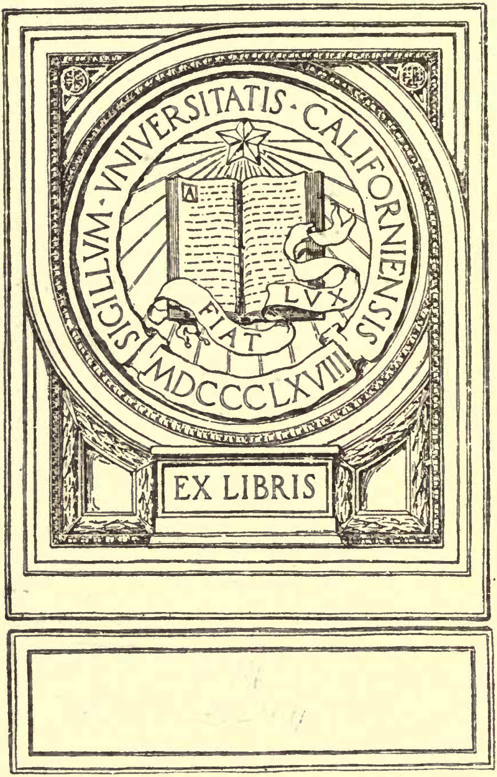

ELECTROPLATING

A TREATISE ON THE
ELECTRO-DEPOSITION OF METALS
WITH A CHAPTER ON METAL-COLOURING
AND BRONZING

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PREFACE

This book has been written primarily as a handbook for the practical electroplater, in the hope that the *modern* practical man will also be or will become, at least in some degree, a scientific student, for the days of "rule-of-thumb" are quickly passing. In our opinion it is essential that a practical book on such a subject as the present, to be of any real value, shall be written from the scientific standpoint.

The art of the electro-deposition of metals arose in the scientist's laboratory, and its growth was fostered largely by the patient work of trained scientific experimentalists; nearly all the important improvements that recent years have witnessed have resulted directly or indirectly from theoretical research, and it is not too much to say that the hope of the future lies almost entirely in this same direction.

On the other hand, it has not been sought to produce either a purely scientific treatise or a laboratory manual—these can be obtained if desired; the authors have, in these pages, endeavoured to combine, along with a simple exposition of theoretical principles, the results of their practical experience.

While it is indisputably true that no book can take the place of workshop training and practice, it is also true that the man who would be a *master* of the art of electroplating must possess considerable workshop experience, and at the same time be a thorough student of the scientific principles upon which it rests. Such a man, to quote the late Prof. Wm. James,* "need have no anxiety about the upshot of his education. . . . If he keep faithfully busy, . . . he can with perfect certainty count on waking up some fine morning to find himself one of the competent ones of his generation."

In its general plan the book is framed partly on the courses of lectures delivered to students in the technical classes of the University of Sheffield, and partly on the syllabus in electro-metallurgy of the City and Guilds of London Institute. On these lines the book would be inadequate unless some account of the elementary principles of electrical engineering were included, and an endeavour has been made to present in a concise manner an outline of the electrical principles involved, together with an explanation of the terms used in connection with them, so that the whole subject may be better understood. It is hoped, therefore, that such matter will assist students and workers in the art of plating, and help to render as easy as possible what appears from our experience to be a thorny part of the subject.

The various formulæ recommended for solutions and directions for carrying out processes of electro-deposition are in nearly all cases those which are in actual use in workshop practice and are not merely laboratory experiments.

The scope of the work does not permit of a very full treatment of the science of electro-chemistry, and those who wish to go more deeply into this fascinating and rapidly developing branch of science are referred to larger works, such as Dr. Allmand's "Principles of Applied Electrochemistry." †

* "Talks to Teachers on Psychology" (Longmans), p. 78.

† London: Edward Arnold, 1912.

We have to acknowledge gratefully the assistance rendered in various ways by our colleagues Dr. Turner, and Messrs. G. B. Brook, F. Mason, and F. W. Bissett.

We are also indebted to Messrs. W. Canning & Co.; the D.P. Battery Co., Ltd.; the Chloride Electrical Storage Co., Ltd., for the use of blocks illustrating types of cells and plant; and lastly, to our friend Mr. E. H. Crapper for his kindness in reading the proofs.

Finally, we should like to take this opportunity of acknowledging the debt of gratitude which we both owe to our old teacher, Mr. Byron Carr, the first—and for over twenty years—lecturer on electroplating in the former Sheffield Technical School, now the Department of Applied Science of the University of Sheffield.

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FUNDAMENTAL CHEMICAL PRINCIPLES

The study of the science and practice of electroplating and the deposition of metals must, like the study of all other branches of applied science, begin with the fundamental facts relative to matter and force, and the theories which have been deduced from these facts.

Matter, Changes of Matter, Force.—We are all more or less familiar with the changes which matter—and by *matter* is meant everything which possesses "mass," *i.e.* bulk and weight—is continually undergoing, and also with the effects which are being produced by "force." Force, of course, is invisible, but we know of its presence by its effects on matter in the way of changes of one kind or another. Scientists usually regard the changes which matter undergoes as of two kinds, *physical* and *chemical*, though it must be said that the dividing line between the two is often not at all distinct; indeed, some physical change always accompanies a chemical change.

Water, in its varied forms, furnishes a familiar and very good example of these changes of matter. We know water under three distinct conditions, (*a*) in its normal state—as a liquid, (*b*) in the form of ice—a solid, (*c*) in the form of steam—gas or vapour. Under each of these conditions it is absolutely different in form and appearance, yet always the same in ultimate composition, external conditions of temperature and pressure determining under which of the three conditions it shall exist. These changes are purely physical—*there is no alteration in the essential nature of the substance.*

On the other hand, if we pass an electric current through water (slightly acidified to render it conductive), and perform the experiment in a suitable apparatus, we shall find that we are able to change the water slowly into two gases, which subsequent experiment would show to be quite different in their properties, both from each other and from water itself in any of its forms. Here we have a chemical change, a change which the student will at once observe to be of a different character to the physical changes previously illustrated.

It will be observed, moreover, that the "forces" at work in these changes are entirely different. Physical or, as they are sometimes termed, "mechanical" agencies, such as heat or pressure, alter the form or appearance or position of substances, whereas *chemical forces* alter the essential composition of the substances. The latter are called "forces" by analogy from the former, but are really quite distinct in nature. It must, however, be borne in mind, as has been previously pointed out, that these changes often merge into each other, and it is often difficult, if not impossible, to draw a sharp line of distinction. Forces which are purely physical, such as are due to heat, often induce or bring about chemical action, and therefore chemical change.

Constitution of Matter.—All substances found in nature may be divided into two classes, "elements" and "compounds."

Elements are those substances such as oxygen, hydrogen, copper, silver, mercury, gold, carbon, etc., which have never yet been decomposed or split up into any other kind of matter. This class, however, is also subdivided usually into two sections, *metals* and *non-metals.*

The principal characteristics of the first section are, that they are good conductors of heat and electricity, that as a rule they are fairly malleable and ductile substances, *i.e.* they can be hammered or rolled into sheets and drawn into wire; with the one exception of mercury they are all solid bodies at ordinary temperatures and pressures, and as will be observed later they all act as cations when undergoing electrolysis (see page 24).

The non-metals are extremely varied in their characteristics; conversely to the metals they are comparatively poor conductors of heat or electricity, and from an electro-chemical point of view act oppositely to the metals in electrolysis. The element hydrogen, however, forms an exception to this rule.

The principal *metals* are—aluminium, antimony, bismuth, copper, gold, iron, lead, magnesium, manganese, mercury, nickel, platinum, silver, tin, and zinc.

The principal *non-metals* are—chlorine, fluorine, hydrogen, nitrogen, and oxygen (all gases at ordinary temperatures and pressures), bromine (a liquid), and carbon, iodine, phosphorus, and sulphur (solids).

Compounds are substances composed of two or more elements, or, in other words, substances which can be split up into other kinds of matter, as, for example, common salt (into sodium and chlorine), water (into hydrogen and oxygen), copper sulphate (into copper, sulphur, and oxygen).

Modern science regards matter under all conditions, whether solid, liquid, or gaseous, as being made up of innumerable particles of two orders or types, to which respectively the names "atoms"—derived from a Greek term meaning indivisible particles—and "molecules"—signifying "little heaps"—have been given.

The *atom* is defined as the smallest particle of matter which can take part in a chemical change, and atoms usually exist in a state of chemical combination with other atoms, either of the same or of some other kind. Molecules are particles usually of a larger order, and consist as a rule of more than one atom. The *molecule* is defined as the smallest particle of matter which can exist in a free state, or perhaps better, the smallest particle in which the original properties of any substance are retained. For example, if one drop of water was taken and divided, and subdivided, until a point was reached where further division was quite impossible so long as the substance was still to possess all the chemical properties of the bulk, we should then have arrived at the molecule. If, however, chemical forces were brought to bear, this molecule could be again divided, but in this case it would be into the essential constituents of the substance, or, in other words, into atoms of the elements hydrogen and oxygen respectively.

This view of matter is due directly to an Italian chemist Avogadro (1811), but it is also the indirect outcome of what is known as the *atomic theory*, which, though originally propounded more than two thousand years ago, is really due, so far as modern chemistry is concerned, to John Dalton of Manchester (1808). It had already been observed that substances which could be decomposed into other substances, or kinds of matter, were of invariable composition. Water, for instance, when decomposed, was always found to consist of eight parts by weight of oxygen, and one part by weight of hydrogen. From this and many other similar facts, Dalton argued that matter must be made up of atoms, or minute particles, having always the same relative weight or mass. This theory affords an explanation of the fundamental principle of chemical science, termed "*the law of definite proportion*," which means that wherever a chemical change occurs in matter, whether it be a separation or a combination, the relative weight of material liberated or used up is a definite quantity, and is always the same for every particular substance. One example, that of water, has already been cited; another simple illustration is that of hydrogen chloride, which when decomposed is always resolved into 1 part of hydrogen, and 35·5 parts of chlorine, by weight. Conversely, whenever these substances are brought together and chemical forces applied, they always combine in these proportions, to form hydrogen chloride.

A further principle of almost equal importance is that named the *law of multiple proportions.* Though the combination or separation of compounds is always definite, yet in many cases the same elements can combine in more than one proportion to give rise to other kinds of matter. Hydrogen and oxygen, for example, when combined in the proportion by weight of 1 to 8 form water; if, however, these two elements are combined in the proportion of 1 to 16, which under certain conditions can be done, an entirely different compound results, viz. hydrogen peroxide. It is indeed a fairly common occurrence in nature, that the same elements combine in different proportions, and give rise to different compounds or forms of matter. But Dalton showed that these proportions have always a simple relationship or ratio to each other; *e.g.* if a certain element, A, is found to combine with a fixed weight of a second element, B, in more than one proportion, the different weights of A which so combine always bear to each other a simple arithmetical ratio, such as 1 : 2 or 1 : 3, and so on. That is, the combining weights are simple multiples of one another.

This principle may perhaps be made clear by reference to two well-known elements, oxygen and nitrogen, which combine in five different proportions, giving the compounds shown below:—

Name.	*Parts by Weight.*		*Formulæ.*	*Ratio of N to O.*
	N	O		
Nitrous oxide	28	16	N_2O	7 : 4
Nitric oxide	14	16	NO	7 : 8
Nitrogen trioxide . . .	28	48	N_2O_3	7 : 12
Nitrogen peroxide . .	14	32	NO_2	7 : 16
Nitrogen pentoxide . .	28	80	N_2O_5	7 : 20

It will be observed from the last column, that the respective ratios of oxygen to each of the other members of the series are as 1 : 2 : 3 : 4 : 5. These facts and a vast number of similar ones can best be explained, so far as our present knowledge goes, by the atomic theory of matter, and its assumption of the existence of the minute particles termed atoms and molecules already referred to.

Chemical Symbols, Formulæ and Atomic Weights.—The atomic theory, in addition to being an aid to some understanding of the chemical changes in matter, has led to the introduction of a system of symbols, which enables these changes to be readily expressed both qualitatively and quantitatively. A *chemical symbol*, often the first or first and some other letter of its English or Latin name, has been assigned to every element, and as all substances are either elements or combinations of elements, we are enabled to express briefly the composition of any substance by means of these symbols, *e.g.* the letter H represents hydrogen, O oxygen, Ag, silver (Latin, *argentum*), Hg, mercury (Latin, *hydrargyrum*), K, potassium (Latin, *kalium*), Na, sodium (Latin, *natrium*).

These symbols have not only a qualitative but a quantitative meaning. Though it is impossible at present to assign an absolute weight to any atom, it is possible by the study of the compounds of atoms to determine their weight relatively to each other. This has been done, and a system of relative weights of the elements has been compiled, known as *atomic weights.*

Up to recent years hydrogen, as the lightest known element, was taken as unity, and the weights of all other atoms were regarded as so many times that of hydrogen. Recently, however, it has been found, that more exact values can be obtained by taking oxygen, to which an atomic weight of 16 is given, as the standard of comparison. In the accompanying table of atomic weights, this standard has been adopted. On this basis of comparison hydrogen is slightly above unity, being 1·008, but for practical purposes round figures are usually taken as given in the last column.

TABLE I.

LIST OF THE COMMONER ELEMENTS WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

Oxygen = 16. Hydrogen = 1·008.

Element.	*Symbol.*	*Atomic Weight.*	*Usual Value taken.*
	SECTION I. METALS.		
Aluminium	Al	27·1	27
Antimony	Sb	120·2	120
Arsenic	As	74·96	75
Barium	Ba	137·37	137
Bismuth	Bi	208·0	208
Cadmium	Cd	112·4	112
Calcium	Ca	40·07	40
Chromium	Cr	52·0	52
Cobalt	Co	58·97	59
Copper	Cu	63·57	63·5
Gold	Au	197·2	197
Iron	Fe	55·84	56
Lead	Pb	207·1	207
Magnesium	Mg	24·32	24
Manganese	Mn	54·93	55
Mercury	Hg	200·6	200
Nickel	Ni	58·68	59
Palladium	Pd	106·7	107
Platinum	Pt	195·2	195
Potassium	K	39·1	39
Silver	Ag	107·88	108
Sodium	Na	23·0	23
Tantalum	Ta	181·5	181·5
Tin	Sn	119·0	119
Zinc	Zn	65·37	65
SECTION II. NON-METALS.			
Bromine	Br	79·92	80
Carbon	C	12·0	12
Chlorine	Cl	35·46	35·5
Fluorine	F	19·0	19
Hydrogen	H	1·008	1
Nitrogen	N	14·01	14
Oxygen	O	16·0	16
Phosphorus	P	31·04	31
Silicon	Si	28·3	28
Sulphur	S	32·07	32

If therefore the symbols described above be regarded as representing one atom of the particular element thus identified, it will be readily understood that a symbol, in addition to indicating the nature of a substance, indicates its relative weight. For example, the symbol O not merely implies oxygen, but one atom or 16 parts by weight of oxygen. By grouping these symbols, therefore, the composition of any substance may be expressed, thus :—H_2O (water) means hydrogen 2 atoms or 2 parts by weight, oxygen 1 atom or 16 parts by weight. HCl (hydrogen chloride) means hydrogen 1 atom or 1 part by weight, chlorine 1 atom or 35·5 parts by weight. Symbols grouped in this way are known as *molecular formulæ*, and represent of course the composition of the molecule. The small figures at the right-hand lower corner of a symbol signify the number of atoms of that particular element.

The foregoing examples are fairly simple, but some molecules are much more complex, ammonium sulphate, for example, being represented thus, $(NH_4)_2SO_4$. In this instance two elements, one atom of one and four atoms of the other, nitrogen and hydrogen respectively, are placed in brackets and a small figure 2 immediately follows at the right-hand lower corner and outside the bracket; this implies that these two elements form a small group, so to speak, inside the molecule, and the formula NH_4 is to be multiplied by 2 to arrive at the total number of atoms included in this group; in addition the molecule also contains 1 atom of sulphur and 4 of oxygen. One molecule of ammonium sulphate therefore contains in all 2 atoms of nitrogen, 8 atoms of hydrogen, 1 atom of sulphur, and 4 atoms of oxygen.

It will thus be seen that by means of its formula and a knowledge of atomic weights, the percentage composition by weight of any substance may readily be determined. A larger figure placed immediately before a symbol or group of symbols and on a level with them signifies the number of molecules. Thus $2H_2O$ represents two molecules of water, 2HCl, two molecules of hydrogen chloride, $2(NH_4)_2SO_4$, two molecules of ammonium sulphate, and so on.

Molecules of elementary substances contain different numbers of atoms. In the commoner elements they often consist of two atoms, and are written down thus: oxygen O_2, hydrogen H_2, chlorine Cl_2, etc. The following well-known elements have only one atom in the molecule:—potassium, sodium, cadmium, mercury, and zinc, and are therefore written K, Na, Cd, Hg, and Zn respectively. In many cases of elements the molecular formula is unknown.

Chemical Equations.—Placed in the form of an equation, the symbols explained in the foregoing paragraphs, are exceedingly useful in expressing chemical changes. For example, the equation,

$$2Na + Cl_2 = 2NaCl$$

denotes that sodium and chlorine have combined or will combine to form sodium chloride, and that this combination must take place in the proportion of 46 parts by weight of sodium, and 71 parts by weight of chlorine, or 39·3 per cent. of sodium, and 60·7 per cent. of chlorine.

Again $$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

The complete meaning of this equation is, that 65 parts by weight of zinc added to 98 parts by weight of sulphuric acid* (hydrogen 2 + sulphur 32 + oxygen 64 = 98) produce 161 parts of zinc sulphate and two parts of hydrogen. The figure obtained by adding up the atomic weights of all the atoms forming a molecule is known as the *molecular weight* of the substance. The figure 98 is therefore the molecular weight of sulphuric acid, while similarly 161 is that of zinc sulphate. It may be advisable to point out that the sign + on the *left*-hand side of an equation signifies that a chemical action has taken place between the two or more substances thus connected.

The extreme usefulness of these equations will be evident

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* In aqueous solution only, however, is this reaction correct.

as the student proceeds; by them we are enabled to make the most exact calculations regarding the composition of any solution used in the electro-deposition of metals, and also to express the results of the decomposition of these solutions by means of electricity.

Acids, Salts, and Bases.—Compound substances are often classified by chemists under three headings, (1) acids, (2) salts, (3) bases.

(1) *Acids* are usually defined as compounds containing hydrogen, from which the hydrogen can be displaced by a metal (only, however, in the presence of water). Hydrogen is consequently a necessary constituent of an acid, though it must be understood that all hydrogen compounds are not necessarily acids.

The following are some well-known acids, and the equations accompanying them will show how they may be decomposed and made to yield up their hydrogen.

Hydrochloric acid (HCl)	$2HCl + Zn = ZnCl_2 + H_2$
Sulphuric acid (H_2SO_4)	$H_2SO_4 + Zn = ZnSO_4 + H_2$
Nitric acid (HNO_3)	$2HNO_3 + Mg = Mg(NO_3)_2 + H_2$

(N.B.—The usual reactions between nitric acid and a metal result in the liberation of hydrogen and oxygen together forming water. Magnesium is an exception.)

Acids have the power of turning blue litmus (a well-known vegetable compound) red, and this fact furnishes a very useful test for the presence of acids.

