ammonium, and barium are available. The sulphide film is conductive, but allows of the ready separation of the deposit from the basis metal.

4. WAX FILM. Quite an old method is that of painting over the surface of the metal cathode a thin film of a solution of paraffin wax in alcohol. The solvent dries off, leaving the merest film of wax which again does not hinder conduction but admits of the easy separation of the deposit.

5. SILVER IODIDE METHOD. This involves the deposition of a film of silver by immersion in a silver solution of composition corresponding to the ordinary silver-plating bath. A few minutes' immersion suffices. The deposit, after rinsing, is then treated with a weak solution of iodine resulting in the conversion of the silver film into silver iodide, upon which copper is easily deposited and from which it may be readily detached.

6. SILVER FILM. For many purposes it will be found that the silver film produced by immersion in the silver cyanide

solution provides an excellent means for the separation of deposits made thereon, without recourse to the addition of iodine. On both smooth and matt surfaces we have found this method to be both simple and very efficient. Even a matt copper deposit from the acid bath treated by this method, and the deposition of copper continued, admits of the separation of the second deposit without difficulty or tearing. The method may be made applicable to other metals by the prior formation of the merest film of copper by electrodeposition.

7. METAL FILMS of bright nickel or chromium offer effective methods of separation. In the case of chromium the separation all too frequently occurs during deposition owing to the stresses in the deposited metal.

Silvering Non-metallic Surfaces. A brief reference to the production of silver coatings on non-metallic surfaces to initiate electrodeposition is relevant here. Examples of the application of these processes are to be found in the production of parabolic reflectors for cinema projectors and heliograph mirrors. The process consists in silvering, by immersion, glass moulds of the required form, the silver deposit providing a conducting base for a subsequent deposit of copper of substantial thickness. When the copper deposit is removed the silver is attached to the copper, thus leaving the glass, and the silvered copper deposit is then rendered immune against tarnishing by a deposit of rhodium.

In an informative review of these silvering processes Hepburn* includes a number of well recognized formulae of the silvering solutions, of which one, using cane sugar as the reducing agent, is as follows—

Stock Solution A.

Cane sugar (loaf or granulated sugar)	100 gm.
Nitric acid (Sp. Gr. 1·22)	5 c.c.
Alcohol	200 c.c.
Water to	1 litre

Stock Solution B.

Silver nitrate	10 gm.
Water to	1 litre

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* *J. Electrodepos. Tech. Soc.*, 1941, xvii.

Stock Solution C.

Strong ammonia solution (·880) . .	200 c.c.
Water to	1 litre

Stock Solution D.

Potassium hydroxide	10 gm.
Water to	1 litre

From these the silvering solution is prepared by taking 200 c.c. of solution B ($AgNO_3$) and adding solution C drop by drop until the brown ppt. first formed (silver hydroxide, AgOH) just redissolves. An addition of 10 c.c. of solution D (KOH) is now made which again effects the pptn. of silver hydroxide the ppt. again being redissolved with the minimum amount of ammonia solution C, avoiding excess. To this prepared solution add 10 c.c. of solution A (sugar). The carefully cleaned glass surface is dipped into, or covered by, this solution, when silvering takes from 5 to 15 minutes. Such silver deposits are quite thin as compared with the usual electro-deposit and also involve loss of silver by the silvering of the containing vessel and also in the form of pptd. silver oxide.

This and similar processes first used in the silvering of glass, are applicable to the wide range of plastics now in considerable use and thus increase the range of electro-deposition on non-conducting surfaces.

Stopping Off. There are many examples in electrodeposition in which portions only of the work require to be plated. Others need to be shielded from deposition. Such examples cover both decorative and industrial purposes. This protection or stopping off is effected by the application of a coating of a material which needs to be (1) insulating, (2) relatively hard to withstand handling, (3) stable against the corrosive action of the solutions, and (4) subsequently easily removable.

For solutions not containing cyanides, an ordinary type of asphaltum varnish suffices. This is applied to the cleaned surface, taking care that the exposed parts do not become touched with the varnish. After thoroughly drying, the work goes either straight to the plating bath, or it may be passed through a dip to ensure the removal of any tarnish resulting from the exposure during the application of the varnish. No mechanical processes can be applied during deposition, and subsequently the varnish is removed by a suitable solvent, such as turpentine, and the work freed from the solvent, ready for further processes of metal colouring or finishing. Where deposition is to be effected in a cyanide solution, copal varnish, coloured with a little yellow chrome, must be used, as asphaltum does not withstand the action of cyanides.