(2) *Salts* are compounds similar in molecular type to the acids, and indeed differing from the latter only in the fact that the hydrogen is replaced by a metal. The compounds shown on the right-hand side of the above equations are "salts," the usual definition of a salt being:—A compound resulting from the reactions between acids and the oxides, or hydroxides * of metals, or the metals themselves.

(3) A *base* is the term usually given to the oxides and

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* The hydroxide of a metal is its combination with HO.

hydroxides of metals, or to any substance having the power of neutralizing an acid to form a salt. Examples:—

$$\overset{\text{(Potassium hydroxide)}}{KHO} + \overset{\text{(Hydrochloric acid)}}{HCl} = \overset{\text{(Potassium chloride)}}{KCl} + \overset{\text{(Water)}}{H_2O}$$

$$\overset{\text{(Copper oxide)}}{CuO} + \overset{\text{(Sulphuric acid)}}{H_2SO_4} = \overset{\text{(Copper sulphate)}}{CuSO_4} + \overset{\text{(Water)}}{H_2O}$$

$$\overset{\text{(Silver oxide)}}{Ag_2O} + \overset{\text{(Nitric acid)}}{2HNO_3} = \overset{\text{(Silver nitrate)}}{2AgNO_3} + \overset{\text{(Water)}}{H_2O}$$

It must be observed, however, that the word "base," as applied above to oxides and hydroxides, is not literally accurate, inasmuch as something is lost from the composition of the so-called "base" which is not found in the salt, viz. the oxygen or the HO combination, which, as will be observed, combines with the hydrogen of the acid to form water. Some authorities therefore contend that the word "base" should be confined to ammonia, and substances like ammonia which really form the base of a salt, and do not lose anything, thus—

$$\overset{\text{(Ammonia)}}{NH_3} + \overset{\text{(Hydrochloric acid)}}{HCl} = \overset{\text{(Ammonium chloride)}}{NH_4Cl}$$

Valency or Quantivalence.—It has been previously observed that hydrogen was originally regarded by chemists as a standard to which the weights of all the other elements are relative. This is so in a sense other than that of atomic weights only. An element is said to have a certain "equivalent" or equivalent weight, and this is not necessarily its atomic weight, though it is always either that or some simple ratio thereof. The *equivalent* of any element may be defined as the proportion by weight which combines with or replaces one part by weight of hydrogen. Hydrogen is here taken as the standard, since it enters into combination in smaller proportions by weight than any other element.

Taking water again as an illustration, we find that oxygen combines with hydrogen in the proportion of 8 to 1 (H_2O =, in round figures, hydrogen 2, oxygen 16).

Therefore oxygen is said to have an equivalent of 8; in this case the equivalent of the element is half its atomic weight.

The ratio of the atomic to the equivalent weight is known as the *valency*, or "quantivalence" of the element, and may be briefly expressed in the following formula:—

$$\frac{\textbf{atomic weight}}{\textbf{equivalent weight}} = \textbf{valency}.$$

Substituting the figures in the example just quoted of oxygen, we have therefore—

$$\tfrac{16}{8} = 2 = \text{valency of oxygen.}$$

In some cases, as has been indicated, the atomic and equivalent weights are equal; for example, chlorine combines with hydrogen in equal atomic proportion, thus $H_2 + Cl_2 = 2HCl$. Similarly sodium replaces hydrogen in equal atomic proportion, $2Na + 2HCl = 2NaCl + H_2$. Obviously, therefore, the numbers which represent the atomic weights of chlorine and sodium also represent their equivalents, *i.e.* 35·5 and 23 respectively. The application of the above formula would thus give 1 as the valency. These elements are consequently known as *univalent.*

Oxygen, on the other hand, is *bivalent*, while similarly elements which have the power of combining with, or replacing 3 parts of hydrogen, have a valency of 3, and are known as *trivalent.* These three classes embrace the majority of the commoner elements, but there are a few which have valencies of four, five, and even six, and are called quadrivalent, quinquivalent, and sexvalent respectively.

Table II. gives the usual valencies of the commoner elements.

TABLE II.

THE USUAL VALENCIES OF THE COMMONER ELEMENTS.

Valency.	1.	2.	3.	4.	5.	6.
	Bromine	Barium	Aluminium	Carbon	*No common elements have a usual valency of five, but occasionally the following show this valency—*	Molybdenum
	Chlorine	Cadmium	Antimony	Iridium		Osmium
	Fluorine	Calcium	Bismuth	Platinum		Tungsten
	Hydrogen	Cobalt	Chromium	Silicon		
	Iodine	Copper	Gold			
	Potassium	Iron	Nitrogen			
	Silver	Lead	Phosphorus			
	Sodium	Manganese				
		Mercury				
		Nickel				
		Oxygen				
		Palladium			Antimony	
		Sulphur			Bismuth	
		Tin			Nitrogen	
		Zinc			Phosphorus	

It must be clearly understood, however, that many of the elements in the above table are capable of appearing in more than one class. Copper, for instance, is usually a bivalent element, but occasionally it enters into combinations which are of the univalent class. Thus in cupr*ic* oxide (CuO), one atom of copper replaces two hydrogen atoms in the corresponding hydrogen compound, H_2O; here, therefore, it possesses its usual bivalent quality. Another oxide of copper, cupr*ous* oxide, happens, however, to be known as existing, having the formulæ Cu_2O, and in this case it is obviously univalent, the copper atom being equivalent to one hydrogen atom only.

There are, of course, some elements which do not either combine with or replace hydrogen directly. In these cases, however, the equivalents have been determined indirectly, by observing their replacing power relatively to some other element, which has a direct action upon hydrogen.

This subject of valency possesses great significance from the electro-chemical point of view, as will be shown later.

Laws of Conservation.—Two great laws of matter, the truth of which has been recognized as the result of long and patient scientific research, must now be mentioned and briefly explained.

The first of these is the law of *The Conservation of Mass.* This law is a broad generalization based on experience, which means that in all changes of matter, whether it be a combination of elements, or a decomposition of compounds, no *mass* is either gained or lost. All that can happen in any such change or series of changes is a rearrangement of atoms or molecules. Matter cannot be either created or destroyed.

The second of these laws is that of *The Conservation of Energy.* This is another broad generalization, confirmed by innumerable experiments, meaning simply that *energy* can neither be created nor destroyed. Its form may be changed. It may have been stored up for ages, and then liberated to manifest itself in some other form. It may exist in one place as heat energy, and from this form it may be changed to electrical energy, and again in turn to chemical energy, but its *quantity* remains exactly the same; throughout any number of such changes, it neither increases nor diminishes.

CHAPTER II

FUNDAMENTAL ELECTRO-CHEMICAL PRINCIPLES

Chemical and Electro-Chemical Action.—In the study of all chemical changes of matter it is essential to bear in mind that no such changes can be effected without the aid of chemical force and also of energy in some form or other. This fact becomes especially evident to the electro-metallurgist or electro-plater, whose chief study is necessarily the decomposition or separation of chemical compounds. In all cases of chemical change there is evidence that energy is being either expended or developed. This is shown by the absorption or evolution of heat in many ordinary cases of chemical combination or decomposition when there is no question of electrical causes or effects. In the majority of cases of elements combining to form compounds there is an evolution of heat, and energy is being developed or liberated. Hence, in order to decompose these compounds when they are formed, as much heat, or a corresponding quantity of energy in some other form, must be applied or expended.

The form of energy which the electro-depositor or electro-plater applies for this object is electrical, but the work actually done is chemical; hence the term "electro-chemical action."

A simple case of the electro-deposition of a metal from a solution of one of its compounds, will furnish an illustration of this action and assist the reader in grasping this most important principle.

Suppose a depositing vat, containing a solution of copper sulphate ($CuSO_4$), is connected up, in a manner which will be explained later, to the connecting wires or "leads," as they are sometimes termed, of a dynamo. The copper sulphate solution is, as a result of the passage of electricity from the dynamo, decomposed, and metallic copper is deposited. Now it will be fairly obvious that in this case electrical energy is delivered into the vat by the dynamo at work. The energy thus delivered is in part expended as an equivalent of the heat energy originally evolved when copper sulphate was formed by the union of Cu and SO_4, and it is only by virtue of this that deposition or liberation of metallic copper takes place.

As will presently appear, exactly the same result can be brought about by using means other than the dynamo for producing electrical energy, and at this point it will be convenient to study briefly the action of a simple voltaic cell, using it as an illustration of electro-chemical action and the inter-convertible nature of energy. Such a cell is constructed by immersing two plates of zinc and copper respectively in a dilute solution of sulphuric acid and water. Pure zinc is not soluble in dilute sulphuric acid (though impure zinc is exceedingly so), but if a sheet of pure zinc and a sheet of copper are both immersed in a vessel containing dilute sulphuric acid, and a metallic connection is made between the two sheets (Fig. 1), it will be observed that while there is no apparent action at the surface of the zinc, the liquid itself is decomposed, and a large number of small bubbles of hydrogen gas collect on the surface of the copper. If also the zinc sheet was carefully weighed at the beginning and at the end of the experiment, it would be found that it had lost weight; part of it therefore must have been dissolved. The resulting action may be described thus:—

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

which is obviously an instance of chemical change. The agency by which it is brought about is, however, electrical, for on investigation by means of suitable apparatus, it would be found that both the metals concerned were in a special state, which is described by saying that they are "electrically charged," one (the zinc) negatively, the other (the copper) positively, and when a complete circuit was established through the liquid and through the connecting wire, that an *electric current* passed from the copper to the zinc outside the liquid, and conversely inside the liquid, as indicated by the arrows in the diagram (Fig. 1). In this experiment, we have illustrated the decomposition of sulphuric acid into H_2 and SO_4 by means of electrical action, and the energy required is produced by the combination of the zinc with the SO_4 group or "radicle," as it is termed, of sulphuric acid.

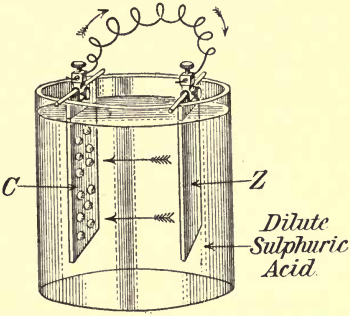

Fig. 1.—Simple voltaic cell,

But now it must be pointed out that not *all* the energy so produced is taken up by the simple decomposition of sulphuric acid. It will be noted that the connecting wire between the two plates becomes heated considerably. Some part, therefore, of the generated energy is occupied in producing heat. Now, this spare energy, as it may be termed, can be utilized, and may indeed take the place of the dynamo in the illustration previously used. To demonstrate this, dissolve in another glass cell (similar to that in Fig. 1) a few crystals of copper sulphate. This cell will now correspond to the copper sulphate vat previously referred to. Immerse in it a strip of copper, and (say) a strip of brass, which have been cleaned by dipping in dilute nitric acid. Disconnect the connecting wire between the zinc and copper in the cell used in the last experiment, and connect in a similar manner the zinc of this cell to the brass strip in the second cell; take another wire and connect the copper strips in each cell together. We have then the arrangement shown in Fig. 2.

The action now observed in the cell containing the zinc and copper will be similar to that found to occur in the former experiment, and no action will, at first, be observable in the other cell. After a few minutes, however, if the strip of brass be taken out of the solution and examined, it will be found that the whole of the surface which has been immersed in the copper sulphate solution, is coated with a fine salmon-pink coloured deposit of copper. In this experiment, electrical energy has been generated in the first cell, and utilized not only in this cell to decompose sulphuric acid, but in the second cell to decompose copper sulphate ($CuSO_4$), thus liberating the copper and depositing it upon the brass strip. The original loss of energy, in the form of heat, undergone by copper when combining with SO_4 to form copper sulphate, is now restored by applying electrical energy, with the result that the copper is recovered in its original metallic condition.

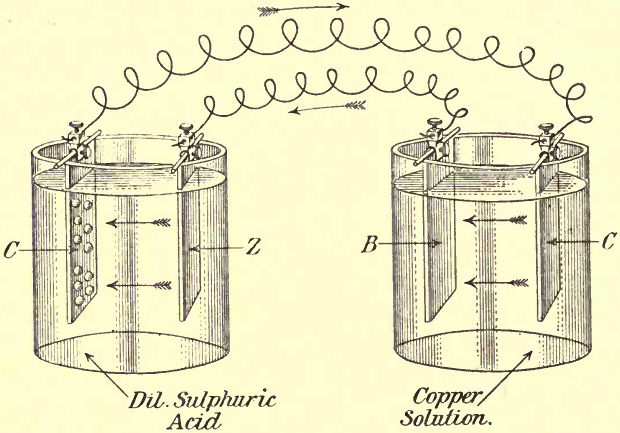

FIG. 2.—Simple voltaic cell connected to copper depositing cell.

It is evident, however, on consideration of the law of the

"Conservation of Energy," that an indispensable condition of such action is that the amount or quantity of electrical energy thus applied must be at least equal to or slightly in excess of the amount of energy evolved in the formation of the original compounds. Much research has been done in the direction of determining quantitatively the amount of heat evolved by the elements in thus combining to form compounds, and it is now possible to assign to them, what may be termed a general order of activity in this respect, those at the top of the list evolving a greater number of heat units in their combinations than those below. Such an arrangement of the commoner metals is given in Table III.

TABLE III.

THE COMMONER ELEMENTS ARRANGED IN ORDER OF THEIR ACTIVITY OF COMBINATION AS SHOWN BY EVOLUTION OF HEAT ENERGY.

Combinations with			
Oxygen O.	*Chlorine* Cl.	*Bromine* Br.	*Iodine* I.
Magnesium	Magnesium	Potassium	Potassium
Calcium	Potassium	Sodium	Sodium
Sodium	Sodium	Calcium	Calcium
Potassium	Calcium	Aluminium	Aluminium
Aluminium	Aluminium	Zinc	Zinc
Zinc	Zinc	Cadmium	Cadmium
Iron	Cadmium	Lead	Lead
Cadmium	Lead	Copper	Copper
Cobalt	Iron	Gold	Gold
Nickel	Cobalt		
Lead	Nickel		
Copper	Mercury		
Mercury	Silver		
Silver	Copper		
	Gold		

As will be observed from the typical compounds shown above, the order varies slightly according to the nature of the compounds formed, some elements having what may be termed a special aptitude for forming particular salts. The general order, however, is only departed from within comparatively narrow limits.

The practical meaning of this feature of chemical combination is, that wherever two or more combinations of elements are possible in any action or series of actions, that in which the greatest amount of heat energy is evolved will, as a general rule, be effected first.

In addition, metals occupying a leading position in the above arrangement, have usually the power of replacing elements lower in the list, in any particular compound; as a consequence they liberate the latter and often deposit them in a metallic condition. For example, if a strip of metallic zinc is placed in a solution of copper sulphate, the heat energy evolved in the combination $Zn + SO_4$ being higher than that of $Cu + SO_4$, the zinc will dissolve and form $ZnSO_4$, and as a consequence metallic copper will be liberated on the surface of the zinc immersed, thus—

$$2Zn + 2CuSO_4 = 2ZnSO_4 + 2Cu.$$

A similar result will be obtained, if iron is used instead of zinc. This principle is the basis of all the "simple immersion" processes for the deposition of metals to which reference will be made later. Effects of this order may also be obtained in the case of fused or melted substances, as well as with substances dissolved in water. Silver may, for example, be readily liberated from fused silver chloride, by placing in the chloride a few small pieces of metallic zinc, according to the equation

$$Zn + 2AgCl = ZnCl_2 + 2Ag.$$

The Electro-chemical Series.—In electro-chemistry another arrangement of the elements is made, which has great practical importance in the deposition of metals. This is known as the *Electro-chemical Series*, being an order or arrangement of the metals showing how they are electrically related to each other, when placed in solutions which have the property of conducting electricity. It will have been observed in the experiment illustrated in Fig. 1, that when a circuit was completed, the electric current passed *inside the liquid from the zinc to the copper*. This result naturally leads us to consider the current as originating at the zinc. If, therefore, we consider a flow of electricity as analogous to a flow of water, which for present purposes we may do, then we may legitimately consider the zinc as being as it were at a higher level—or, as it is termed, at a higher *potential* (see Chap. III.)—than the copper. Similarly, if any other pair of unlike metals were placed in sulphuric acid as the conducting liquid, it would be found in all cases where a current was produced, that one metal was at a higher potential than the other.

TABLE IV.

Arrangement of the Principal Elements in Electro-Chemical Series.

	+
Positive Elements	Potassium
	Sodium
	Calcium
	Magnesium
	Aluminium
	Manganese
	Zinc
	Iron
	Cadmium
	Cobalt
	Nickel
	Lead
	Tin
	Bismuth
	Copper
	Silver
	Mercury
	Palladium
	Platinum
	Iridium
	Gold
	Hydrogen
	Antimony
	Carbon
	Arsenic
	Phosphorus
Negative Elements	Iodine
	Bromine
	Chlorine
	Nitrogen
	Sulphur
	Oxygen
	−

In this order, any single element is electro-negative to any one placed above it, and positive to any below it.

Negative elements are, in electrolysis, always given off at the anode, or positive electrode. Positive elements are given off at the cathode.

Experiments of this nature have been made, with the result shown in Table IV., in which the principal metals are placed in such an order that if any two of them are taken, the current will flow within the cell *from the higher to the lower*, the higher metal being termed *electro-positive*, and the lower *electro-negative*. It must be clearly understood, however, that the terms "electro-positive" and "electro-negative" are only relative. Thus, if two metals are taken almost from the middle of the list, *e.g.* gold and tin, although both are considered electro-positive, yet the lower one, gold, would necessarily be electro-negative to the other if placed in the same solution. As in the case of the table of heat evolution, which, as might be expected, the present table closely resembles, the order varies slightly with different solutions, but the general arrangement holds good for most solutions.

Electrolysis.—Terms employed in connection therewith.—Electrolysis is the term used to describe the operation of decomposing by electricity any substance, whether in solution or in a state of fusion (*i.e.* molten), and in this connection other terms are used which may here be defined and explained.

(*a*) *Electrolyte* is the term applied to substances dissolved in a liquid undergoing decomposition, or to any liquid which can be decomposed by electricity. All liquids or solutions may be divided into two classes, electrolytes and non-electrolytes. The former are conductors of electricity, and during conduction are decomposed. The latter class includes liquids that either do not conduct electricity at all, such as oils, paraffin, turpentine, etc., or, if conductive, are not decomposed, such as mercury.

(*b*) *Electrodes* are the plates or conducting mediums, by means of which electricity enters or leaves an electrolyte. That which is at the higher potential and by which the current enters is termed the ANODE, that which is at a lower potential and by which the current leaves is termed the CATHODE.

(*c*) *Ions, anions and cations.*—The meaning and use of these terms will be understood, by a brief consideration of the chief points of the theory of electrolysis as given in the following section.

The Theory of Electrolysis.—It may be said that the distinguishing feature of electro-chemical or electrolytic action, as contrasted with chemical action, is that the products of the former only appear at the surface of the electrodes, the anode and cathode respectively, whereas the products of the latter action permeate the entire mass. In order to explain this fact and other phenomena of electrolysis, the molecules which make up an electrolyte are regarded as existing, at least partly, in what is termed a "dissociated" condition, *i.e.* they are not simply molecules in the mere chemical acceptation of the term, nor even atoms, but particles endowed with a special nature, by reason of which they are called "*ions*"—a term due originally to Faraday, and derived from a Greek word meaning "moving" or "going."