The process of stopping off finds its largest application in the more recent methods of building up (page 292) in which large surfaces require to be shielded from the deposition which is applied to relatively small areas for the purpose of increasing the diameter of a part by the application of a deposit of considerable hardness.

For this purpose, paraffin wax was first applied up to the limit of the required deposit. Time of immersion must allow of the metal attaining the temperature of the wax bath for the production of a relatively thin and uniform coating. The work is withdrawn from the wax bath and then allowed to drain. A second immersion may be required to attain the requisite thickness of wax to permit of perfect insulation, and also to withstand subsequent handling. Some subsequent touching up of the wax film may be required to obtain the sharp line marking the boundary of the surface to be deposited upon. In the subsequent plating process, care must be taken to keep the temperature of the depositing solution well below that of the softening point of the wax. After deposition, which may be a matter of hours, days, or in some cases even weeks, the wax can be removed by re-immersion—after rinsing—in the hot wax bath, and subsequently in boiling water. During the removal process, a thin film of wax will spread over the deposited metal, but this will not interfere with the further grinding process to bring the thickness or diameter to the required specification.

More recently, waxes of the chlorinated naphthalene type have been largely employed.

Further variations in the composition of waxes for this purpose of stopping off now permit of the immersion of the whole of the part in the wax bath, subsequently removing the wax from that portion upon which the deposit is to be made. Where obtainable, higher melting and softening points for these waxes are advantageous, together with lower specific gravity. Increased hardness will also permit of a larger factor of safety in subsequent handling.

The work is first degreased in trichlorethylene, with a subsequent treatment in a hot alkali solution, and, after rinsing, dried. Those portions to be plated are then painted over with either glycerine or a paste of glycerine and chalk in the proportion of four of chalk to five or six of glycerine. The work is then immersed in the wax pot, the temperature of which may be maintained thermostatically and the tank suitably lagged for the conservation of heat. After the work has acquired the temperature of the wax, it is withdrawn and allowed to drain and cool. A second immersion can then be given to increase the thickness of the wax film. After removal, draining, and cooling down, those areas which have been treated with the glycerine composition can then be easily stripped of the wax film. The stripping is started by means of a sharp knife. The exposed surface is then cleaned again in a luke-warm electrolytic bath, after which it is transferred, after rinsing, to the depositing bath.

After deposition the wax is removed by immersion in the hot wax bath, followed by immersion in hot water, or by degreasing. The boiling water method has the advantage of leaving a thin film of wax on the surface, which provides some measure of preservation in the case of ferrous metals.

Parkerizing. While not in any sense an electrolytic process, this method of rendering iron and steel rustproof calls for brief mention. It has attained a considerable vogue, though more recently has been largely replaced by the process of "Bonderizing." The Parkerizing process consists in treating the suitably cleaned surfaces with a nearly boiling solution of a soluble phosphate of iron (ferrous di-hydrogen orthophosphate). By the interaction of the soluble phosphate with the metal of the articles treated, there is formed on the surface an insoluble phosphate of iron which is very adherent and protective. There are many variations in the patented materials used for this purpose, other soluble phosphates, such for example as that of manganese, being introduced into the composition of the rustproofing material. A satisfactory deposit involves lengthy boiling, about an hour being required. On account of this, modifications have been worked out in the process to reduce the time required for producing a protective coating.

This more rapid process is called Bonderizing and provides a surface which is an excellent ground work for the application of coatings of paints or enamels.

Bonderizing. Owing to the fairly long time of immersion necessary to the Parkerizing process, where large mass production is carried out, the Bonderizing process has been developed, by which means conversion of the steel surface into insoluble basic phosphates can be effected in seven to ten minutes. Steel surfaces that have been cold rolled and therefore superficially hardened by cold working, are difficult to attack, and that is why the Parkerizing process requires about sixty minutes' immersion.

The Bonderizing solution effects the change in about one-sixth of this time, and can be advantageously employed for treating mud-guards, motor-car wings, wheel rims, etc., on the conveyer principle.

Parkerizing can be accelerated by using a sand or shot-blasted surface. Bonderizing eliminates this necessity.

Parkerizing has a rust-proofing value which Bonderizing does not claim. The latter is considered as a chemical primer, and a base for paint, lacquer, or enamel. Operations in Bonderizing are similar to those in Parkerizing. The solution is maintained solely by the addition of Bonderite Powder.

The various stages in the process can be enumerated as follows—

1. Degreasing either by—
   (*a*) Trichlorethylene, or
   (*b*) In an aqueous alkaline solution.
2. Rinsing in clean, hot water, if an alkaline cleaner has been used.
3. Bonderizing in a nearly boiling solution for seven to ten minutes.
4. Rinsing in clean hot water.
5. Drying out in a heated oven.

The articles thus treated are ready for a final coating by either spray or dip methods.

The Bonderizing solution should be contained in a steel tank, and kept at 208° to 210° F. Steam coils should be used for heating, to enable any sediment formed to settle freely at the bottom of the tank. The deposit which gradually forms on the heating coil itself, tends to impair the heat transference to the solution, and therefore coils should preferably be arranged so as to permit of easy removal for cleaning, and should be made of brass, which does not scale up as readily as steel, and is more easily cleaned.

The stock solution is made up of a definite strength, by dissolving Parco Powder (manganese dihydrogen phosphate), in water, and then adjusting the final strength by the addition of Bonderite Powder which is principally Parco Powder containing an accelerator.

The strength of the solution is determined by titrating 10 c.c., which is removed by means of a pipette, with deci-normal sodium hydroxide, using phenolphthalein as indicator. By this means, the total content of phosphate radical is determined. For convenience, the strength of the solution is determined by "points"; that is, the number of c.c. of deci-normal sodium hydroxide required to neutralize 10 c.c. of solution. It is recommended that initially, the solution made by dissolving the Parco Powder, should give 26 points. The final adjustment is now made by the addition of Bonderite Powder, until the strength reads 29 to 30 points.

After a good boiling to effect complete solution of the powders, the mixture is then ready for use.

Immersion of the steel articles occupies about ten minutes, after which they are removed, well washed in a hot water rinse or spray, and then finally dried out in a heated oven. The latter is imperative in the case of articles which possess seams or overlapping metal joints. The surface of the steel is thus given a matt finish of a plum colour.

After about six weeks use, the sludge and deposit at the bottom of the tank accumulates to such an extent, that it is advisable to clean out the tank.

The strength of the solution is not the only important factor for successful working. Temperature is equally important, and should be maintained as aforementioned, at 208°–210° F. Should the plum-coloured surface be crystalline and sparkling, this indicates that the degreasing process prior to rust-proofing. has not been perfect, due to the incomplete removal of alkalis in the rinsing operation.

The best results are obtained by controlling the ratio of free acid to total phosphate in solution. This ratio can be easily and simply found by titrating 10 c.c. of the solution with deci-normal caustic soda, using both phenolphthalein and methyl orange together as indicators.

On titrating, the first colour change due to the methyl orange, gives the number of c.c. of alkali necessary to neutralize the free acid present, while complete neutralization denoted by the pink colour of the phenolphthalein, gives the total alkali to react with the total phosphate present.

The ratio of free acids to total phosphates, should be at least 1 : 6. If the ratio drops to say 1 : 5, "smudge" will be produced. Should this condition exist, i.e. the amount of free acid is excessive, sodium hydroxide or carbonate should be added to the bath to effect a partial neutralization.

It has also been found that if this ratio is kept at above 1 : 6, "smudge" is never produced, and the speed of the reaction is increased.

CHAPTER XXIV

METAL COLOURING

INTRODUCTION—General methods—Properties of chemical films—General procedure—Colouring of copper—Copper "oxidize"—Florentine bronze—Steel bronze—Colouring of brass—Various colours—Black on brass—Steel bronze on brass—Colouring of silver—Metallochromes—Lacquering

Introduction. Subsequent to electro-deposition many metals are subjected to chemical processes by which they acquire relatively thin films of compounds which, in addition to their pleasing colour, are more permanent in air than the metals themselves.

Reference has already been made to the permanence acquired by metals owing to the formation of thin and stable films of oxides. A suggestion, therefore, forces itself into notice that the designed production of such oxide films might play an important part in the longer preservation of metals exposed to corrosive conditions.

If this is possible with oxides it might be equally attainable and effective with films of sulphides, and the processes of forming these films of metallic compounds for the dual purpose of decoration and protection are generally known as *metal colouring*.

General Methods. These films are producible by at least four entirely different ways—

1. Mechanical methods comprising those similar to painting and including spraying and dipping processes.

2. Thermal methods which employ an elevation of temperature to bring about the desired chemical change.

3. Chemical methods, which are the most largely used, whereby the metals are immersed in appropriate chemical solutions in order to acquire these films by chemical action.