The nature of the difference may be explained by an example. For instance, when crystals of copper sulphate are dissolved in water an electrolyte is formed, and when the solution is complete, it is assumed that some of the molecules of the salt, $CuSO_4$, become dissociated into what may be termed a metallic part or radicle, and an acid part or radicle, the word "ion" being applied to both. It is obvious, however, that Cu and SO_4 respectively do not exist merely as chemical individvals. "Cu" is the chemical symbol for metallic copper. "SO_4" is a compound of sulphur and oxygen, which is not known to exist in a free state. The ions of a solution of copper sulphate must therefore differ from their atomic or molecular constituents in some important essential, and from considerations which need not here be entered into, this difference is regarded as consisting in their possessing in the ionic state an *electrical charge*, which has both a qualitative and quantitative value. The Cu section of the molecule with its charge is then known as *cuprion*, and the SO_4 section with its charge as *sulphion*.

The former is charged with positive electricity, the latter with negative.

To a reader unfamiliar with electrical matters, this may require some further explanation. The theory of electrical science supposes all bodies to be charged with equal amounts of positive and negative electricity, which normally neutralize one another, and thus no state of electrification is exhibited externally. The act of electrifying a body is to separate the positive and negative charges; the body then exhibits the phenomena of "electrification." For example, a rod of sealing wax may not exhibit any signs of electrification; but rub it with a piece of dry flannel and then present it near to some bits of paper, bran, or sawdust; the latter are attracted towards the rod.

Now, even in this simple experiment it can be shown that after rubbing, the rod and the flannel are in different states; the rod is said to be negatively charged, and the flannel positively charged; thus the act of rubbing may be looked upon as a means of separating the positive and negative charges. Further, a positively charged body attracts a negatively charged body, and repels a body which is positively charged like itself. That is, charges of opposite "sign" attract one another; charges of like sign repel one another.

Now, as will be more fully explained later, the terminals or poles of a voltaic cell are in the state which is described as being electrically charged, the one positively and the other negatively. When, therefore, they are connected to the two electrodes of the depositing cell, and these become positively and negatively charged, they will exert an attraction on the oppositely charged ions, the positive electrode or anode on the negatively charged ions, and the negative electrode or cathode on the positively charged ions. Hence the positive ions move to the cathode plate, and are therefore called *cations;* the negative ions move to the anode plate, and are therefore called *anions*. In our instance the positively charged cuprions of Cu are the cations; the negatively charged sulphions of SO_4 are the anions.

Now, when these moving ions touch each their respective electrode by which they are attracted, they give up their charge and immediately return to their natural chemical state. The cuprion losing its electrical charge becomes simply metallic copper, and deposits itself as such on the surface of the cathode. The sulphion, SO_4, chemically combines with the metal of the anode and forms copper sulphate.

	Cathode	*Ion*	*Ion*	*Anode*	
Before		Cu	SO_4		
		←	→		
After	Cu		SO_4		
			$SO_4 + Cu$		$= CuSO_4$

As the charges carried by the ions are, from the above, of an opposite kind to that on the electrodes to which they migrate, some neutralization takes place, and the action would soon cease were it not for the fact that the cell or battery tends to maintain the electrodes in a charged state, *i.e.* to keep up the potential difference (see p. 33) between them. Thus, so long as the action proceeds, electricity is drawn from the battery, and as it is termed a current "flows" round the circuit.

The following diagram (Fig. 3) will perhaps make the matter clearer, the signs + and − denoting positive and negative electrical charges respectively.

Electrolysis continues, therefore, so long as the electrodes are recharged from the source of current, and so long as any ions remain to be discharged; in the present instance the ions are continually replenished in the solution by means of the action of the sulphion SO_4, which being liberated at the anode, combines with it to reform $CuSO_4$, and so enables the process of deposition to continue, by furnishing successive series of dissociated ions.

Laws of Electrolysis.—As has been already observed, the ions of an electrolyte not only possess an electrical charge of a definite quality, but also of definite *quantity*. Faraday, whose brilliant genius laid the foundations of the science of electro-chemistry, investigated this part of the subject exhaustively, and formulated certain laws or principles, which are now considered fundamental.

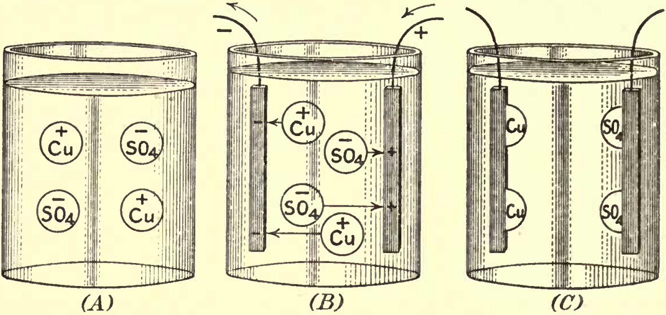

Fig. 3.—Diagram to illustrate the dissociation theory of electrolysis.

(A) Ions in motion but possessing no definite direction. (B) On electrolysis ions in motion in definite directions. (C) Illustrating action at electrodes.

Note.—If the anode is *not* soluble, the SO_4 attacks the water present, and liberates oxygen with the formation of sulphuric acid, thus $2SO_4 + 2H_2O = 2H_2SO_4 + O_2$.

These laws may be summarized thus:—

I. The weight of any substance liberated or deposited from an electrolyte is directly proportional to the quantity of electricity flowing through the circuit.

II. The weights of different substances liberated or deposited by the same quantity of electricity are proportional to their respective chemical equivalents.

In the light of the "ionic" theory of electrolysis, the first of these laws may be also stated as follows: The number of ions liberated, or in other words, giving up their electrical charge, is directly proportional to the quantity of electricity flowing through the circuit. If, therefore, a definitely measured quantity of electricity, flowing through an electrolyte, is found to deposit one gram of the metal concerned, then double this quantity of electricity, flowing through the same electrolyte, will result in the deposition of two grams. How a "quantity" of electricity is measured will appear later.

The meaning of the second of these laws is that the actual weight of metal deposited from a solution, depends not only upon the current, but upon the nature of the metal, *i.e.* if the same quantity of electricity is passed successively through solutions of silver, copper, gold, and nickel, the weight of each metal deposited will bear the same ratio to the others as their respective chemical equivalents.

This law is of extreme importance to the electroplater, and it may also be advisable to point out, that because of it the question of the valency of metals assumes first-rate significance, for it is evident from this law, that the weight of any metal liberated in electro-chemical action depends not only on its atomic weight, but also on its valency.

Suppose two electrolytes, containing, for example, silver and copper respectively, were electrolyzed by the same current; it would be found that the proportion of silver liberated to that of copper would be as 108 : 31·75, which of course agrees with Faraday's law (II.). Now, the respective atomic weights are 108 and 63·5. If, therefore, the ions of silver and copper were simply regarded as the chemical atoms Ag and Cu, a serious theoretical difficulty would arise. When consideration is given to the valencies of the two metals, however, the apparent discrepancy is overcome by regarding the bivalent copper ion as carrying a double electrical charge, corresponding to its valency, viz. 2, while the univalent silver ion carries only a single charge. The copper ion therefore demands, proportionately to the silver, twice the charge at the electrodes to enable it to be discharged, with the result that the weight of copper obtained is relatively only half its atomic weight, while the corresponding amount of silver obtained is equal to its atomic weight. Further, it will be found that the elements of greater valencies behave similarly; trivalent ions carrying three electrical charges, quadrivalent four, and so on.

Indeed, from the electro-chemical point of view, valency means simply the number of electrical charges associated with the elements, when in solutions undergoing electrolysis. Arithmetical illustrations of Faraday's laws, which will further elucidate their meaning, will be given in Chapter IV.

CHAPTER III

FUNDAMENTAL ELECTRICAL PRINCIPLES

To those engaged in the work of plating, or kindred processes, a grasp of the fundamental principles of electricity is becoming more and more essential.

Whenever electricity is used for lighting, traction, electroplating, electrotyping, the working of machinery by means of electric motors, etc., it is the so-called "electric current" which is the agent, or to speak more strictly it is the electrical energy associated with the "flow" of electricity which in doing the work accomplished is converted into some other form of energy. In all cases where electricity is the agent doing work, one or other of the properties or effects resulting from the "flow" of an electric current is utilized, and it is only through these properties that work can be done. The properties of an electric current must therefore first be considered.

Properties of an Electric Current.—From the preceding chapter it will have been gathered that a current of electricity has the property of "electrolyzing" or decomposing compound solutions called electrolytes. This effect is generally spoken of as the CHEMICAL EFFECT.

There are, however, two other effects, namely, the *Thermal* or *Heating* effect, and the *Magnetic* effect.

Although the chemical effect is the one which is of primary importance to the electroplater, a knowledge of the others is necessary in order better to understand the working of electricity, so that they will first be briefly mentioned.

The Magnetic Effect.—If a wire through which a "current" is said to be "flowing" is held in almost any position near to a pivoted magnetic needle at rest, the needle is deflected, thus showing that a mechanical force has acted on the needle, and this force is of the same nature as that which would be exerted on the magnetic needle by another magnet. We see therefore that the "current" has a magnetic effect.

Again, a piece of soft iron if dipped into iron filings will exert little or no attractive effect upon them. But when a wire carrying a current is coiled round the iron in a close spiral of many turns, the iron behaves quite differently, and will readily pick up a mass of the iron filings; it is "magnetized," and this magnetic state has been brought about by the current flowing spirally round the iron.

The Thermal or Heating Effect.—Whenever a current flows through a conductor, electrical resistance is overcome, and since this resistance is analogous to friction, heat is produced. If the rate of production of heat is sufficiently rapid, the conductor becomes quite warm to the touch, or even has its temperature raised to the point of incandescence as in an ordinary electric glow lamp.

Before dealing in greater detail with the properties and effects of electric currents, it will be advisable to get a clear understanding as to what is meant by the flow of electricity in an electric circuit, and to consider the electric circuit in general, so as to explain the meaning of some of the terms used in connection with electrical apparatus.

The Electric Circuit.—An electric circuit is the complete path which an electric current traverses, and in which electrical energy is transformed into other kinds of energy. It contains essentially the "generator" or source, the apparatus to be worked, and the necessary transmitting and distributing wires connecting the whole together to form a continuous conducting path.

Every electric circuit containing a generator at work is divisible into two portions, the *internal* and *external* portion. The internal portion is the path through the generator from one of its terminals to the other; the external portion is the path from one terminal through the apparatus worked by the current to the other terminal. Thus in Fig. 4 (*a*) when the switch is closed, the part from D to A through the dynamo is the internal, and the part ABCD the external portion. These are frequently called the *internal circuit* and the *external circuit* respectively.

As the "flow" of electricity in a circuit is in many respects quite analogous to the flow of water through a pipe, the analogy will be helpful. When a battery or direct-current dynamo is joined up as shown in Fig. 4 (*a*) in an incomplete or "open" circuit ("open" because the switch is "off"), it may be likened to a pump (Fig. 4 (*b*)) with its inlet D and outlet A connected by a pipe, in which a stop-cock turned to the "off" position is interposed, the whole being filled with water. Working the pump will produce a difference of water pressure between the two sides of the stop-cock, that on the left being, say, greater than that on the right. Mark these + and − respectively. This difference of pressure will depend on the "water-moving force"

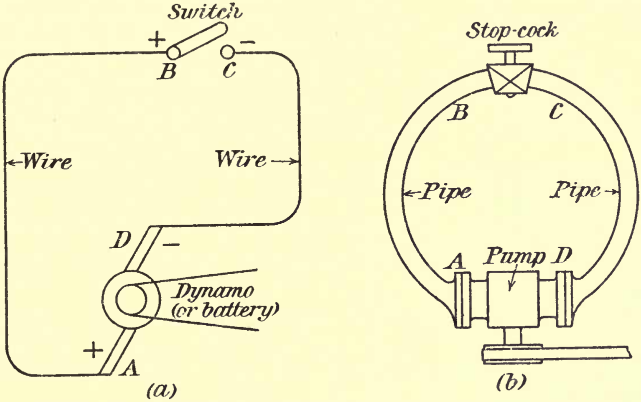

FIG. 4.—The electric and hydraulic circuits compared.

of the pump. Obviously, however, no water will flow so long as the stop-cock is "off," but on turning the cock "on," the pressure difference will set the water in motion, and a flow will be maintained so long as the pump is at work.

Potential and Difference of Potential.—Referring now to the electric circuit, and accepting the statement that all bodies contain within them electricity "at rest," then when the dynamo is working, or the battery is charged, the wire AB connected to the + terminal of the generator is in a different physical state to the wire CD connected to the − terminal. From the electrical standpoint the wire AB is described as being at a higher *electrical potential* or as having an electric potential which is *positive*, while CD is at a lower potential or is said to have a *negative* potential. Thus when the generator is working there is a *difference of electrical potential* between any point on AB and any point along CD, but *the electricity is still "at rest,"* since the conducting circuit is interrupted by the switch.

The term "electrical potential" is perhaps rather puzzling, but its meaning may be illustrated by the term "pressure" used in a mechanical sense. For instance, if the pressure of the steam in a boiler is measured by a pressure gauge, the gauge indicates the pounds per square inch *above atmospheric pressure*, which inthe case cited is taken as the zero of pressure for practical purposes; in other words, the gauge indicates the difference of pressure between the absolute boiler pressure and the atmospheric pressure. Similarly, the electrical potential at any point in an electric circuit is for practical purposes reckoned as the difference between the electrical potential of the point in question and that of the earth which is arbitrarily taken as the zero of potential.

For most purposes, however, the actual potential at a point in a circuit is of little or no moment, and it is only a knowledge of the *difference of potential* between two points which is of vital importance, since this is the cause of the electricity being set in motion. Electricity and water at rest are of no commercial value so far as doing work is concerned, but when in motion they at once assume commercial importance, for both are capable of doing work.

Electromotive Force.—Returning now to the case of Fig. 4 (*a*), when the circuit is completed by the closing of the switch, the potential difference (expressed in an abbreviated form by the letters P.D.) existing between A and D sets electricity in motion, starts the "current" in fact. But the dynamo or battery is a machine or apparatus devised for the express purpose of *maintaining* the potential difference across its terminals; hence while it is operative a continuous flow of electricity results, just as in the case of the pump which maintains a difference in pressure between the discharge and suction pipes. The function of an electrical generator is therefore to set up an *electricity-moving-force*, termed the *electromotive-force* (in abbreviated form expressed by the letters E.M.F.).

Common usage has introduced such expressions as "electricity-generating station"; "a dynamo generates electricity," etc. Nobody would say, however, that the pump in Fig. 4 (*b*) generated water, and, therefore, strictly speaking, expressions such as the above are incorrect. The cell, battery, or dynamo generates the E.M.F. which sets the electricity in motion, and so they may in a sense be said to generate an electric current, but they do not generate the electricity which is thus moved.

The manner in which an E.M.F. is set up by cells, or dynamos, is dealt with in Chapters V. and VI.

Rate of fall of P.D.—Consider now Fig. 5 (*a*) in which A_1B_1 is a horizontal pipe of uniform bore, to which are attached at points along its length open-ended vertical glass stand-pipes T_1, T_2, T_3, T_4, T_5, the end A_1 being attached directly to the discharge pipe M of a centrifugal pump, while B_1 is connected to the suction side of the pump through a return pipe $B_1C_1D_1$, on which there are similar stand-pipes not shown on the drawing. S_1 is a stop-cock. The electrical equivalent is depicted in Fig. 5 (*b*), analogous parts being similarly lettered. The electrical circuit consists of a dynamo corresponding to the pump, a switch S_2 corresponding to the stop-cock, and conductors MA_2, A_2B_2, and $B_2C_2D_2$ corresponding to the pipes. In both circuits it will be assumed that

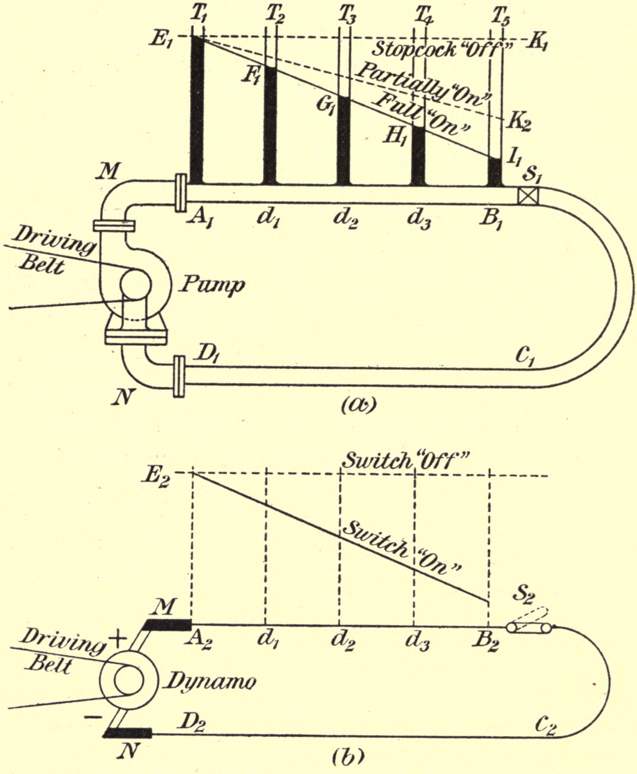

FIG. 5.—The rate of fall of (*a*) by hydraulic pressure, or (*b*) electric potential in circuit of uniform resistance.

the points A_1 or A_2 and M are close to one another or connected by pipes or wires of large area as shown, and likewise points D_1 or D_2 and N, so that virtually A_2 and D_2 are connected to the terminals MN of the dynamo, while in the water circuit A_1 and D_1 are joined to the discharge and suction ends respectively of the pump.

Let the entire pipe circuit now be filled with water to a level, say, halfway up all the glass tubes, *i.e.* to G_1. All the water is then at rest, its surface being at atmospheric pressure which forms our zero starting-point from which to measure pressures. In the case of the electrical circuit the electricity is already within it and at rest.

Now let the stop-cock S_1 be closed, so that the pipe line is interrupted, and let the pump be started. It will be found that the water will *rise* in all the stand-pipes on A_1B_1 to exactly the same height, the line E_1K_1 joining the tops of these columns being horizontal. Conversely in the stand-pipes on C_1D_1 it will *fall* to a uniform level. Since the water cannot circulate owing to the stop-cock being closed, it still remains at rest (except for the whirling going on in the pump which may for our purpose be disregarded), but at different levels on the discharge and suction sides respectively. The extra height to which the water is forced up in the stand-pipes T_1, T_2, etc., is a measure of the water pressure above the atmosphere at those points where they are connected, and the vertical pipes could be replaced by ordinary pressure gauges which would register the pressure above the zero of the atmosphere (corresponding to the higher or positive potential in the electrical case). On the other side the fall of the water in the stand-pipes would measure the suction, and these pipes could be replaced by vacuum gauges, registering the fall of pressure (corresponding to the lower or negative potential in the electrical case).

Evidently, then, in the case illustrated the distribution of pressure in each pipe is uniform; it has one uniform value in A_1B_1, and another uniform value in C_1D_1. Also, it is clear that the difference of pressure between any point of A_1B_1 and the return pipe is a constant.