4. Electrolytic methods, when usually the metal is made the anode in the solution and is then oxidized.

Properties of Chemical Films. These films of compounds offer several points of interest. They are, as may be anticipated, quite thin. Several attempts have been made to determine their thickness. Thus the colouring effects on copper may be removed by a solvent which will not effect the basis metal. Potassium cyanide or dilute sulphuric acid will serve this purpose, and from the loss of weight per unit area, and an assumed density for the deposit, the thickness can be calculated. Thus a copper oxide film obtained on copper by immersion in a solution of the nitrate, and subsequently heating, gave a weight of 99 mg. per sq. dm. or 14 grains per sq. ft. A similar deposit obtained from an ammmoniacal solution of copper nitrate gave a weight of 37 mg. per sq. dm. or 5·3 grains per sq. ft. A simple calculation shows that a film weighing 60 mg. per sq. dm. or 0·55 gm. per sq. ft. has, with an assumed density of 2, a thickness of approximately one eight-thousandth of an inch, that is, one-eighth of a mil. This is not much, but it does provide some measure of protection of the underlying metal in addition to enhancing its appearance.

Again, quite uniform coloured films of oxides may be obtained by merely heating. The discolourment of copper is well known and is capable of a considerable amount of control. Steel is another case in point. In fact, the colours of these films of oxide on steel are so well marked that they may be—and indeed are—used by the toolmaker as sufficiently accurate computations of the temperatures required in the tempering of hardened steel. These temperatures with their corresponding colours are as follows—

Temperature (deg. C.)	*Temper Colour*
220	Pale yellow
230	Straw yellow
255	Brownish yellow
265	Purple yellow
277	Purple
288	Bright blue
293	Dark blue
316	Blackish blue

In this case, as in many others, careful control of temperature is necessary for the attainment of uniform effects.

These and other colour effects are not to be wondered at when it is remembered that copper sulphate, for example, is definitely blue in the crystalline form, while it is much lighter in the powdered state, due, no doubt, to the much greater reflection of light from the much more numerous though smaller crystal faces. Again, mercuric iodide can be readily transformed from the red to a yellow state by gently heating. Mercuric sulphide is red in its natural form, but black by precipitation in Group 2 of the usual analysis scheme, while the yellow colour of gold by reflected light, and green by transmitted light, provides yet another example of colour change with change of state or subdivision. Further, apart from pleasing colour, the chemical films must possess properties which will make for permanence.

In a general way it may be taken for granted that the compounds formed are less active than the metals from which they have been produced. Similarly, the removal of oxide films during the process of pickling is not infrequently more or less mechanical, the porous oxide films admitting the acid to the metal beneath, which becomes attacked with surface solution, whereby the film of oxide drops from the corroding surface of the metal. This has been very clearly shown. Chemical compounds are as a general rule more stable than the metals from which they have been formed.

They should then be non-hygroscopic, that is, they should not attract atmospheric moisture.

This quality is conspicuously absent in the case of iron rust, which, attracting moisture from the air, encourages further oxidation and rusting, rusting being an operation subsequent to the surface corrosion of the metal.

These films must be reasonably hard and able to withstand abrasion. As regards colour, this may be inherent or acquired by the passage of light through films of differing thickness.

Ultimately, for a still further degree of permanence, such films are lacquered, as it must be recognized that such chemical compound films cannot be regarded as altogether free from the possibility of corrosion.

General Procedure. The preparation of metallic surfaces prior to metal colouring necessitates the same degree of care as with electrodeposition, possibly even more so because the colouring solutions employed are almost entirely free from any substance with cleansing properties. Many of the solutions are practically neutral. Absolute chemical cleanliness may be regarded as essential. Where successful results are not at first obtained, the complete removal of the imperfect colour film is of the utmost importance. The exact matching of colours and shades is difficult in the case of small scale operations. On the larger scale uniform results are the much more frequent rule, there being greater control over the composition of the solution and its temperature, both important factors.

Differing effects again may be obtained by the use of different types of surface. These may be bright by polishing, or dead by dipping, sand-blasting, or by the application of the colouring process directly on to the matt surface obtained, for example, from the acid copper or silver baths. Again, variations of effects are possible by the light scratch-brushing of the somewhat dull colours at first produced, or with greater contrast, relieving may be applied by removing the colour films from the "high lights" by the application of a heavier scratch-brushing or of fine pumice powder. In the latter case, the colour is frequently completely rubbed through and the too sharp contrast may be toned down by a momentary dip in the colour solution.

Still further, the colour effects may be those due to the natural colours of the films of sufficient thickness to be opaque, or they may be due to light effects brought about by the passage of light through very thin films, which in themselves are of insufficient thickness to give the natural colour of the compound. The light transmitted through these exceedingly thin films is then reflected from the metal surface beneath, and during this reflection is broken up in much the same way as when passing through a prism of varying thickness, thus producing effects similar to those of the spectrum, or what may be called "rainbow" effects.