Analogously to this in the electric circuit (Fig. 5 *b*), the electrical potential at all points from M to the switch *viâ* A_2 and B_2 is *exactly the same* so long as the switch S_2 is "off," and a similar remark applies to the potential at all points from S_2 to D_2, *viâ* C_2. But the potential of the portion MA_2B_2 is higher than that of $S_2C_2D_2$, if M is the positive terminal of the dynamo. This P.D. could be measured by means of a suitable *voltmeter*—an instrument for measuring difference of potential, and electrically analogous to a boiler pressure gauge. Such an instrument would indicate that the P.D. was a constant, providing that one of its terminals be joined to any point on the conductor MA_2B_2, the other to any point on the conductor $S_2C_2D_2$, and that no change except the moving of the voltmeter wires be made. Hence, when a generator is running, so long as the circuit is "open," the *P.D. between the conductors leading from its terminals is a constant quantity*, and further, *this constant quantity is equal to the E.M.F. developed by the generator.*

Now let the stop-cock S_1 be fully opened, and let a steady stream of water be allowed to flow through the pipe of Fig. 5 (*a*), in the direction A_1 to B_1. The pipe being full throughout, the whole of the work of the pump is expended in forcing water round the circuit, and in doing this work the total difference of pressure between inlet and outlet is absorbed. The height of the water in the stand-pipes will then be different in the different pipes; those nearer the end A_1 will indicate a greater pressure than those more remote towards B_1, and the level in the stand pipes on C_1D_1 will fall as we approach N. It follows, therefore, that the water pressure at points in the pipe diminishes in the same direction as that in which the stream flows. As the pipe A_1B_1 has been assumed straight and of uniform cross section, the tops of the water columns in the stand pipes will be found to lie all in one straight line $E_1F_1G_1H_1I_1$, but sloping. If the length d_1d_2 along the pipe A_1B_1 equals the length d_2d_3, the difference between the height of water in the stand-pipes T_2 and T_3 is the same as that between stand-pipes T_3 and T_4. Also, if d_1B_1 be n times d_3B_1, the difference between F_1d_1 and I_1B_1 is n times that between H_1d_3 and I_1B_1. In other words, *when a steady stream of liquid flows through a uniform pipe the* *difference in pressure between any two points is proportional to the distance between those points*, and this is true whether the tube AB is horizontal or inclined.

Again, if the stop-cock S_1 be partially shut the rate of flow of water is diminished and the pressure distribution altered; the statement above (in italics), however, still holds good, but the *slope* of the pressure line will now be, say, E_1K_2, and the pressure difference between, say, d_1d_2 will be less than formerly.

A restriction made in the bore of the tube, say, between d_2d_3 (Fig. 6) diminishes still further the rate of flow, and the pressure line may now be $E_3F_3G_3H_3I_3$.

Now, the difference in pressure between any two points of the pipe is dependent upon the rate of flow of the water, and the frictional resistance offered by the pipe to its passage. As, however, in the example taken the rate of flow is exactly the same at all points along the pipe when the stream is steady, the explanation of the greater difference of pressure between T_3 and T_4 than between T_2 and T_3 must be put down to the extra resistance introduced by the restriction between d_2d_3. The rate of flow of water in the pipe circuit, however, depends upon the resistance of the pipe as a whole, and the difference of pressure or "head" between the discharge and suction pipe.

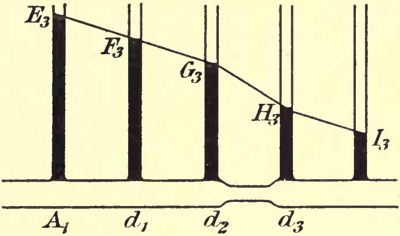

FIG. 6.—Fall of pressure in circuit not having uniform resistance.

Analogously in the electric circuit when the conducting path is completed by the closing of the switch, a current of electricity results, flowing in the direction $MA_2B_2C_2N$, that is, from the + terminal of the generator round the external circuit to the − terminal, and through the internal circuit from − to +. The potential at points along the conductor is no longer uniform, but falls in the direction M to N, *i.e.* in the direction in which the current flows. Assuming A_2B_2 to have a constant cross-sectional area, the *fall of potential* is indicated by the full straight line E_2A_2, representing to scale the potential at A_2 with respect to zero or the earth's potential; similarly the heights to the full straight line represent the potentials at d_1, d_2, etc. If, therefore, the length $d_1d_2 =$ the length d_2d_3, then the P.D. between d_1 and $d_2 =$ the P.D. between d_2 and d_3, and from the same reasoning, if $d_1B_2 = n$ times d_2d_3, their respective P.D.'s are in the same proportion. In other words, *when a steady current of electricity flows through a uniform wire the P.D. between any two points is proportional to the length of the conductor between the two points.*

In the electric circuit this is true whether the wire is straight or bent so long as its area is not altered, and whatever be its position. The statement could be verified by means of a voltmeter placed across d_1d_2, d_2d_3, or other points along the wire.

Again, the rate of flow of electricity in a circuit where there is only one path provided for the passage of electricity, viz. $MA_2B_2S_2C_2D_2N$, is the same at all points, for if *ammeters*—instruments for measuring the rate of flow—be inserted at various points in the circuit, they will all indicate the same value.

Resistance and Ohm's Law.—Now, with a metal conductor at a constant temperature, innumerable experiments have shown that the rate of flow is directly proportional to the P.D. between the ends of the conductor, and that the ratio $\frac{\text{P.D.}}{\text{rate of flow}}$ is a constant quantity, a relationship first announced by Dr. Ohm in 1827.

This constant quantity is called the *electrical resistance* of the conductor, while the rate of flow of electricity is expressed as the current. Thus the relationship enunciated by Dr. Ohm may be written

$$\frac{\textbf{P.D.}}{\textbf{current}} = \textbf{Resistance},$$

and is known as **Ohm's Law.**

The use of the term "resistance" having now become customary, all circuits or parts of a circuit are regarded as possessing obstructive properties, so that the P.D. existing between two points must be looked upon as the electrical pressure used up in forcing the current against the resistance offered to its passage between these points.

The introduction of an extra resistance (the equivalent of the restriction in the water circuit of Fig. 6) in a circuit containing a generator of fixed E.M.F. will reduce the current, and there will be a redistribution of the potential and of the P.D.'s across the various parts, just as in the water circuit.

The analogy between water circuits and electric circuits is a useful one, but like most analogies it must not be pressed too far, since there are certain points of difference. Electricity, for example, is not a material substance like water, and consequently cannot be strictly looked upon as "flowing" in the same sense as water flows; the word "flow" is merely a metaphor, yet by its aid, probably a better grasp of certain electrical phenomena may be obtained than by any other explanation.

Electrical Units and their Definitions.—Although electricity is not a material substance, yet nevertheless some means must be adopted in order to express the magnitude of the various quantities used in electrical science in ways similar to those adopted in other sciences. For example, the quantity of water contained in a tank may be expressed by using the unit, the gallon, and further, if a pipe be inserted and the water allowed to run out, the rate at which the water runs out may be expressed as so many gallons per minute, or pints per second. Here the gallon has been adopted as the unit of quantity, and the gallon per minute as the unit rate of flow, the latter expressing, of course, the rapidity with which the water flows from the tank.

So with electricity, units are required to express quantity of electricity, and rate of flow. As the presence of an electric current is only manifested by its properties, such units must be based on one or other of the effects mentioned at the beginning of the chapter and on the magnitude of these effects.

For reasons which need not be entered into here the practical definitions of the above units are based on the chemical effect.

Definition.—*Unit quantity of electricity* is that quantity which, when passed through a solution of silver nitrate in water will deposit 0·001118 gram of silver, and is called the **Coulomb.**

Definition.—*Unit rate of flow of electricity or the current* is that unvarying current which when passed through a solution of silver nitrate in water will deposit silver at the rate of 0·001118 gram per second; it is thus the rate corresponding to the passage of a *coulomb per second*, and is called the **Ampere.**

If the *rate of flow*, *i.e.* the current, be multiplied by the *time* for which it lasts, the product must give the total *quantity* of electricity that passes in the given time, the relationship between the above units may therefore be expressed as follows:—

$$\begin{array}{c}\textbf{Quantity}\\ \textbf{in coulombs}\end{array} = \begin{array}{c}\textbf{current in}\\ \textbf{amperes}\end{array} \times \begin{array}{c}\textbf{time in}\\ \textbf{seconds}\end{array}$$

Symbolically $Q = I \times t$,

where Q = quantity in coulombs,
I = current strength in amperes,
t = time during which the flow lasts in seconds..

The coulomb, however, is a very small unit, so a secondary unit called an **ampere-hour** is often employed for practical purposes.

Since 1 ampere flowing for 1 second = 1 coulomb,
then 1 ,, ,, 3600 seconds = 3600 coulombs.

But 3600 seconds = 1 hour.

∴ 1 ampere flowing for 1 hour = 3600 coulombs,
or 1 ampere-hour = 3600 coulombs.

Examples.—1. A plating vat has a current of 50 amperes flowing through it for 6 hours, what quantity of electricity passes through the vat?

$$Q = I \times t$$

Substituting, we get $Q = 50 \times 6 = 300$ ampere-hours,

or $Q = 50 \times 6 \times 3600 = 1{,}080{,}000$ coulombs.

2. One thousand three hundred ampere-hours pass through an electric circuit in 10 hours 50 minutes: what is the average current?

$$I = \frac{Q}{t}.$$

Substituting, we get $I = \dfrac{1300 \text{ ampere-hours}}{10\frac{5}{6} \text{ hours}}$

$= 120$ amperes.

Current Density.—For electrolytic purposes current density is defined as the amperes per square centimetre, or per square inch of area of electrode immersed in the electrolyte. The current density, together with other factors which will be discussed as occasion arises, has an important bearing on the kind of deposit obtained. A very simple experiment readily shows this to be the case. Take a little coppering solution (see page 252) and immerse in it two clean and smooth copper plates of about 4 square inches area to form an anode and cathode respectively. Pass a current of about one ampere for 5 to 10 minutes. Observe that the copper deposited is salmon pink in colour, dull, but smooth. Now pass 5 or 6 amperes for a similar period and notice that the deposit is much rougher and more crystalline than before.

Resistance and Conductance.—All substances, whether solids, liquids, or gases, are regarded as possessing from an electrical point of view a property which may be described from two opposite points of view as either its "resistance," or its "conductance," the one being the converse of the other. In the case of a water pipe of small section, if we try to force through it a large quantity of water, we know that the smallness of the bore presents considerable resistance to the effort. The pipe might, therefore, be described either as a "good resister" to the flow, or as a "bad conductor" of the flow. In the same way that property of any substance which *resists* the flow of electricity is called its **Resistance**, and from the opposite point of view the facility offered to the flow is called its **Conductance.**

All metals are fairly good conductors of electricity, but the four metals, silver, copper, gold, and aluminium, stand pre-eminent in this respect, their relative conducting powers being of the order 1 : 0·92 : 0·67 : 0·56 respectively. Of these silver and gold are obviously too expensive to employ for electrical conductors, and in consequence, as copper and aluminium are relatively cheap, it is usual to find that conductors are composed of one or other of these metals, copper being used to a far greater extent than aluminium.

On the other hand, substances such as gutta-percha, india-rubber, ebonite, mica, glass, porcelain, etc., are extremely bad conductors, so much so that they are termed **insulators**, and are used to confine currents of electricity along definite conducting paths and prevent leakage. This, in fact, is the object of covering electrical conductors with some substance which has good insulating properties. Bitumen, oiled paper, vulcanized india-rubber, cotton and silk, are among the chief insulating materials used for this purpose, vulcanized india-rubber being employed to a very large extent for cables, while silk and cotton (well varnished) are used for winding electrical instruments and machines respectively.

The unit of resistance is called the **ohm**, and is defined as the resistance offered to an unvarying current of electricity by a column of pure mercury having a uniform cross-sectional area of 1 sq. mm., a length of 106·3 cms. and a mass of 14·4521 grams at 0° C.

As a fairly close approximation, $42\frac{1}{3}$ yards of No. 20 S.W.G. (0·036″ diam.) copper wire has a resistance of 1 ohm at a temperature of about 15° C. (roughly 60° F.). Other equivalents of the ohm are given in Table IX. on page 129.

The unit of conductance is called the **mho**, a term suggested by the late Lord Kelvin. It may be defined as the facility offered to the passage of an unvarying current by a column of mercury having the dimensions and particulars given above.

The relationship between these units is as follows:—The measure of the conductance of a wire or circuit is given by the reciprocal of its resistance; if R = its resistance in ohms, then $\frac{1}{R} = K$, its conductance is mhos, and *vice versâ* $\frac{1}{K} = R$.

It is, however, more usual to speak of the resistance of a material, rather than of its conductance, and this more general usage will be adhered to in the majority of cases for present purposes. But from the above relationship, if one of the two expressions be known, it is easy to see how it may be converted if we wish to express the property in question in its second form.

Two other terms, namely, "specific resistance" or "resistivity," and "specific conductance" or "conductivity," are frequently employed when dealing with the resisting, or oppositely the conducting, property of *different kinds of material*, and as these terms are frequently confused with those of resistance and conductance it will be well to state their precise meaning. **Resistivity** and **conductivity** are terms used to denote the resistance and conductance respectively of 1 cm. (or 1 in.) length of the material having a cross-sectional area of 1 sq. cm. (or 1 sq. in.) at 0° C. Their numerical values are spoken of as the resistivity in ohms per cm. per sq. cm. (or per in. per sq. in.) and the conductivity in mhos per cm. per sq. cm. (or per in. per sq. in.), according to whether the dimensions are in centimetre units or in inch units.

These terms therefore denote respectively, the resistance and conductance of a specified length of material, of specified cross-sectional area, whereas the terms resistance and conductance are used to express the obstruction and facility respectively offered to the passage of electricity by a material of *any* length, and *any* cross section. The resistivity of copper is less than that of German silver, but it is quite possible to have a copper wire of greater resistance than one made of German silver.

The term "resistivity" is of value in calculating the resistance of a conductor (as will be seen below), or for comparing the relative resistance of wires composed of different materials but of similar length and area. The resistivity of copper, for example, is 0·000000614 ohm per in. per sq. in., that of German silver 0·00000828 ohm in the same units at 0° C. The relative resistances are therefore as 0·000000614 : 0·00000828 or as 1 : 13·48. Owing to the low order of magnitude of the resistivity of metals, it is more usual to express resistivity values in microhms; 1 microhm $= \frac{1}{1,000,000}$ (one millionth) of an ohm.

Table V. gives the values of the resistivity of the common materials used for electrical purposes.

TABLE V.

RESISTIVITIES OF METALS AND ALLOYS.

Metals.	*Microhms at 0° C.* *per cm. per sq. cm.*	*per inch per sq. in.*
Silver, annealed	1·47	0·58
Copper, annealed	1·56	0·61
,, hard drawn	1·62	0·64
Aluminium	2·66	1·05
Gold	2·20	0·87
Zinc	5·75	2·26
Wrought iron, mild steel	10·0	3·94
Platinum	10·92	4·30
Nickel	12·32	4·85
Tin	13·05	5·12
Lead	20·38	8·0
Mercury	94·1	37·0
Alloys.		
German silver (varies with composition)	21·0	8·3
Platinoid	41·7	16·4
Eureka	44·2	17·4
Ferry	47·2	18·6

Laws of Resistance.—The resistance of a conductor depends upon four distinct factors :—

(1) Length.
(2) Area of cross section.
(3) Kind of material.
(4) Temperature;

to which may be added (5) the degree of purity and the hardness or softness of the material, these being really special variations that come more properly under (3).

Taking the effect of the dimensions and kind of material, it is found that the resistance is directly proportional to the length, inversely proportional to its cross section, and is obviously proportional to the resistivity of the material.

Expressing the above in algebraic form,

if
$$\left.\begin{array}{l} R = \text{resistance} \\ l = \text{length} \\ A = \text{area of cross section} \end{array}\right\} \text{of the conductor,}$$
$$\sigma = \text{resistivity of the material,}$$

then
$$R = \sigma \text{ for unit length having unit area,}$$
$$R = \sigma \times l \text{ for a length } l \text{ having unit area,}$$

and for area A
$$R = \frac{\sigma \times l}{A},$$

which is the fundamental equation expressing the resistance of a conductor as influenced by conditions (1), (2), (3). As fairly reliable data of the resistivity are given in the table above, it is possible to calculate the resistance of a given piece of wire, or to determine what length of a particular wire would be necessary to make a resistance of definite value. Owing, however, to the different units which may be employed, the law is expressed in more precise forms below,

$$(a)\ R_{\text{(ohms)}} = \frac{\sigma_{\text{(ohms per cm./sq. cm.)}} \times l_{\text{(cms.)}}}{A_{\text{(sq. cms.)}}}$$

$$(b)\ R_{\text{(ohms)}} = \frac{\sigma_{\text{(microhm per cm./sq. cm.)}} \times l_{\text{(cms.)}}}{10^6 \times A_{\text{(sq. cms.)}}}$$

$$(c)\ \mathrm{R}_{(\text{ohms})} = \frac{\sigma_{(\text{ohms per in./sq. in.})} \times l_{(\text{ins.})}}{\mathrm{A}_{(\text{sq. ins.})}}$$

$$(d)\ \mathrm{R}_{(\text{ohms})} = \frac{\sigma_{(\text{microhm per in./sq. in.})} \times l_{(\text{ins.})}}{10^6 \times \mathrm{A}_{(\text{sq. ins.})}}$$

Example.—The two copper leads from a dynamo to a plating vat are each 30 ft. long, and composed of wire $\frac{1}{4}$ in. in diameter. What will be the resistance of these leads? Resistivity of copper 0·61 microhm per in. per sq. in.

Taking expression (*d*) above, $\mathrm{R} = \dfrac{\sigma \times l}{10^6 \times \mathrm{A}}$

substituting, $\mathrm{R} = \dfrac{0{\cdot}61 \times 30 \times 2 \times 12}{10^6 \times 0{\cdot}7854 \times (0{\cdot}25)^2}$

from which $\mathrm{R} = 0{\cdot}00895$ ohms.

For practical purposes, tables such as are given on p. 129 are far more convenient and handy for resistance calculations, and examples are there given, but nevertheless the student should familiarize himself with the matter given above.

With respect to the resistance of conductors as influenced by temperature and purity, hardness or softness, little need be said here, as they are relatively unimportant to the electroplater. As a general rule the resistance of pure metals, with few exceptions, increases about 0·38 per cent. per 1° C. rise in temperature. In the case of alloys such as German silver, platinoid, eureka, etc., the percentage increase due to a rise in temperature is very much smaller. The degree of purity has a very great influence on the resistivity, as may be judged by reference to the resistivity table, and a hard-drawn wire offers a slightly higher resistance than one which has been subjected to an annealing process subsequent to drawing.

Resistivity and Conductivity of Electrolytes.—Strictly speaking, the resistivity of an electrolyte is the same property as that of any other conducting medium. It varies with temperature, in many cases *decreasing* with *increase* of temperature, and thus an electrolyte behaves in this respect in an opposite manner to most metals. Since, however, the resistivity of an electrolyte is so greatly influenced by the degree of dissociation and rate of migration of its ions, and comparatively so little influenced by its dimensions, it is more convenient to refer to the conductivity, as this expresses the ease with which the ions migrate. It will therefore readily be understood that the conductivity of electrolytes is a more complex problem than that of solid metal conducting mediums. At present it is regarded as being due to the power of the water or other solvent (called the "dissociant") to break up the dissolved salt into the two kinds of ions, which have been already described in Chap. II.