Another important feature of these metal colouring processes is the difference in colour produced on two metals of slightly differing composition. As an extreme case copper and brass behave very differently in the same solution but, more relevant to the case in point, two samples of copper, one of ordinary commercial composition and another produced by electrolysis, give markedly different effects in the same solution.

Still further, where metals, such for example as iron, are not in themselves amenable to simple colouring effects, they may be rendered more susceptible by the application of a thin deposit of another metal, this also increasing the range of colour obtainable. Iron and steel work is, on this principle, frequently coppered either in the cyanide solution alone, or subsequently thickened in the acid solution, thus rendering possible the application of the colours usually associated with copper to the baser metal iron.

Another principle which can be effectively employed is that of parcel deposition, whereby two either slightly or markedly different colours may be obtained on the same piece of work with pleasing results.

It will thus be appreciated that the processes of deposition and subsequent metal colouring provide wide scope for decorative effects on many metals which normally possess no attractive features.

Subsequent to colouring the usual processes of rinsing call for the same degree of perfection as with plating, and drying is frequently followed by lacquering with either colourless or coloured lacquers.

A few typical examples will now be referred to, a much wider range being available from other works dealing more exclusively with this phase of decorative metal work.

COLOURING OF COPPER

A wide range of colour and shade is effectively obtained on copper by the use of a number of solutions, the chief constituent of which is one of the soluble sulphides. These sulphides include those of sodium, potassium, barium, and ammonium. With different concentrations, temperatures and times of exposure the colours may vary from the lightest brown to black, and still further variations are possible according to whether the copper surface is smooth or matt, the latter surface generally yielding the darker colour.

These colours also lend themselves to relief with still further possible variations of effect. The processes are widely used.

Copper "Oxidize." A typical solution is—

Potassium sulphide (Liver of sulphur)	2 oz.	12·5 gm.
Ammonium chloride	2 lb.	200 ,,
Water	1 gal.	1 litre

The solution is used cold. If warmed a weaker solution will serve the purpose better. In case of an unsatisfactory result the colouration may easily be removed prior to a further attempt being made. The process is very elastic in operation, the film being one of copper sulphide—not oxide.

Florentine Bronze. This very pleasing effect is produced by the application of a paste composed of red oxide of iron and blacklead and drying at 100° C. for about half an hour. The copper is oxidized at the expense of the iron oxide thus—

$$2Cu + Fe_2O_3 = Cu_2O + 2FeO$$

The paste or dry powder is then removed with a stiff bristle brush. Darker shades are obtained at a higher temperature. The most pleasing result is obtained with electrolytic copper, so that all other examples of metals are amenable to this process by the prior application of copper from an appropriate solution.

Steel Bronze.

SOLUTION—

Arsenious oxide . .	20 oz.	125 gm.
Copper sulphate . .	10 ,,	62 ,,
Ammonium chloride .	2 ,,	12·5 ,,
Hydrochloric acid . .	1 gal.	1 litre

The oxide of arsenic readily dissolves in the warmed acid, the other materials being subsequently added. The solution at 120° F. gives a quick result, but in cold solution the simple deposition of the arsenic (for such the process is) takes place more slowly. Either relief effects or finishing with a soft mop may then be resorted to, to enhance the effect.

COLOURING OF BRASS

In view of the fact that traces of impurity in copper profoundly influence the colour effects chemically developed, it becomes quite impossible to predict with certainty the results of the same solutions on brass. A number of well-defined colours are, however, readily and repeatedly obtainable.

Various Colours.

SOLUTION—

Sodium thiosulphate "Hypo" .	12 oz.	75 gm.
Lead acetate . .	8 ,,	50 ,
Water	1 gal.	1 litre

The salts are added together to the water and raised to 180° F. Clean brass acquires in this solution the following succession of colours: pale gold, dark gold, orange, brown, crimson, purple, and through various iridescent shades to deep blue, and finally to steel grey. Careful manipulation will succeed in arresting the process at any desired shade.

The succession of colours appears to be due to the reflection of light from the metal below, through the increasingly thicker film of deposited lead sulphide. When the film becomes appreciably thick, the observed colour is that of the opaque film. The colours are rendered much more permanent by lacquering. The film which is lead sulphide appears to be due to the following chemical changes—

$$Pb\,(C_2H_3O_2)_2 + Na_2S_2O_3 = PbS_2O_3 + 2NaC_2H_3O_2$$

$$PbS_2O_3 + H_2O = PbS + H_2SO_4$$

Black on Brass. Several solutions are available for this effect. They usually comprise ammoniacal solutions of copper salts such as—

(*a*)	Copper sulphate	4 oz.	25 gm.
	Water	1 gal.	1 litre
	Ammonia .880	q.s.	q.s.

The copper salt is dissolved in a part of the water. Ammonia is added until the green hydroxide of copper first formed is nearly all redissolved. A small residue of undissolved copper hydroxide is a guarantee of the absence of a large excess of ammonia in the presence of which the black film (a black hydrate of copper oxide) is soluble, and therefore not produced. The solution gives a quick result when used hot. The action is slower when cold.

(*b*) Copper nitrate may be used in place of the sulphate, and

(*c*) A similar effect is obtained by dissolving copper carbonate in ammonia, which again must not be in excess.

Steel Bronze.

SOLUTION—

White arsenic (As_2O_3)	12 oz.	75 gm.
Hydrochloric acid (conc.)	1 gal.	1 litre

The arsenious oxide readily dissolves in the warmed acid—

$$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O$$

and by immersion the arsenic is substituted by the copper (or zinc) of the brass—

$$2AsCl_3 + 3Cu = 2As + 3CuCl_2$$

Care must be taken to avoid the inhalation of the extremely poisonous fumes.

Again, the reaction is slow in cold solutions and more rapid on warming.

Very many other chemical solutions are available for the colouration of brass with a wide variety of results. Further compositions with manipulative details may be obtained by consulting relevant works on the subject.

COLOURING OF SILVER

While silver is not susceptible to direct combination with oxygen, it readily discolours under ordinary atmospheric conditions. This is mainly due to the presence of sulphuretted hydrogen, which, acting on silver thus—

$$2Ag + H_2S = Ag_2S + H_2$$

produces thin films of silver sulphide of various shades.

Such films may therefore be produced by design with solutions containing soluble sulphides as in the case of copper. The effect obtained is commonly but erroneously known as "oxidizing," and further decorative effects are obtained by relieving as in the case of copper.

A very satisfactory, though much more expensive, method of "oxidizing" silver involves its immersion in a solution (necessarily dilute) of platinum chloride. The metal platinum comes down by replacement thus—

$$4Ag + PtCl_4 = Pt + 4AgCl$$

The relatively small amount of silver chloride formed is washed away and good tones are produced.

Many other metals are also amenable to the processes of chemical metal colouring. The subject is altogether too broad to enlarge upon here.

Metallochromes. These purely decorative effects are produced on polished metals, usually iron or nickel, by making them anode in a solution of lead salt when, by electrolysis, thin films of di-oxide of lead are deposited upon them giving rise to what may be called rainbow effects due to "interference."

A solution suitable for this purpose is—

Litharge (PbO)	62·5 gm.
Caustic potash	100 ,,
Water	1 litre

Other lead compounds, including especially the acetate, are also available. The polished plate is made anode and a cathode is provided by a copper or other wire held with its end facing the plate and close to it. Lead di-oxide is formed opposite to the cathode wire, the deposit spreading from this initial centre and decreasing in thickness with distance.

It is this varying thickness which breaks up the light as it passes through and is reflected from the polished surface below. The ornamental character of the effects may be increased by shaping the cathode wire and varying its distance from the polished anode. The results are striking, but cannot be said to be of large application.

Lacquering. Few metal finishes, whether obtained by polishing, dipping, deposition or metal colouring, are quite free from oxidation or discoloration under atmospheric conditions. They seem to call for some final covering which, by its inertness and continuity, will completely insulate the metal from the atmosphere. Years ago, large quantities of brass were used in many different domestic forms in which the polished metal was conspicuous. Some protection from the air was a vital necessity. For this purpose coverings known as lacquers are applied. Formerly, these for the most part were solutions—or more correctly suspensions—of the different forms of lac in a volatile spirit. After applying to the metal surface, the spirit evaporated away, leaving a very thin yet continuous layer of the lac over the surface of the metal. Such lacquers were first applied by a hot process. In the case of small work, this was wired in batches, warmed on a stove, immersed in the lacquer, allowed first to drain, and then to dry. Larger work was dealt with individually and by hand. This involved considerable skill on the part of the operator, but could be satisfactorily accomplished with the necessary speed. Drying required from 10 to 15 minutes. Temperature control was a matter of importance, especially as in a moist atmosphere, vapour could condense from the air by the cooling effect of the evaporating spirit, giving rise to a "bloom" which was undesirable.

Cold processes, therefore, offered some attraction, and were adopted on quite a large scale as they eliminated any special skill, the lacquers being applied by dipping, brushing, or spraying. The lacquers contained notable quantities of higher alcohols, these preventing the undesirable bloom. They could also be tinted, thus enhancing the appearance of many metals, while a green tint improved the effect of an antique finish.