Unit of Electrical Pressure.—It is now necessary to introduce the unit of electrical pressure, which has been deferred until the ampere and the ohm had received consideration, in order that the most practical definition could be given. On page 38 the relationship known as Ohm's Law has been quoted. We had there the ratio—

$$\frac{\text{Potential Difference}}{\text{Current}} = \text{Resistance.}$$

Symbolically $$\frac{V}{I} = R$$

where V represents the P.D.

If, then, I and R each be unity, V must be unity, and in the practical system of units, *the unit of electrical pressure is that potential difference which will cause one ampere to flow through a resistance of one ohm.* It is called the **Volt.**

We shall now enlarge upon the above relationship between the quantities, pressure, current, and resistance, in order that the law may be correctly applied to any particular case, and with the recognized terminology. Generally, one or other of four expressions will be applicable to most circuit conditions.

I. *For part of an external circuit consisting solely of a resistance.*

$$\text{Current (amps)} = \frac{\text{P.D. (volts)}}{\text{Resistance (ohms)}}$$

or

$$I = \frac{V}{R}$$

where I = current through the part considered.

V = P.D. across ,, ,,

R = resistance of ,, ,,

II. *For the whole circuit.*

$$\text{Current (amps)} = \frac{\text{E.M.F. (volts)}}{\text{Total resistance (ohms)}}$$

$$I = \frac{E}{R}.$$

III. *For the whole circuit when there are two E.M.F.'s acting in it*—a case frequently arising in practice—

$$I = \frac{E \pm e}{R}$$

where E = the principal E.M.F.,

e = the other E.M.F.,

R = the total resistance of the circuit.

In words, the current is proportional to the *resultant* E.M.F. acting in the circuit and inversely proportional to the total resistance. The resultant E.M.F. is the sum of the separate E.M.F.'s if they both tend to send current in the same direction, in which case the + sign must be used. On the other hand, the E.M.F.'s may oppose one another; the resultant is then the difference between the E.M.F.'s, and the − sign is used. The direction of the current will always be the same as that in which the larger E.M.F. is acting.

IV. *For part of a circuit containing a resistance and an opposing or "back" E.M.F.*

$$I = \frac{V - e}{R}$$

where V = P.D. across the part in question,

R = resistance of the part,

e = the opposing E.M.F.

The following examples may help to elucidate difficulties arising from a consideration of the above.

Examples.—(1) A plating dynamo having an internal resistance of 0·02 ohm and developing an E.M.F. of 10 volts, is joined to an external circuit of resistance 0·105 ohm. What current will flow in the circuit?

From (II) above $$I = \frac{E}{R}$$

$$\therefore I = \frac{10}{0{\cdot}105 + 0{\cdot}02}$$
$$= 80 \text{ amperes.}$$

(2) Two batteries having E.M.F.'s of 4 and 2 volts respectively and of negligible resistance, are joined in opposition and their free terminals are connected by a wire of 10 ohms resistance. What current will flow through the wire?

From (III) we have—

$$I = \frac{E \pm e}{R}$$

Substituting, $$I = \frac{4 - 2}{10}$$

Since the E.M.F.'s *oppose* one another, the resultant E.M.F. $= 4 - 2 = 2$ volts.

$$\therefore I = \frac{2}{10}$$
$$= \frac{1}{5} \text{ ampere.}$$

If the batteries had been joined so that their E.M.F.'s *assisted* each other, the current would have been—

$$I = \frac{4 + 2}{10}$$
$$= \frac{6}{10} \text{ or } \frac{3}{5} \text{ ampere.}$$

(3) The copper leads in the example on page 46 were found to have a resistance of 0·00895 ohm. If 80 amperes

pass along them what will be the fall of potential or "drop" in the leads?

From (I) $V = IR$

$$\therefore V = 80 \times 0{\cdot}00895$$
$$= 0{\cdot}716 \text{ volt.}$$

Electrical Work, Energy, and Power.—When a current of electricity flows in a circuit work is done at a definite rate and energy is dissipated, and we must now introduce units in terms of which these quantities are measured.

The work done in raising a mass of one pound through a difference of level of one foot against gravitational attraction is taken as the unit of mechanical energy and called the foot-pound, the work done being obtained by multiplying the mass in pounds by the number of feet through which it is raised.

Somewhat similarly the unit of electrical energy is the work done in moving one coulomb of electricity between two points in a circuit between which the P.D. is 1 volt. It is called the **Joule**. But as the quantity of electricity conveyed by one ampere flowing for one second = 1 coulomb, the unit of work or of energy is usually defined as follows: The **joule** is the work done per second by 1 ampere flowing between two points in a circuit, when the P.D. between them is 1 volt.

The total work or energy expended in t seconds when the current is I amperes, and the P.D. V volts, is given by the product of these three quantities,

i.e. **Total work done = amperes × volts × time** (secs.)
or No. of joules $= I \times V \times t$.

The joule, however, is much too small a unit for practical electrical purposes. It is customary, therefore, to express electric energy in terms of a secondary unit, the watt-hour, or in terms of the commercial unit called the **Board of Trade Unit** or Kelvin. This latter is the unit by which—to use the common but inaccurate expression—"electricity" is bought and sold, and the meters which are installed on consumers' premises are designed expressly for the purpose of measuring the energy consumed in terms of this unit.

Power is defined as the rate of doing work, and we are familiar with the term *horse-power* used to express a standard rate of doing mechanical work, equivalent to 33,000 ft.-lbs. per minute.

Electrical power signifies the rate at which electrical work is done in a circuit. The average rate can always be found by dividing the amount of work done by the number of seconds taken for its performance. The rate of working, however, may not be constant over a large time, and the result arrived at in this manner only expresses the average rate. But if we multiply together the P.D. and the corresponding rate of flow, *i.e.* the current at the same moment, the product of the volts and amperes will then give the instantaneous rate of doing work, and we obtain the power directly.

The unit of electrical power is the *joule per second*, more commonly termed the **watt**, and is the power developed or absorbed in a circuit when the product volts × amperes = unity.

Thus 1 watt = 1 volt-ampere.

We see, then, that if I be the current in amperes, V the P.D. in volts, and W = the watts,

$$W = I \times V$$

watts = current × potential difference.

A kilowatt (= 1000 watts) is also employed as a unit of power, where the watt is inconveniently small.

Example.—If the P.D. of a plating dynamo is 10 volts and 150 amperes flow in the circuit to which it is connected, what is its rate of working?

$$W = I \times V$$
$$W = 150 \times 10$$
$$\therefore \text{rate of working} = 1500 \text{ watts.}$$

If the dynamo in question were capable of delivering a maximum of 300 amperes at the same voltage, what would be its capacity, *i.e.* the maximum power which could be safely taken from it for long periods?

$$\begin{aligned} W &= I \times V \\ W &= 300 \times 10 \\ &= 3000 \text{ watts} \\ &= 3 \text{ kilowatts.} \end{aligned}$$

But as 300 is the maximum current, then 3 kilowatts is the maximum power and represents its capacity.

We may, however, express power in ways other than as above, and as shown below.

Since $$W = I \times V,$$

and from Ohm's Law $I = \frac{V}{R}$ where $R =$ the resistance of the circuit across which the P.D. is V, then by substituting this value of I in the former expression we get

$$\begin{aligned} W &= \frac{V}{R} \times V \\ &= \frac{V^2}{R}. \end{aligned}$$

or $$\textbf{watts} = \frac{\textbf{(potential difference)}^2}{\textbf{resistance}}.$$

Again, $V = IR$, and substituting in the same expression this value of V we get

$$\begin{aligned} W &= I \times IR \\ &= I^2R, \end{aligned}$$

or $$\textbf{watts} = \textbf{(current)}^2 \times \textbf{resistance.}$$

It is obvious, then, that providing any two of the three quantities, I, V, R, be known, the power expended may be readily determined.

The connection between these units of work, power, and energy may be tabulated as follows:—

$$\begin{aligned} 1 \text{ joule} &= 1 \text{ volt-ampere-second}, \\ 1 \text{ watt} &= 1 \text{ volt-ampere}, \\ 1 \text{ H.P.} &= 746 \text{ watts}, \\ 1 \text{ watt-hour} &= 1 \text{ volt-ampere-hour}; \end{aligned}$$

but as there are 3600 seconds in one hour—

$$1 \text{ watt-hour} = 3600 \text{ joules}$$

Again,

$$\begin{aligned} 1 \text{ kelvin} &= 1000 \text{ watt-hours}, \\ \therefore 1 \text{ kelvin} &= 1000 \times 3600 \text{ joules} \\ &= 3{,}600{,}000 \text{ joules}. \end{aligned}$$

From the Law of the Conservation of Energy, it follows that when energy is used up in a circuit it must reappear in some other form or forms, and to the exact equivalent of that supplied electrically.

In general, for industrial purposes we wish it to reappear as either mechanical energy, heat energy, or chemical energy. The form in which we get it again, however, depends entirely on the nature and disposition of the path through which the current flows and the actions which result; in other words, on what happens in the apparatus when a current passes through it. Some simple illustrations have already been given which bear out the statement in dealing with the effects of a current (p. 29). But whatever the path may be, the flow of a current is always accompanied by the generation of heat which warms the conducting medium. Heat so produced represents so much energy wasted, unless indeed its production is the only thing aimed at. But if it is desired to do chemical work in an electrolytic cell, energy used up in the production of heat in the cell is wasted, since that is not the purpose in view.

It must, however, be clearly understood that the heat energy here referred to is distinct from the heat energy absorbed or liberated in chemical reactions. The former is produced by the current in overcoming the electrical resistance of the conducting path, as explained below, while the latter is due to the chemical decomposition set up by the current.

We shall dismiss any consideration of the conversion of electrical into mechanical energy, as it does not concern us.

Heat produced by a Current, Joule's Law.—Referring to Fig. 5 (*b*) (p. 34), it is obvious that in the elementary circuit there considered there is no device, such as an electric motor or an electrolytic cell, for the conversion of electrical into mechanical energy and chemical energy respectively, yet the circuit absorbs energy. Taking two points such as d_1 d_2, we have explained the fact that a P.D. exists between them when a current flows. Let the P.D. be V volts, the current I amperes, and R the resistance of d_1 d_2, then the energy used up in the portion considered in t seconds is $\mathrm{IV}t$ or $\mathrm{I}^2\mathrm{R}t$ joules. This energy is spent in overcoming the resistance and reappears as heat energy. The rate of production of heat is therefore IV or $\mathrm{I}^2\mathrm{R}$ joules per second. When a circuit acts simply as a resistance, the *whole* of the energy given up by a current flowing through it is converted directly into heat.

From the investigations of Joule, Prof. Rowland, and others a relationship between the joules expended and the number of units of heat (calories *) produced can be found. This relationship is called **Joule's Law** and is expressed as follows:—

$$\mathrm{H} = \mathrm{I}^2\mathrm{R}t \times 0{\cdot}24$$

where H = number of heat units in calories.

Rate of doing Chemical Work by a Current.—E.M.F. set up by Chemical Decomposition.—Suppose a current of I amperes to be passed through a decomposable solution—copper sulphate, for example—provided with *insoluble* electrodes, and let V be the P.D. which is maintained across them. The rate at which energy is given to the arrangement is V × I joules per second, part of which is used in doing chemical work, and from previous considerations

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* A *calorie* is defined as the heat required to raise the temperature of 1 gram of water 1° C. when the water is initially at a temperature of 15° C.

part is wasted in the production of heat. Let $R =$ the resistance of the electrolytic cell; then

$$VI = w + I^2R$$

where $w =$ rate of doing chemical work in joules per second or watts.

$$I^2R = \text{rate of production of heat.}$$

Dividing the expression by I, we get

$$V = \frac{w}{I} + IR.$$

$$\therefore \quad IR = V - \frac{w}{I}$$

and

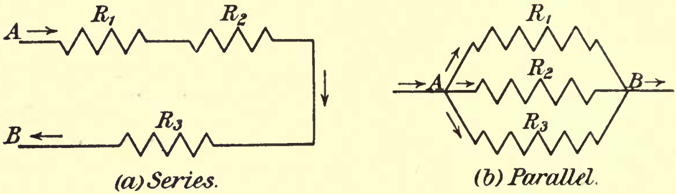
$$I = \frac{V - \frac{w}{I}}{R}.$$

This is the form of an expression which is not wholly unfamiliar, for on comparing it with case IV on p. 48, we recognize Ohm's Law.

Now, as $\frac{w}{I} = \frac{\text{rate of doing chemical work (watts)}}{\text{current}}$, and as $\frac{\text{watts}}{\text{current}} = \text{volts}$, $\frac{w}{I}$ represents an electrical pressure, and as its sign is negative, it must be an opposing or "back" E.M.F.—one, in fact, acting in opposition to V, the P.D. forcing current through the arrangement. Again, if there were no chemical work $\frac{w}{I} = 0$, and there would be no opposition E.M.F. We see, then, that when a solution is decomposed by a current of electricity, the electrodes being insoluble, there is an E.M.F. set up by the chemical decomposition of the solution, which opposes the E.M.F. of the source from which the current is derived. Further, let the opposing E.M.F. be denoted by e, as was done on p. 48, then $\frac{w}{I} = e$ or $w = Ie$, *i.e.* the rate of doing chemical work is expressed by the product of the current and the opposing E.M.F. produced.

The method of calculating this E.M.F., together with examples, and a consideration of the case when *soluble* electrodes are used is given under the heading "E.M.F. required for electrolysis" (pp. 65 ff.).

Series and Parallel Circuits.—There are two general ways of joining "elements"* together to form an electric circuit, namely, *in series*, or *in parallel*; and circuits so formed are spoken of as *series circuits* and *parallel circuits* respectively. These methods of connection are represented diagrammatically in Fig. 7, in which the elements R_1, R_2, R_3 are shown connected in *series* at (*a*) and in *parallel* at (*b*).



(a) Series. (b) Parallel.

Fig. 7.—Conductors in series and in parallel.

A simple way of noting the distinction between them is to trace the path provided for the passage of electricity from one end of the circuit to the other. By doing so it will be seen that in a series arrangement *there is only one path* by which a current entering at A can flow to B, and that is by passing in succession along the elements R_1, R_2, R_3. In (*b*) it is seen that the current has the choice, so to speak, of three paths between A and B, and in consequence it divides at A into three portions, flowing through the three branches simultaneously, in a similar manner to that of a river dividing at one point into two or more channels which eventually unite again at some other point. "In parallel," therefore, means that arrangement which provides several paths along which current may flow simultaneously from one point to

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* The term "element" is here used to denote any single device which can be placed in an electric circuit, such as a vat, an ammeter, a voltmeter, a resistance, a cell, etc.

another. In practical cases (including plating shop vats) the circuit connections as a whole conform more closely to Fig. 8, but on examination this is readily seen to be a combination of the methods outlined above. For instance, between the wires AC and BD we have four branches along which current may flow from the positive wire AC to the negative wire DB; the elements R_1, R_2, R_3, R_4 are therefore in parallel, and we must regard the wires AC and DB as being the practical equivalent of the points A and B respectively in the theoretical diagram (Fig. 7). The current from the dynamo, however, must necessarily pass along the single path MA to the elements, returning by the single path BN, and then through the machine from N to M to complete its circuit; the main leads must therefore be regarded as being in *series* with the remainder of the circuit.

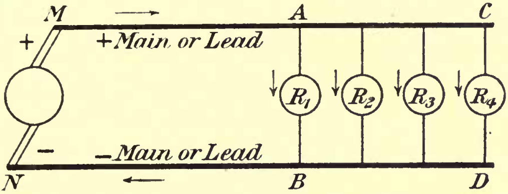

Fig. 8.—Parallel circuit with connections to dynamo.

It must not be assumed, however, that elements may be joined in series or in parallel indiscriminately. There are theoretical and practical reasons which prescribe to us the most suitable method. Some of these will be fairly obvious by considering the characteristic features of the series and parallel methods with respect to the resistance, the distribution of the current, and the potential. For brevity these will be given in the form of a summary.

Series Circuits.—(1) When elements are in series, the total resistance is the *sum* of their individual resistances. Thus in Fig. 7 if R_1, R_2, R_3 represent the resistance of the respective elements, then

$$R \text{ (the total resistance)} = R_1 + R_2 + R_3.$$

(2) The current *has the same value at all parts of the circuit;* there is no "*loss of current.*" This point and also the next one (3) have been explained in detail in connection with Fig. 5, p. 34.

(3) The P.D. between any two points is proportional to the resistance between the points, and is numerically equal to the product of current and resistance according to Ohm's Law.

(4) A break, disconnection, or the opening of the circuit *at any point* with a switch interrupts the current through the *whole* of the elements.

Parallel Circuits.—(1) When elements are connected in parallel, the resistance of the combination is *always less* than that of any of its elements taken separately.

Let us suppose that in Fig. 7 the only element present is R_1, of resistance R_1 ohms, and therefore of conductance $\frac{1}{R_1}$. Now introduce the element R_2 of conductance $\frac{1}{R_2}$, the total conductance is then $\frac{1}{R_1} + \frac{1}{R_2}$, and similarly when R_3 is also introduced the total conductance $= \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3}$, and so on for any number. The total conductance is, however, the reciprocal of their combined resistance, R, therefore

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3}.$$

Example:—Let $R_1 = 4$ ohms, $R_2 = 4$ ohms, $R_3 = 6$ ohms,

then
$$\frac{1}{R} = \frac{1}{4} + \frac{1}{4} + \frac{1}{6}$$
$$= \frac{2}{3}$$
$$\therefore \quad R = \frac{3}{2} \text{ or } 1{\cdot}5 \text{ ohms.}$$

It is useful to note that when a number of elements each having the *same* resistance are joined in parallel, the resistance of the combination $= \dfrac{\text{resistance of one branch}}{\text{number of branches}}$.

(2) The division of the total current into the various branches is dependent on the conductance of the branches. If they are all alike in this respect the current divides equally among them. In any case, however, the ratio between the current in any branch and the total current is equal to the ratio of the conductance of that branch to the total conductance of all the branches.

For example, taking the figures above, what current (I_1) flows through the branch R_1, if the total current (I) is 40 amperes?

$$\begin{aligned} &\text{Conductance of branch } R_1 = \tfrac{1}{4} \\ &\text{Total conductance} \qquad\quad\; = \tfrac{2}{3} \end{aligned}$$

$$\therefore \frac{I_1}{I} = \frac{\frac{1}{4}}{\frac{2}{3}}$$

$$\frac{I_1}{40} = \frac{3}{8}$$

from which $I_1 = 15$ amperes.

Similarly $I_2 = 15$ amperes,

$I_3 = 10$ amperes.

(3) The fall of potential along each branch is the same. For as they are all connected to a common point A at the commencement of the circuit, and terminate at the common point B, then whatever P.D. exists between these common points is also the P.D. across the ends of each branch.

(4) Any branch may be disconnected by the mere opening of a switch placed in it, without interrupting the current flowing through the other branches.

It will be clear, then, that it would be inadvisable to work two plating vats in series, when the work in them requires different currents. If this were done the rate of deposition in one would be too slow, or in the other too rapid, and the work would be spoilt. The invariable plan in practice is to work plating vats in parallel. By so doing any vat can have work put in, or taken out, and further, by the addition of resistance to the branch containing the vat the current may be regulated to a suitable value, without interfering with the deposition going on in other vats. For details of the practical arrangement of vat connections see page 123.

CHAPTER IV

QUANTITATIVE ELECTRO-DEPOSITION

It will now be possible to consider more fully the meaning and value of Faraday's Laws. These laws have already been stated in Chapter II., but for convenience they are here repeated.