More recently, other materials have been applied. Thus in 1916, nitro-cotton of the form of mononitrocellulose came into use. This compound is produced by the action of a mixture of strong nitric and sulphuric acids on cotton wool. After "nitrating," the product is thoroughly washed in many changes of water and dried with care. It then contains about 12 per cent of nitrogen, and is dissolved or dispersed in a mixture of solvents, such as acetone, amyl acetate, and a number of hexane derivatives, avoiding too large a proportion of the more volatile constituents. A further addition is that known as the plasticizer, the purpose of which is to displace brittleness by toughness in the lacquer film. For thinning down such lacquers other solvents of the benzol and toluol types are used. The resulting lacquer is more resistant to abrasion than those from gum lacquers. The materials, especially the nitro-cotton, are highly inflammable, but a little care in their manipulation provides an adequate check, while the resulting thin film can hardly be said to present any risk. Still more recently, synthetic resins similar to the natural gums have been largely applied. In addition to producing a hard glossy finish, they may still be improved by stoving, and then offer considerable resistance to all the usual forms of corrosive attack. Where tints are required on lacquered articles, they may be applied either in the form of a tinted lacquer, in which case unevenly applied lacquer brings variations of shades, or, alternatively, the tint may be applied by immersion in a dye subsequent to lacquering with the production of a more uniform finish.

APPENDIX

USEFUL INFORMATION

Metric System

1 Metre = 10 decimetres = 100 centimetres = 1000 millimetres = 39·37 inches
1 Kilogram = 1000 grams = 2·204 lb.
1 Litre = 1 cubic decimetre = 1000 cubic centimetres = 1¾ pints
1 cub. cm. and 1 milli-litre are the same for all practical purposes

Conversion Tables

one inch	=	2·54 cm. = 25·4 mm.
one sq. in.	=	6·45 sq. cm. = 645 sq. mm.
one sq. ft.	=	9·2 sq. dm.
one cub. in.	=	16·4 cub. cm.
one gram	=	15·432 grains
one pound (avdp.)	=	7000 grains
,, ,, ,,	=	453·6 grams
1 ounce (avdp.)	=	28·4 grams
1 ounce (troy)	=	31·1 grams
1 kilogram	=	2·204 lb. (avdp.)
1 pint	=	20 fl. oz. = 567 c.c.
1 fl. oz.	=	28·4 c.c.
1 Imp. gallon	=	4·536 litres
1 Imp. gallon	=	1·2 U.S.A. gal.
1 U.S.A. gallon	=	3·78 litres
1 U.S.A. quart	=	·946 litre
1 gallon	=	276·5 cub. in.
20 fl. oz.	=	34·5 cub. in.
1 litre	=	1·76 pints
1 cub. ft.	=	28·4 litres
1 cub. ft.	=	6·25 gallons (Imp.)
	=	7·5 gallons (U.S.A.)
1 lb. (avdp.) per gallon	=	100 grams per litre
oz. per gal. × 6¼	=	gm. per litre
lb. per gal. × 100	=	gm. per litre
oz. per U.S.A. gal. × 1·2	=	oz. per Imp. gal.
grains per gal. are parts per 70,000		
$\therefore \dfrac{\text{grains per gal.}}{70}$	=	gm. per litre

Conversion Tables—(contd.)

gm. per litre × ·133 = oz. (avdp.) per U.S.A. gal.
„ „ × ·16 = oz. (avdp.) per Imp. gal.
„ „ × ·122 = oz. (troy) per U.S.A. gal.
„ „ × ·146 = oz. (troy) per Imp. gal.
„ „ × 2·44 = dwts per U.S.A. gal.
„ „ × 2·92 = dwts per Imp. gal.

Electrical Quantities

1 coulomb = 1 ampere-second and deposits ·000329 gram Cu or ·001118 gram Ag.
1 ampere deposits 1·182 gm Cu per hour
1 „ „ 4·024 „ Ag per hour
1 ampere-hour = 3600 coulombs
96,540 coulombs or 26·8 Ah } deposit one gram-equivalent of any metal
amp. per dm.^{2} × 9·2 = amp. per ft.^{2}
oz. per ft.^{2} for ·001″ = $\frac{\text{Sp. Gr. (approx.)}}{12}$
1 watt = 1 volt-ampere
1 horsepower = 746 watts
1 kilowatt hour = 1000 watt hours = 1 Board of Trade Unit (B.o.T.U.) = 1⅓ horsepower hours.