Law I.—The weight of any substance liberated or deposited from an electrolyte is directly proportional to the quantity of electricity flowing through the circuit.

Law II.—The weights of different substances liberated or deposited by the same quantity of electricity are proportional to their respective chemical equivalents.

Electro-chemical Equivalent.—From the second law the amount of chemical decomposition per coulomb depends upon and is *proportional to* the chemical equivalent of the substance liberated. Taking, for example, silver and copper (cuprous) and their chemical equivalents as 107·88 and 31·78 respectively, then these numbers express the *relative* weights of silver and copper deposited per coulomb from suitable solutions, not the *actual* weight. To connect together the chemical and electrical side more closely on this point, and materially to assist the electro-chemist, the term **Electro-chemical Equivalent** (E.C.E.) is used.

This may be defined as the *number of grams weight of any ion liberated in electrolytic action by one coulomb of electricity.* The distinguishing feature between the chemical equivalent, and electro-chemical equivalent, is that the former is a numerical ratio, whilst the latter denotes the weight in grams, which in the case of any ion is set free by the passage of the specified quantity of electricity.

Referring to the definition of the coulomb (p. 40), obviously 0·001118 is the electro-chemical equivalent of silver when deposited from a solution of silver nitrate in water. Taking this value for silver we may readily calculate the E.C.E. of other ions as follows :—

Let $\mathcal{E}_s$ = E.C.E. of silver,

$\mathcal{E}_i$ = E.C.E. of another ion,

a_s and a_i = their respective atomic weights,

v_s and v_i = their valencies.

Then the number of grams of Ag set free is proportional to the chemical equivalent of silver.

Symbolically $$\mathcal{E}_s \propto \frac{a_s}{v_s}$$

Similarly, for the other ion

$$\mathcal{E}_i \propto \frac{a_i}{v_i}$$

$$\therefore \frac{\mathcal{E}_i}{\mathcal{E}_s} = \frac{a_i}{v_i} \div \frac{a_s}{v_s}$$

from which $$\mathcal{E}_i = \left(\frac{a_i}{v_i} \times \frac{v_s}{a_s}\right) \times \mathcal{E}_s$$

whence by substitution $\mathcal{E}_i$ may be found.

Example.—What is the electro-chemical equivalent of copper? Given that its atomic weight is 63·57, its valency two, while silver has an atomic weight of 107·88, and valency one,

$$\mathcal{E} \text{ (for copper)} = \frac{63{\cdot}57}{2} \times \frac{1}{107{\cdot}88} \times 0{\cdot}001118$$
$$= 0{\cdot}0003294$$

In the deposition of copper from copper sulphate solution a certain amount of free acid (sulphuric acid) is present in the bath, and the value obtained by the above calculation is higher than that usually taken in practice. The difference may be observed by comparison with the value given in the following table.

TABLE VI.

Electro-chemical Equivalents of Metals.

Metal.	E. C. E.		*Ozs. (avoirdupois) per amp.-hour.*	*Ozs. (troy) per amp.-hour.*
	Grams per coulomb.	*Grams per amp.-hour.*		
Silver	0·001118	4·025	0·1411	0·1285
Gold	0·000681	2·452	0·0860	0·0783
Nickel	0·000304	1·095	0·0384	—
Copper (ous)	0·000328	1·186	0·0416	—
,, (ic)	0·000659	2·372	0·0831	—
Zinc	0·000337	1·219	0·0427	—
Iron (ous)	0·000289	1·042	0·0365	—
,, (ic)	0·000193	0·694	0·0243	—
Lead	0·001073	3·863	0·1354	—
Tin (ous)	0·000617	2·220	0·0778	—
,, (ic)	0·000308	1·110	0·0389	—
Cadmium	0·000582	2·097	0·0735	—
Cobalt	0·0003056	1·100	0·0386	—
Platinum	0·0005057	1·8206	0·0638	0·0581
Palladium	0·0005541	1·9904	0·0698	0·0636

Note.—These figures are based on the generally accepted value for silver, viz. 0·001118 gram per coulomb.

Faraday's Laws, with the introduction of the term "electro-chemical equivalent," may now be put into equational form, and when so expressed the relationship is invaluable for quantitative electro-deposition.

Let Q = number of coulombs,
I = current in amperes,
t = time in seconds,
W = weight deposited in grams,
$\mathcal{E}$ = electro-chemical equivalent.

For 1 coulomb $W = \mathcal{E}$
and from Law I $W \propto Q$
Then for Q coulombs $W = Q\mathcal{E}$
But $Q = It$

$$\therefore \quad W = I \times \mathcal{E} \times t$$

or

$$I = \frac{W}{\mathcal{E} \times t}$$

The Electro-chemical Unit Quantity of Electricity, the "Faraday."—Referring again to Faraday's Second Law, suppose the same quantity of electricity to be passed through solutions of HCl, $AgNO_3$, and $CuSO_4$ respectively; then chemically equivalent quantities of substances are produced at all the electrodes. At the electrodes H, Ag, and Cu will be liberated in the proportion of 1·008 : 107·88 : 31·78, or as 1 : 107·02 : 31·52; thus for every one gram of hydrogen, there will be 107·02 grams of silver and 31·52 grams of copper, and these numbers may be called 1-*gram equivalents* (*i.e.* they are the chemical equivalent weights taken in grams). In other words, 107·02 and 31·52 are the equivalent weights in grams of silver and copper respectively corresponding to the liberation of one gram of hydrogen. Other substances (ions) may be regarded in a similar way.

Now, to liberate 1 gram of hydrogen requires the passage of 96,540 coulombs,* from which it follows that *96,540 coulombs are required for the deposition of one gram-equivalent of any substance* (ion). This fundamental quantity of electricity is called by the Germans a "**Faraday.**"

Consequently, the passage of one faraday through an electrolyte is accompanied by the liberation at the anode and cathode respectively of one gram-equivalent of new material. To render this as clear as possible, take the electrolysis of water as another example and pass through it a faraday of electricity; then as the chemical equivalents of oxygen and hydrogen are 8 and 1·008 respectively, 8 grams of oxygen and 1·008 grams of hydrogen will be set free at the electrodes.

Examples of the application of Faraday's laws:—

1. Find the current which was used in depositing 50 grams of silver, the time occupied in deposition being 45 minutes. The electro-chemical equivalent of silver is 0·001118 gram.

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* This is obtained by dividing the weight liberated—1 gram—by the E.C.E. of hydrogen.

$$\text{Now } I = \frac{W}{\mathfrak{Z} . t}.$$

By substituting the given figures, $W = 50$; $\mathfrak{Z} = 0{\cdot}001118$; $t = 45 \times 60$.

$$I = \frac{50}{0{\cdot}001118 \times 45 \times 60}$$

$$I = 16{\cdot}5 \text{ amperes.}$$

2. What weight of copper would be deposited by a current of 16·5 amperes passing through a solution of copper sulphate for 45 minutes? The electro-chemical equivalent of copper is 0·00033 gram.

$$W = I \times \mathfrak{Z} \times t$$

Substituting the given figures,

$$W = 16{\cdot}5 \times 0{\cdot}00033 \times 45 \times 60$$

$$\therefore W = 14{\cdot}7 \text{ grams.}$$

3. Find the electro-chemical equivalent of copper from the data obtained in Example 2.

$$W = I \times \mathfrak{Z} \times t$$

Therefore $$\mathfrak{Z} = \frac{W}{I \times t}$$

Now, W was found to be 14·7 grams. $I = 16{\cdot}5$, $t = 45 \times 60$.

By substitution $$\mathfrak{Z} = \frac{14{\cdot}7}{16{\cdot}5 \times 45 \times 60},$$

$$\therefore \mathfrak{Z} = 0{\cdot}00033 \text{ gram.}$$

4. During a certain plating operation 321 grams of silver are deposited. How many faradays have been used?

107·02 (say 107) grams are deposited by 1 faraday.

1 gram is deposited by $\frac{1}{107}$,,

$\therefore$ 321 grams are deposited by $\frac{321}{107}$,,

$= 3$ faradays.

E.M.F. required for Electrolysis.—Hitherto in our consideration of the relationships existing between electricity and chemistry our attention has been confined to the study of the meaning and applications of Faraday's laws.

These laws are, however, only an expression of one feature of these relationships. It is necessary now to consider not only the *quantity* of electricity which passes or is moved through an electrolyte, but the total amount of work done or energy expended in moving this quantity; and further, not only the amount of chemical action resulting, but the intensity or affinity (as it has been termed) of this action. In other words, attention must be paid to the **E.M.F.** required in electrolysis as well as to the quantity of electricity to obtain an exact amount of electrolytic product.

On page 18 we explained that when an electric current is passed through an electrolyte a definite amount of energy is used up and a definite amount of work done in the form of chemical decomposition, *e.g.* in an electrolyte of copper sulphate the substance is resolved into the products Cu and SO_4. But by reason of the fact that *work* is done during this operation these two products possess a certain potential energy, in virtue of which they can re-unite, and if by any means they do re-combine, then their potential energy is given up in some form or other. This may occur either in the form of electrical energy or heat energy or both, but in any case it must be re-applied before the substance can be again decomposed.

Briefly, then, the amount of energy produced by combination must be equal to that expended in decomposition. Thus, suppose the product of combination to be heat energy, then:—

$$\left.\begin{matrix}\text{Electrical energy}\\ \text{of decomposition}\end{matrix}\right\} = \left\{\begin{matrix}\text{Heat energy of}\\ \text{re-combination.}\end{matrix}\right.$$

This, of course, is only in accordance with what has been previously stated in describing the law of the conservation of energy.

It has already been explained (in Chap. II.) that the amount of heat absorbed or evolved in chemical reactions varies according to the affinity of the substance concerned, and a definite value can be attached to every particular combination.

If we take any column of Table III., p. 19, the nearer a substance is to the top of the column, the higher as a *general* rule is its heat of combination, *e.g.* that of zinc is higher than that of copper. When, therefore, zinc replaces copper in combination with their respective sulphates a certain amount of energy is evolved or given out in the form of heat and dissipated. The practical result is that a lesser amount of energy is required to decompose copper sulphate than zinc sulphate.

These points are obviously of great importance in either the theoretical or practical study of the applications of electro-chemistry.

One or two examples of methods of calculation will no doubt assist the reader to understand more thoroughly this important principle. It has already been explained that the *quantity* of electricity required to deposit or liberate one gram-equivalent of any substance is 96,540 coulombs; the practical point under discussion now is, therefore, what pressure is required to move this quantity of electricity in any electrolytic reaction?

Since our basis of calculation is the heat energy evolved in any combination, we make use of Joule's Law (page 54), from which we get that

$$1 \text{ calorie} = 4{\cdot}2 \text{ joules},$$

or

$$1 \text{ joule} = 0{\cdot}24 \text{ calorie}.$$

Now, suppose that, as our first example, a simple univalent compound be taken, sodium chloride.

The number of calories evolved during the combination of one gram-equivalent ($23 + 35{\cdot}5 = 58{\cdot}5$ grams) of NaCl has been found to be 97,900 calories (see Table VII.).

Now, the amount of electrical energy equivalent to this figure is found by a very simple calculation :—

If 0·24 calorie = 1 joule,

then $$\frac{97{,}900}{0{\cdot}24} = 407{,}916$$

= number of joules equivalent to 97,900 calories.

This figure represents, therefore, the total energy required to decompose one gram-equivalent of NaCl.

Now we know that the *quantity* of electricity required is 96,540 coulombs;

∴ since $$\text{volts} = \frac{\text{joules}}{\text{coulombs}},$$

the electrical pressure required is—

$$\frac{407{,}916}{96{,}540} = 4{\cdot}22 \text{ volts.}$$

Another example which may be taken (almost a classical one) is acidulated water, H_2O.

In this case we have a bivalent compound, and according to Faraday's Laws the number of coulombs required for the decomposition of one gram-equivalent is $96{,}540 \times 2 = 193{,}080$.

The number of heat units evolved in this combination is 68,400 calories (see Table VII.).

$$\text{Equivalent in joules} = \frac{68{,}400}{0{\cdot}24} = 285{,}000.$$

∴ by the formula $$\text{volts} = \frac{\text{joules}}{\text{coulombs}},$$

the pressure required for electrolysis is—

$$\frac{285{,}000}{193{,}080} = 1{\cdot}47 \text{ volts.}$$

Recent research has determined the number of heat units evolved in a large number of combinations, and particulars of these may be obtained from any good text-book on Thermo-chemistry, but a few of the best-known compounds are given in Table VII.

TABLE VII.

HEAT UNITS EVOLVED IN COMBINATIONS OF CERTAIN COMPOUNDS.

Compound.	*Formula.*	*No. of Calories.*
Magnesium chloride	$MgCl_2$	217,300
Potassium hydroxide	KOH	103,200
Potassium chloride	KCl	104,300
Sodium hydroxide	NaOH	101,900
Sodium chloride	NaCl	97,900
Zinc chloride	$ZnCl_2$	97,200
Cadmium chloride	$CdCl_2$	93,240
Ferric chloride	$FeCl_3$	96,100
Ferrous sulphate	$FeSO_4$	235,600
Nickel sulphate	$NiSO_4$	229,400
Cupric chloride	$CuCl_2$	51,630
Cupric sulphate	$CuSO_4$	182,600
Silver nitrate	$AgNO_3$	28,700
Gold chloride	$AuCl_3$	22,800
Water	H_2O	68,400

In applying these theoretical principles to practical electroplating, and so obtaining results such as are tabulated in Table VIII., it is, however, necessary to point out that they are only exactly applicable in cases where insoluble anodes are used. If the particular compound formed by the union of the liberated product at the anode surface with the metal of the anode is soluble, then the anode in such a case is spoken of as a *soluble* anode, in the opposite event as *insoluble.* If now the anodes are soluble in the particular electrolyte being decomposed, as, for example, is the case when copper anodes are used in the electrolysis of copper sulphate, then under perfect conditions of electro-deposition $CuSO_4$ is *re*-formed by combination of SO_4 with the metal of the anode as quickly and to the same equivalent amount as the deposit occurring at the cathode. Obviously, therefore, the amount of heat of re-formation will equal the amount of decomposition, and the minimum voltage in this case is that required to overcome the electrical resistance only; theoretically, no E.M.F. is necessary for decomposition.

This point constitutes the principal difference between *soluble* and *insoluble* anodes in electrolysis, and it will be noted that a higher voltage is required when the latter are used than when the former are employed.

TABLE VIII.

ELECTRODE PRESSURES NECESSARY FOR DECOMPOSITION OF VARIOUS SOLUTIONS (LE BLANC).

Normal solutions of	*Values in volts.*	*Normal solutions of*	*Values in volts.*
Zinc sulphate, $ZnSO_4$ . .	2·35	Sodium hydroxide, NaOH	1·69
Nickel ,, $NiSO_4$ . .	2·09	Ammonium hydroxide, NH_4OH	1·74
,, chloride, $NiCl_2$ . .	18·5	Cadmium nitrate, $Cd(NO_3)_2$	1·98
Lead nitrate, $Pb(NO_3)_2$.	1·52	Cobalt sulphate, $CoSO_4$.	1·92
Silver ,, $AgNO_3$ . .	0·70	Sulphuric acid, H_2SO_4 .	1·67
Nitric acid, HNO_3 . . .	1·69	Hydrochloric Acid, HCl .	1·31

It should be stated that it is not strictly accurate to describe the foregoing calculations (as is sometimes done) as the determination of the P.D. required for electrolysis. What is determined is, strictly speaking, *the tendency of a specific electrolyte to set up an E.M.F.*; the chemical affinities described being those which in the primary cell, as will be shown in the following chapter, are so manipulated as to set up an E.M.F. for external use. Consequently, whatever current is used for electrolysis, it must have a P.D. sufficiently high to overcome (*a*) the "back" E.M.F. of the electrolyte; and (*b*) the mass resistance of the liquid itself, or in other words the "R" of Ohm's Law.

Soluble and Insoluble Anodes contrasted.—It will at this point be necessary for the sake of clearness to consider the difference between the actions occurring in the use of *soluble* and *insoluble* anodes respectively in electrolysis.

Taking as an example of the former, one of its simplest illustrations, let it be proposed to electrolyse a solution of copper sulphate by means of copper electrodes. The actions taking place, expressed in the simplest form, are—

$$\text{Cathode} \leftarrow \text{Cu} \mid SO_4 \rightarrow \text{Anode.}$$

Cu is consequently deposited as metallic copper, and SO_4 is left, which, however, is liberated in contact with a fresh supply of metallic copper, and we get the re-formation of $CuSO_4$ to undergo the same cycle of change. Therefore the chemical changes taking place exactly neutralize each other, and no chemical *work* is done; consequently no back E.M.F. is set up, and the pressure required for electrolysis is that needed only to conform to the terms of Ohm's Law.

On the other hand, suppose that the same electrolyte is submitted to electrolysis by means of platinum electrodes. In this case the anode is insoluble, but the same reactions occur as previously—

$$\text{Cathode} \leftarrow Cu \mid SO_4 \rightarrow \text{Anode.}$$

Cu is deposited as metallic copper, and SO_4 is liberated in contact with the Pt anode. Now, however, it is evident that no re-formation of $CuSO_4$ can take place, and what happens is that the SO_4 (sulphion) being liberated resumes its normal chemical nature, and instantly breaks up in contact with the water of the electrolyte into sulphuric acid and oxygen, thus

$$SO_4 + H_2O = H_2SO_4 + O.$$

Here, then, are exactly the conditions necessary for the setting up of a back E.M.F., *i.e.* an E.M.F. whose tendency is in the opposite direction to that of the current being applied for the purpose of electrolysis; and consequently the P.D. of the latter must be high enough to overcome both this *and* the second factor previously referred to, namely, that of the mass resistance.

This point, known in electrotechnical literature as "polarization," will be made clearer as the student proceeds to the study of primary cells in the succeeding chapter.

Reactions at Anodes and Cathodes.—Faraday's laws apply not only to the reactions due to electrolysis at the cathodes, but also at the anodes. In the case of the decomposition of water, for example, a definite current will liberate a definite amount of hydrogen at the cathode, and a correspondingly equivalent amount of oxygen at the anode surface. It will be clear, therefore, that if this amount of oxygen completely combined with the metal of the anode, then the weight of metal thus taken up would be chemically equivalent not only to the amount of oxygen, but to that of hydrogen liberated by the current's action.

In the case of an electroplating bath, it is *generally* sought to obtain such a composition of solution that the particular compound formed at the anode surface with the metal of the anode *is* soluble in the electrolyte.

Anode and Cathode Efficiencies.—It is also the object of the electroplater in designing a solution for a particular branch of the electro-deposition of metals not only to obtain one which will give a deposit of good quality and suited to his requirements, but also one which will be *efficient*, that is, yield an amount of deposit as closely as possible approximating to the theoretical yield as given by Faraday's laws. These laws have always been found correct, but it must be borne in mind that the products of electrolysis are not necessarily one only in each solution. Indeed, it rarely happens that this is so; other products as well as the particular metal concerned are set free at the cathode. For example, in most solutions hydrogen is liberated in addition to the metal, and that portion of the current which is occupied in doing this is wasted so far as the prime object of electrolysis is concerned. Similarly, even in the case of soluble anodes there may appear products of electrolysis at the *anode* which do not combine with it to form a soluble compound, and in this event again the current is so far wasted from the point of view of solution of the anode metal.

The general *efficiency*, therefore, of a plating solution is determined by the proportion which the products of electrolysis actually yielded in some given time bear to the theoretical amount that should be yielded by the current passing for the time in question, and this proportion may be measured both at the anode and cathode. The terms anode and cathode efficiencies are thus given rise to.

In determining the efficiency of an electroplating process, the following data must be obtained.

(1) Exact current passing (determined by means of a measuring instrument).

(2) Time of experiment.

(3) Nett weight of metal deposited (obtained by weighing the cathode before and after electrolysis).

(4) Nett loss of weight of anode (obtained by weighing the anode before and after electrolysis).

If a soluble anode is used it will be of the same metal as that deposited, the chemical equivalent will, of course, be the same, and consequently the loss of weight of anode should be equivalent to gain of weight of cathode, and both correspond to the requirements of Faraday's laws. In such an event (which would never occur except under very special precautions) the efficiency of each would be 100 per cent. To calculate the actual percentage of efficiency at each electrode, it is only necessary to divide the figure, obtained by experiment in each instance, by the theoretical figure and multiply by 100.

Example.—Calculate the cathode efficiency of a zinc depositing solution, on the electrolysis of which 10 amperes deposited 10·5 grams of zinc in 1 hour.

$$\begin{aligned}\text{Theoretical yield} &= 10 \times 3600 \times 0{\cdot}000337 \text{ (E.C.E. of zinc)}\\ &= 12{\cdot}1 \text{ grams.}\\ \text{Actual yield} &= 10{\cdot}5 \quad ,,\end{aligned}$$

$$\therefore \text{ efficiency at cathode} = \frac{10{\cdot}5}{12{\cdot}1} \times 100 = 86{\cdot}77 \text{ per cent.}$$

CHAPTER V

PRIMARY AND SECONDARY CELLS

It has already been stated that the various forms of energy are convertible in accordance with the Law of the Conservation of Energy, and that certain physical and chemical changes are accompanied by the evolution or absorption of heat. For example, if a stick of solder is bent rapidly backwards and forwards, it becomes perceptibly hot at the bend, due to the strain put upon it; the mechanical energy expended during the process thus reappears in the form of heat. Again, when a small piece of potassium or sodium is thrown into water a violent chemical action ensues, owing to the great affinity of these elements for oxygen, and the evolution of heat is so great that the liberated hydrogen spontaneously ignites. Further, the energy imparted in effecting both physical changes and chemical actions will under certain conditions reappear, in part at any rate, in the form now called electrical energy. Obviously, then, electrical energy is a form that may be derived from some other form, and for practical purposes there are two modes by which the transformation of energy into its electrical form may be effected, namely:—

(1) By placing certain metals in dilute acids or some alkaline oxidizing solution. Such an arrangement is called a *voltaic cell*, and a number of cells joined together is termed a *battery*.

(2) By utilizing a *dynamo* driven by some form of mechanical prime mover.

For all work on a large scale, the dynamo is the most economical means, as far as cost per unit is concerned. This is in spite of the inefficiency attendant on the conversion of, say, coal into electrical energy, through the medium of the boiler, engine, and dynamo, and is due to the fact that coal is a comparatively cheap commodity.

In the case of voltaic cells, the conversion is a more direct one, and the efficiency greater. The "fuel" is usually zinc—an expensive one in comparison with coal—and this is chemically "burnt" by the oxidizing agent in which it is placed. This "burning" tends to keep up the supply of energy when once the current has been established.

PRIMARY CELLS.

The Simple Voltaic Cell.—If a plate of zinc and one of copper are immersed in a solution of dilute sulphuric acid, so that the metals are not in contact with one another, the arrangement forms a simple cell. When such a cell is made up, then

(1) If the zinc is pure, no action whatever is observed to take place.

(2) If the zinc is impure, chemical action is shown by the bubbling which ensues. Impure zinc readily dissolves in dilute sulphuric acid due to local action (see p. 77), but if the zinc be amalgamated, *i.e.* coated with mercury, no such action takes place.

(3) No action is so far observed to take place at the copper plate.

(4) But if the two plates are connected externally by a wire, it will be found that (*a*) the zinc plate gradually dissolves, (*b*) a gas—hydrogen—is given off at the copper plate, some of which adheres to the surface of the plate in the form of bubbles, (*c*) a current of electricity passes round the circuit, as shown by the fact that when the wire is held near to and parallel with a magnetic needle the needle is deflected.

Now, as currents of electricity are always associated with an electricity-moving force or E.M.F., the cell must be the seat of an E.M.F., since the wire is quite inert when disconnected. Some idea of how the E.M.F. is set up will not be out of place, and without entering too much into the theory or theories which have been advanced, the following may assist the reader.

As previously stated (p. 17), when a plate of zinc and a plate of copper are immersed in dilute sulphuric acid, it may be experimentally demonstrated that both plates are in a state of electrical charge, the copper positively, the zinc negatively, and a P.D. exists between them. According to modern theory this may be explained by considering (1) that part of the molecules contained in solution are dissociated into positively and negatively charged ions, "H_2" and "SO_4" respectively, (2) that at the moment of immersion, owing to what may here be termed the "electro-chemical activity" of zinc, a few "Zn" ions are sent off into this solution. These, like the hydrogen ions, possess positive charges, and the zinc plate is made relatively negative. Simultaneously there occurs the passage of a few (H) ions to the copper plate, which on contact render it positive. Now when the copper plate of the cell is made to touch the zinc or, which is the the same thing, is brought by a wire into metallic contact with it, a current passes and the copper takes the same charge as the zinc and becomes negative. Thus more + (H) ions are attracted to the copper and coming into touch with it give up their charges and again render this plate *positive.* The P.D. is thus maintained, and a current still passes. More "Zn" ions now go into solution, the H ions being thus further replaced by Zn, and as long as the circuit is complete, an E.M.F. is continuously exerted in the direction from copper to zinc *viâ* the wire.

The *chemical action* resulting from the working of a simple cell may be expressed as follows:—

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Zinc and sulphuric acid are therefore used up in the formation of zinc sulphate and hydrogen gas, the latter being of course given off at the copper plate.

It will now be advisable to mention that as some misunderstanding frequently occurs through an apparent ambiguity in the designation of the "plates" and "poles" of primary cells, that plate which dissolves during working is generally termed the positive plate or positive element, and the other plate is termed the negative plate or negative element; whereas the terminal of the latter is, according to the direction of the current in the external conductor, the positive pole, and the terminal of the former the negative pole. Thus the *positive plate* forms the *negative pole*, and *vice versâ*. To avoid confusion the plate dissolved, zinc, in all the cells to be considered will be referred to as the lower potential element, the other the higher potential element; there is then no doubt as to which pole is positive to the other.

Local Action.—Common zinc contains impurities, such as iron, lead, arsenic, etc., and dissolves readily in sulphuric acid, an effect which may be ascribed to electrical causes, for these impurities, together with the zinc, being in contact with the dilute acid, give rise to a number of local currents which circulate between the impurities and the zinc. This *local action* is prevented by amalgamating the zinc, and as common zinc is always used in the construction of cells, it should always be amalgamated to prevent the zinc being eaten away more rapidly than corresponds to the rate at which electrical energy is developed in the circuit as a whole.

Polarization.—The hydrogen which accumulates on the copper plate during working is very deleterious, inasmuch as it sets up a back E.M.F., and in consequence weakens the E.M.F. available for sending a current. This accumulation of bubbles of hydrogen is termed *polarization*, and the more practical forms of primary cells are mainly devices for the elimination of this effect. In all modern cells the hydrogen is got rid of by placing in the cell some chemical compound which contains oxygen, and which will readily give up its oxygen in the presence of hydrogen. Such a substance is called a "depolarizer," and the following are the ones used in the cells to be considered next:—

(1) Copper sulphate,
(2) Bichromate of potash,
(3) Chromium trioxide,
(4) Nitric acid,

and several others.

The Daniell Cell.—This cell is made up in a variety of forms, according to the class of work for which it is intended.

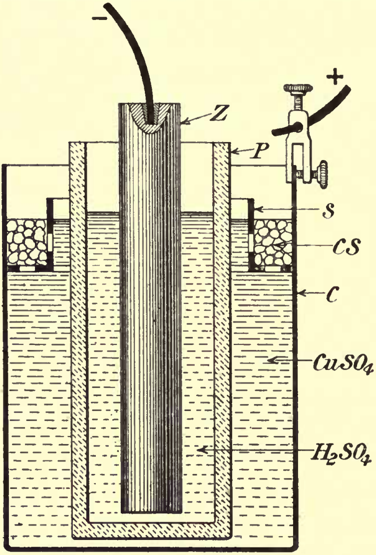

Fig. 9.—Section of the Daniell Cell.

C, copper containing vessel; P, porous pot; Z, zinc rod; S, perforated copper shelf; CS, copper sulphate crystals; H_2SO_4, dilute sulphuric acid; $CuSO_4$, copper sulphate solution.

The form shown in Fig. 9 may be taken as being typical of one frequently used. The high potential element is a sheet of copper bent into a cylindrical containing vessel, holding a saturated solution of copper sulphate. In this solution is also immersed a porous earthenware pot containing the low potential element—zinc—and a solution of sulphuric acid diluted to a strength of about 1 part of acid to 12—20 parts of water.

Action of the cell.—When the cell is in action oxygen is given off at the zinc, and the hydrogen ions are transported towards the copper plate. The oxygen attacks the zinc, forming zinc oxide, which, however, in the presence of the acid ultimately becomes zinc sulphate and dissolves in the solution. The hydrogen before reaching the copper plate comes in contact with the copper sulphate solution, which being decomposed forms sulphuric acid and liberates copper, the latter being deposited on the copper plate.

The resulting reactions may be shown by the following equations :—

(1) In porous vessel $Zn + H_2SO_4 = ZnSO_4 + H_2$.
(2) In outer vessel $H_2 + CuSO_4 = H_2SO_4 + Cu$.

Hence the result of the reactions is such that :—

(1) The zinc is consumed.

(2) The sulphuric acid in the porous vessel is used up in the formation of zinc sulphate.

(3) The copper sulphate in the outer vessel is changed into sulphuric acid.

(4) Copper is deposited on the copper plate.

The cell will not polarize so long as the above action proceeds, and so long as the copper sulphate solution is not allowed to become weak, but to ensure immunity when required to work for long intervals, a perforated copper shelf, or a muslin bag, containing crystals of copper sulphate is suspended in the solution, and these crystals gradually dissolve as the solution weakens. In making up Daniell cells it is advisable to have the level of the acid solution a little higher than that of the copper solution, to prevent the latter from too readily diffusing into the vessel containing the zinc; for in the event of this happening the zinc is attacked, oxide of copper is deposited on it, and the action of the cell is interfered with. The use of the porous pot is, in fact, to keep the solutions in contact—so preserving the electrical continuity—but yet to prevent their mixing too freely. Most of the depolarizers in use will attack zinc, and hence they are kept in a compartment separated from the zinc by the porous walls of the pot.

The Bichromate and Chromic Acid Cell.—In both these cells the depolarizer is chromium trioxide (CrO_3), popularly called "chromic acid," as it has a strong acid reaction when dissolved in water. Formerly this material (CrO_3) was prepared by the user, by acting on potassium bichromate ($K_2Cr_2O_7$) with sulphuric acid, but as chromium trioxide can now be purchased ready prepared, it is often used in preference to potassium bichromate. Consequently, as the cells in other respects are identical, one description will suffice. Figs. 10 and 11 show two types of the cell, the "bottle" and "Fuller" respectively. The former is useful for portable purposes, but for general working where the cells are more or less stationary, the latter has several advantages; it is easier to clean and its parts are easier to replace when worn or broken, and it can be left set up out of work without appreciable wastage of zinc.

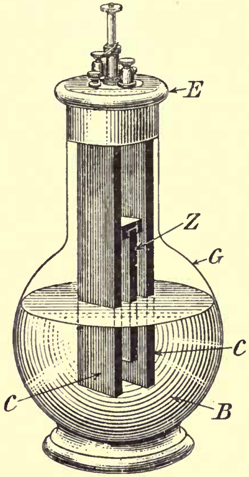

Fig. 10.—Bottle form of Bichromate Cell.

G, glass containing bottle; CC, carbon plates; Z, zinc plate; E, ebonite cap; B, bichromate or chromium trioxide solution.

In the Fuller pattern the outer glazed earthenware vessel contains the depolarizing solution made up from one or other of the following formulæ:—

Chromium trioxide	2 ozs.
Sulphuric acid	2 ozs. (by weight).
Water	1 pint.

Bichromate of potash	2 ozs.
Sulphuric acid	3·5 ozs. (by weight).
Water	1 pint.

One or more carbon plates electrically connected are immersed in the solution, forming the high potential element.

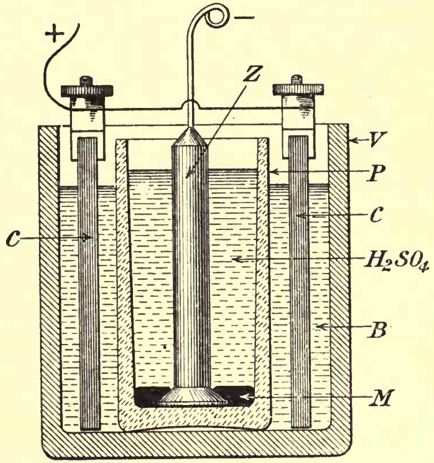

Fig. 11.—Section of Fuller's Bichromate Cell.

V, glazed earthenware vessel; P, porous pot; *cc*, carbon plates electrically connected; Z, zinc rod; M, mercury; B, bichromate or chromium trioxide solution; H_2SO_4, dilute sulphuric acid.

The low potential element is a zinc rod with an enlarged base as shown, immersed in a solution of dilute sulphuric acid (1 in 10) and standing in a small pool of mercury contained at the bottom of a porous pot. The mercury ensures the zinc being kept amalgamated automatically.

Action of the cell: The chemical reaction in the porous cell is similar to that of the Daniell, viz. :—

$$(1) \qquad 3Zn + 3H_2SO_4 = 3ZnSO_4 + 3H_2.$$

The chemical reactions taking place when the hydrogen reaches the depolarizing solution are best shown in several stages.

With solution made from potassium bichromate,

(2) mixing—

$$K_2Cr_2O_7 + 7H_2SO_4 + H_2O = \underset{\text{(chromic acid)}}{2H_2CrO_4} + \underset{\text{(potassium sulphate)}}{K_2SO_4} + 6H_2SO_4.$$

$$(3) \qquad \underset{\text{(from (1))}}{3H_2} + 2H_2CrO_4 = \underset{\text{(chromium trioxide)}}{Cr_2O_3} + 5H_2O.$$

$$(4) \qquad Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O.$$

$$(5) \quad K_2SO_4 + Cr_2(SO_4)_3 = K_2Cr_2(SO_4)_4.$$

The net result of the reactions is therefore :—

(1) The zinc is consumed, zinc sulphate formed, and sulphuric acid used up.

(2) The original potassium bichromate and some sulphuric acid are changed into chrome alum ($K_2Cr_2(SO_4)_4$).

(3) Water is substituted for the remaining sulphuric acid.

When the depolarizer is made directly by dissolving chromium trioxide in water, equations (3) and (4) show the reactions which take place.

The Bunsen Cell.—The usual form of this cell is illustrated in Fig. 12. An outer glazed earthenware vessel contains a solution of dilute sulphuric acid (1 in 10) in which is immersed a plate of stout sheet zinc bent into a cylindrical form, constituting the low potential element. Inside this is a porous pot containing the depolarizer—strong nitric acid—and a rectangular carbon block forming the high potential element.

Action of the cell : When the cell is at work the chemical reactions may be thus represented :—

(1) In outer vessel $Zn + H_2SO_4 = ZnSO_4 + H_2$.

(2) In porous pot $H_2 + 2HNO_3 = \underset{\text{(nitrogen peroxide)}}{2NO_2} + 2H_2O$.

In working, therefore, zinc and sulphuric acid are used up in the formation of zinc sulphate and the liberation of hydrogen; the nitric acid becomes diluted by the formation of water, nitrogen peroxide being liberated. This latter is a gas, and its formation results in very objectionable reddish-brown fumes being given off, especially after the cell has been working for a time and the nitric acid has become weakened. For this reason such cells should be placed where a current of air will carry the poisonous fumes away from the user.

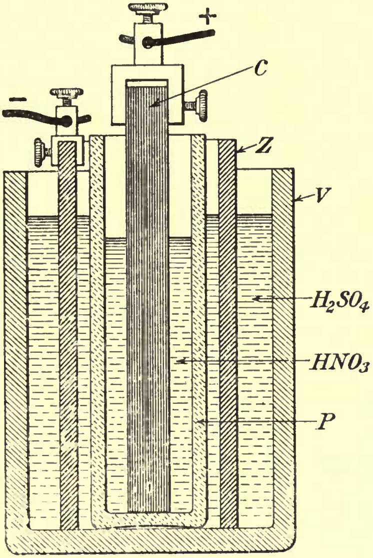

FIG. 12.—Section of Bunsen Cell.

V, glazed earthenware vessel; P, porous pot; C, carbon plate, Z, zinc; H_2SO_4, dilute sulphuric acid; HNO_3, concentrated nitric acid.

The Edison-Lalande Cell.—The chief feature in the construction of this cell is in the high potential element, which consists of finely ground copper oxide compressed into plates and held in a suitable copper framework. Two well amalgamated zinc plates, electrically connected, form the lower potential element; they are arranged one on each side of the copper oxide plate (Fig. 13). The elements are suspended from the lid of a glazed earthenware vessel in a solution of caustic potash, made up in accordance with the following formula.

Caustic potash . . .	2 lbs.
Water	5 pints.

Action of the cell: When a current is taken from the cell, potassium zincate is formed, and the hydrogen reduces the copper oxide to metallic copper. The oxygen in the copper oxide serves as a depolarizer. The chemical equations are as follows:—

$$(1)\ Zn + \underset{\text{(caustic potash)}}{2KHO} = \underset{\text{(potassium zincate)}}{K_2ZnO_2} + H_2.$$

$$(2)\ H_2 + \underset{\text{(copper oxide)}}{CuO} = H_2O + Cu.$$

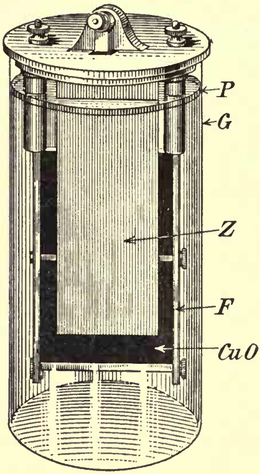

Fig. 13.—The Edison-Lalande Cell.

G, glass or glazed earthenware containing vessel; Z, zinc plate; CuO, copper oxide plate; F, framework supporting copper oxide plate; P, layer of paraffin oil.

Care and Management of Cells.—To maintain primary cells in good working order the following points should be observed:—

(1) Keep the zincs well amalgamated. To amalgamate a plate, first clean it by immersion in dilute sulphuric acid (1—6) and allow it to gas freely for a few minutes. Pour on the cleaned surface a little mercury and rub briskly with a swab of rag until the surface is covered. New zinc is liable to have a greasy surface; so before attempting amalgamation, dip it several times in a hot potash solution to dissolve the grease, scour well with sand to remove the film of potash solution, and afterwards thoroughly wash it with water. It may then be

immersed in the sulphuric acid and rubbed over with mercury as directed above.