TABLE LXXI

Temperature Scales

°C	°F	°C	°F
0	32	55	**131**
5	41	60	**140**
10	50	65	**149**
15	59	70	**158**
20	68	75	**167**
25	77	80	**176**
30	86	85	**185**
35	95	90	**194**
40	104	95	**203**
45	113	100	**212**
50	122		

degrees Fahr. = (degrees Cent. × $\frac{9}{5}$) + 32
degrees Cent. = (degrees Fahr—32) × $\frac{5}{9}$

TABLE LXXII

Specific Gravities and Weights of Metals

Metal	Sp. Gr.	Wt. 1 cub. in. oz. avdp.
Aluminium	2·7	1·56
Cadmium	8·6	4·97
Chromium	6·9	3·98
Cobalt	8·8	5·08
Copper	8·95	5·18
Gold	19·4	10·2 (troy)
Iron	7·8	4·5
Lead	11·4	6·6
Magnesium	1·75	1·01
Manganese	7·4	4·26
Mercury	13·6	7·9
Nickel	8·8	5·08
Platinum	21·4	11 (troy)
Silver	10·5	5·53 (troy)
Tin	7·3	4·2
Zinc	6·9	3·98

TABLE LXXIII

THICKNESS OF WIRES

Standard Wire Gauge (S.W.G.)	Diameter	
	Inch	Centimetre
0	0·324	0·823
2	0·276	0·701
4	0·232	0·589
6	0·192	0·488
8	0·160	0·406
10	0·128	0·325
12	0·104	0·264
14	0·080	0·203
16	0·064	0·162
18	0·048	0·122
20	0·036	0·0915
22	0·028	0·071
24	0·022	0·056
26	0·018	0·046
28	0·0148	0·038
30	0·0124	0·032

TABLE LXXIV

RESISTANCE OF WIRES

Metal	S.W.G.	Ohms per foot	Feet per ohm
Copper	12	0·000944	1060
	14	0·001595	628
	16	0·00249	402
	18	0·00443	226
	20	0·00787	127
	22	0·013	77
	24	0·021	47·5
Iron	12	0·00566	177
	14	0·00957	105
	16	0·01496	67
	18	0·0266	37
	20	0·0472	21
Nickel silver	12	0·0189	53
	14	0·0319	31
	16	0·0498	20
	18	0·0886	11·3
	20	0·1574	6·3
Platinoid	20	0·21	4·75
Manganin	20	0·262	3·8

0 21 4·71

TABLE LXXV

HYDROMETER SCALES AND SPECIFIC GRAVITIES

Beaumè (Nickel-ometer)	Twaddell	Specific Gravity	Beaumè (Nickel-ometer)	Twaddell	Specific Gravity
0	0	1·000	39·8	76·0	1·380
2	2·8	1·014	40·0	76·6	1·383
2·7	4·0	1·020	41·2	80·0	1·400
4·0	5·8	1·029	42·0	82·0	1·410
5·4	8·0	1·040	42·7	84·0	1·420
6·0	9·0	1·045	44·0	87·6	1·438
8·0	12·0	1·060	44·1	88·0	1·440
10·0	15·0	1.075	45·4	92·0	1·460
10·6	16·0	1·080	46·0	93·6	1·468
12·0	18·2	1·091	46·8	96·0	1·480
13·0	20·0	1·100	48·0	99·6	1·498
14·0	21·6	1·108	48·1	100·0	1·500
15·4	24·0	1·120	49·0	103·0	1·515
16·0	25·0	1·125	50·0	106·0	1·530
17·7	28·0	1·140	51·0	109·2	1·546
18·0	28·4	1·142	52·0	112.6	1·563
19·8	32·0	1·160	53·0	116·0	1·580
20·0	32·4	1·162	54·0	119·4	1·597
22·0	36·0	1·180	55·0	123·0	1·625
24·0	40·0	1·200	56·0	127·0	1·635
26·0	44·0	1·220	57·0	130·0	1·650
27·9	48·0	1·240	58·0	134·2	1·671
28·0	48·2	1·241	59·0	138·2	1·690
29·7	52·0	1·260	60·0	142·0	1·710
30·0	52·6	1·263	61·0	146·2	1·731
31·5	56·0	1·280	62·0	150·6	1·753
32·0	57·0	1·285	63·0	155·0	1·775
33·3	60·0	1·300	64·0	159·0	1·795
34·0	61·6	1·308	65·0	164·0	1·820
35·0	64·0	1·320	66.0	168·4	1·842
36·0	66·4	1·332	67·0	173·0	1·865
36·6	68·0	1·340	68·0	178·2	1·891
38·0	71·4	1·357	69·0	183·2	1·916
38·2	72·0	1·360			

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