(2) Porous pots when not in use should be left soaking in water and not allowed to dry before being thoroughly washed, or they will soon fall in pieces.

(3) After a cell is exhausted, thorough washing and the addition of fresh solution will put it in order again.

(4) Nitric acid is useless in cells when it has turned green. Similarly, bichromate solution should be thrown away after it has turned a dark colour with a greenish tint.

(5) In making up cells in which the depolarizer is in a separate compartment, avoid the possibility of its getting to the zinc, by having the sulphuric acid solution a little higher than the other (about ¼ inch).

(6) When diluting H_2SO_4 with water, slowly add the acid to the water, and not *vice versâ*, since a rapid evolution of heat takes place during the mixing. Allow the mixture to cool before using.

SECONDARY CELLS OR ACCUMULATORS.

Principle of the Lead Cell.—If two clean lead plates be immersed in dilute sulphuric acid, and their extremities connected with a low-reading voltmeter, no evidence of an E.M.F. is obtained, and no current can be derived from the arrangement. But if a current of electricity be sent through it for a few minutes from some external source, then, after disconnecting the source and again applying the voltmeter a reading of about 2 volts will be shown. Further, on examining the plates, the anode will have a chocolate coloration on its surface, while the cathode is unaltered. What has happened is that oxygen and hydrogen have been liberated by electrolytic action, the former at the anode, the latter at the cathode. The oxygen has combined with the lead surface of the anode forming lead peroxide (PbO_2), while the hydrogen at the cathode mostly rises to the surface of the liquid and leaves the plate unaffected. Hence the surfaces of the plates have two different chemical compositions; this difference gives rise as in the case of a primary cell to an E.M.F., and a current may be drawn from it for a few seconds, or until the resulting chemical action forms on both plates lead sulphate. The cell is then inert, but the process may be repeated theoretically *ad infinitum*, for on again passing a current through, the lead sulphate on the anode is re-formed into lead peroxide, while that on the cathode is reduced to metallic lead.

Such is the principle of a *lead secondary cell* or *accumulator*. It differs therefore from a primary cell in that its elements or plates have first to be put into the necessary chemical condition by electrolysis. In other words, the plates have to be "polarized."

It has been shown that polarization is detrimental to the proper working of a primary cell, chiefly on account of the back E.M.F. introduced thereby, but in an accumulator polarization is directly aimed at. During the chemical conversion of the plates by electrolysis—a process called "charging" the cell—the cell itself exerts an E.M.F. which is always in opposition to that of the charging source, and electricity has to be forced through the cell against this back E.M.F.; consequently a pressure greater than 2 volts per cell has to be available for charging purposes. On the other hand, after it has been charged and the charging source removed, it is this polarization E.M.F. which serves to maintain the current during the discharge of the cell.

An accumulator may therefore be looked upon as a cell in which energy is kept in store to be used as occasion requires. The reader should particularly observe that there is no accumulation or storing of electricity; fundamentally in forming the cell electrical energy is transformed into chemical energy, and when used to supply a current the energy transformation is merely reversed.

The Modern Accumulator.—Very little need be said here on the usual mode of construction; so many are in use, small cells especially, that their general make-up is well known. A brief reference to the plates, however, may be advantageous. Two distinct types are in use, namely :—

(1) Planté, or so-called unpasted plates. For +ve plates only.

(2) Faure, or pasted plates. For both +ves and −ves. The distinction arises from the mode of forming the active material on the plates, *i.e.* the lead peroxide and the spongy lead on the positives and negatives respectively. The plates are made in the form of grids ingeniously arranged to bind the material to the grids, and a few representative types are shown in Figs. 14, A, B and C.

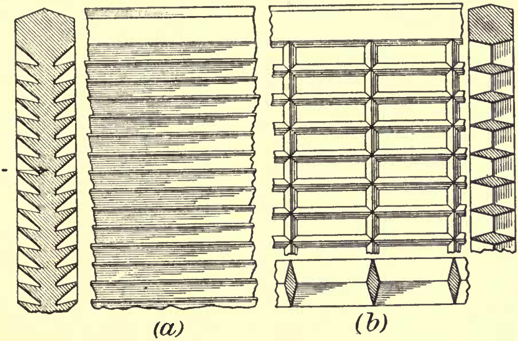

FIG. 14 (A).—E.P.S. grids : Faure type of plate.

(*a*) positive ; (*b*) negative.

For Planté plates the lead peroxide is formed from the lead grid itself by chemical and electro-chemical means, a process which takes some time.

For Faure plates the chemical formation is accelerated by filling the interstices of the grids with a mixture of red-lead (Pb_3O_4) and sulphuric acid, the mere mixing of which forms a certain amount of PbO_2 according to the following equation :—

$$Pb_3O_4 + 2H_2SO_4 + H_2O = PbO_2 + 2PbSO_4 + 2H_2O.$$

Subsequent electro-chemical action, when they are placed in dilute sulphuric acid and joined up as anodes, results in the following reaction due to the oxygen liberated,

$$PbO_2 + 2PbSO_4 + 4H_2O = 3PbO_2 + 2H_2SO_4 + 2H_2.$$

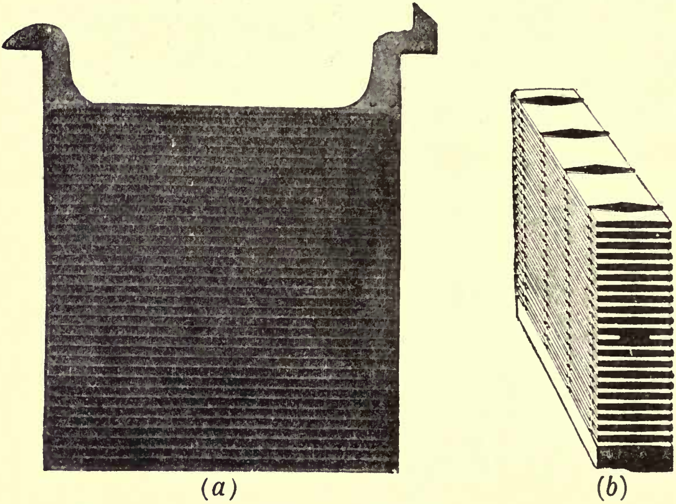

Fig. 14 (b).—D.P. plates.

(*a*) Positive; (*b*) section of positive plate to a larger scale.

Faure negative plates are pasted with a mixture of litharge (PbO) and sulphuric acid, which forms $PbSO_4$ (lead sulphate),

$$PbO + H_2SO_4 + H_2O = PbSO_4 + 2H_2O.$$

Electro-chemical treatment, by making them cathodes in dilute sulphuric acid, reduces the $PbSO_4$ to spongy lead, due to the action of the hydrogen liberated, thus:—

$$PbSO_4 + H_2 = Pb + H_2SO_4.$$

Chemical Changes during Discharge.—Assume that a cell is fully charged and that a current is being taken from it. The direction of the current outside the cell is from the positive or peroxide plate to the negative plate, and *vice*

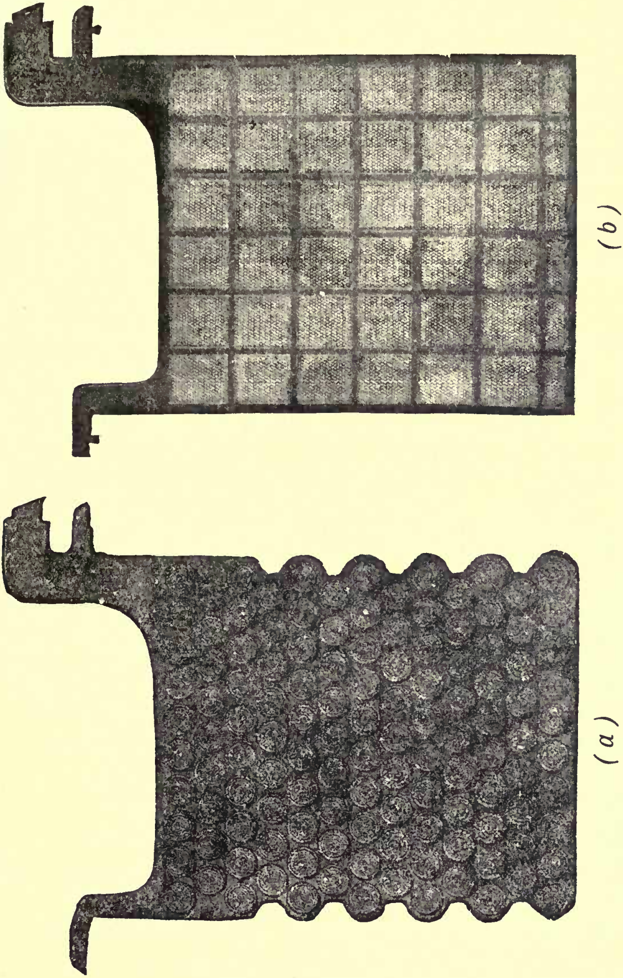

FIG. 14 (C).—Chloride Electrical Storage Co.'s plates.
(*a*) positive; (*b*) negative.

versâ inside.* Owing to the electrolysis of the electrolyte,

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* When referring to the accumulators it is now common practice to

oxygen is given off at the negative plate, hydrogen at the positive. The spongy lead at the negative becomes oxidized, and in the presence of sulphuric acid changed into $PbSO_4$, while the peroxide plate is converted into $PbSO_4$, due to the hydrogen liberated there. During both reactions sulphuric acid is used up and water formed.

The reactions may be shown as follows :—

At the negative plate

$$Pb + H_2SO_4 + O = PbSO_4 + H_2O.$$

At the positive plate

$$PbO_2 + H_2SO_4 + H_2 = PbSO_4 + 2H_2O.$$

Chemical Changes during Charge.—During charging oxygen is liberated at the positive and hydrogen at the negative plate. The $PbSO_4$ on the plates is reconverted into PbO_2 and Pb respectively, water is used up and sulphuric acid formed, the reactions being—

At the positive plate

$$PbSO_4 + 2H_2O = PbO_2 + H_2SO_4 + H_2.$$

At the negative plate (negative plate.)

$$PbSO_4 + H_2 = Pb + H_2SO_4.$$

It must be understood that there is still doubt as to the precise actions which take place in these cells, but the above equations showing the ultimate result are generally accepted.

Capacity.—The capacity of an accumulator is reckoned in ampere-hours. Since the product of a current multiplied by time is a quantity of electricity, this is the quantity of electricity which the cell will give before it is considered to be discharged. The capacity may range from 10 to 20 ampere-hours in small portable cells, to several thousand ampere-hours in large stationary cells. The capacity is

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call the element whose pole is positive, the positive element or plate, and the one whose pole is negative, the negative element or plate. The usage of terms is therefore different from that in the case of primary cells (p. 77).

dependent upon the amount of active material entering into the reactions, and to make it up to the requisite amount it is customary to use 2, 3, 4, etc., positive plates, arranged so that each of them is between two negatives; all positives and likewise all negatives are connected together, so that they form virtually one large plate of each kind, plates of opposite polarity being kept completely apart by insulating separators. It must not be assumed, however (as is frequently the case), that because a cell is marked, say, 60 ampere-hours, that it will give 60 amperes for 1 hour, or 30 amperes for 2 hours, although it may give 15 amperes for 4 hours. Generally speaking, there is a certain maximum rate which ought not to be exceeded, otherwise the cell may show signs of decay prematurely, and the marking of the cells presupposes that the maximum permissible rate of discharge is not exceeded.

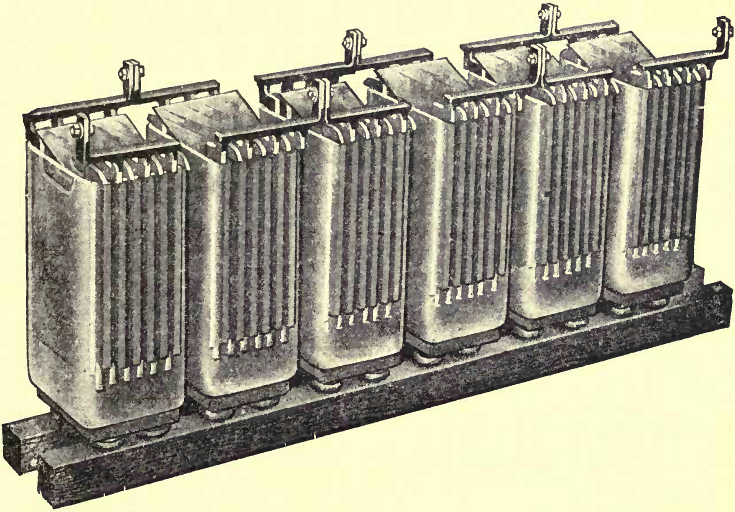


Fig. 15.—Method ot erecting large accumulators.
(6T type; D.P. cells with bolted connections on single-tier stand.)

Erection, Care, and Management of Accumulators.—The general mode of erecting cells of large size for stationary purposes may be gathered from Fig. 15. They are placed on a wooden tier protected from the ravages of acid and acid spray, by being coated with acid-resisting enamel. The cells are supported at each corner on glass or earthenware insulators containing oil, and arranged with their connecting lugs alternately positive and negative. Connections between adjacent cells are made either by bolting the lugs together with special bolts well protected with vaseline, or by welding them together with an oxy-hydrogen flame.

By strict attention to the following points cells may be kept in good condition for many years, although like other things they naturally deteriorate in course of time.

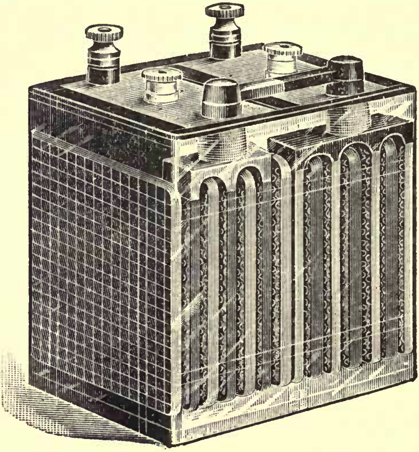


Fig. 16.—Portable accumulator in celluloid case.

(1) Never allow them to stand for any length of time in a discharged or partially discharged condition.

(2) If not required for use, do not empty out the acid; give them a full charge periodically.

(3) Keep the level of the solution well above the top edges of the plates, and make up any evaporation by the addition of distilled water.

(4) Periodically test the density of the acid and see that it complies with the maker's recommendations.

(5) With small portable cells in celluloid cases (Fig. 16), it is advisable to replace the acid once every six months. To do this, charge up fully, empty out the acid, wash the cells out quickly with distilled water, empty, and immediately add fresh acid of proper density, and "gass up" again.

(6) Accumulator manufacturers send instructions with their cells with respect to the charging current, density of acid, and other details, which should be adhered to as closely as possible. They also will supply suitable acid, but if the user wishes to make up his own, it is important to use distilled water, and either pure sulphuric acid or the variety known as brimstone sulphuric acid. Never be tempted to use the commercial acid, and ordinary tap water.

Charging Arrangements.—The only satisfactory method of obtaining current for charging is to use a dynamo, or to make use of the public electricity supply mains, if such be fed with direct current. In either case the number of cells which may be charged in series is dependent on the voltage of the source; 2·5 volts per cell must be allowed for ensuring a full charge with the normal charging current. Thus suppose that a plating dynamo gives a voltage of 10 volts, it would be just possible to charge four cells in series. The arrangement and connections are shown in

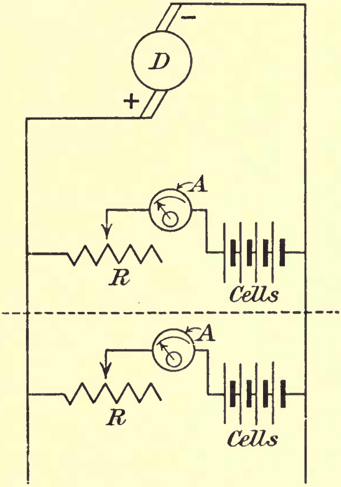


FIG. 17.—Connections and accessories for charging accumulators.

A, A, ammeters; R, R, variable resistances; D, dynamo.

Fig. 17. Connect the positive pole of the dynamo through a suitable variable resistance, to the positive pole of the cells, putting an ammeter and a switch in circuit; connect the negative pole of the cells to the negative pole of the dynamo. With all the resistance in circuit, close the switch, and then adjust the resistance to give the required current. Keep the current constant by readjusting the resistance as occasion requires. If the dynamo is of ample capacity, another set of four cells could be charged at the same time by arranging them as shown below the dotted line.

E.M.F. of Cells.—The following table gives the approximate E.M.F. of the various cells considered.

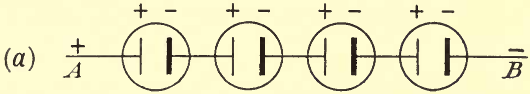
TABLE IX.

Kind of cell.	*Approx. E.M.F.*
Simple cell	1·0 volts
Daniell ,,	1·07 ,,
Chromic acid	1·95 ,,
Bunsen	1·9 ,,
Edison-Lalande	0·75 ,,
Storage	2·0 ,,

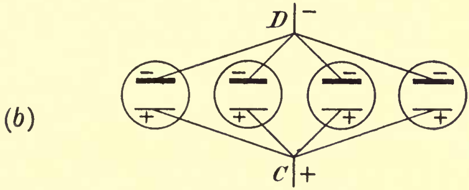
Arrangement of Cells in Series and in Parallel.—The preceding table shows that the E.M.F. of a single cell is only of the order 0·75 to 2 volts, but a larger E.M.F. can be obtained by the employment of a number of cells and connecting them up in *series*. Cells are said to be "*in series*" when the negative pole of the first cell is connected to the positive pole of the second, the negative of the second to the positive of the third, and so on. Fig. 18 (*a*) shows four cells connected in this manner. The thick strokes on the diagram represent the negative poles, and the thin ones the positive poles. As the E.M.F. of each cell acts in the direction from negative pole to positive pole *through* the cell, we have a number of E.M.F.'s, each of them acting in the same direction along the conducting path, and the resultant E.M.F. of the arrangement as a whole is the sum of their separate E.M.F.'s. Thus four Daniell cells in series would have an E.M.F. of 4 × 1·07 = 4·28 volts.

It is clear also from previous considerations that the internal resistance of the battery is the sum of the individual resistances of the cells composing it. Connecting in series, therefore, not only increases the E.M.F., but also the resistance of the battery.

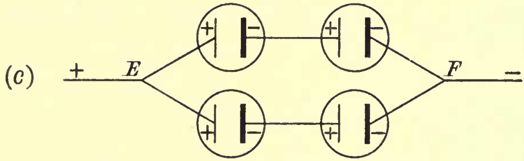
It is also important to remember that *the E.M.F. of a given kind of cell is the same whatever be its size,* but a large cell will have a *lower* internal resistance than a small one.



Series.



Parallel.



Series-Parallel.
(2 in series, 2 rows in parallel.)

FIG. 18.

Another way of arranging a number of cells is to join them "*in parallel.*" To do this all the positive poles are connected together to form a common positive, and likewise all the negative poles to form a common negative. Fig. 18 (*b*) illustrates the method, using four cells, but any number may be added in a similar manner.

With this arrangement it is very necessary that all the cells should be of the same kind or have the same E.M.F., and for preference they should be of similar size. If, for instance, the E.M.F. of two of them differs materially, it is easy to see that a current, independent of any current in the external circuit, will circulate round the closed circuit which the arrangement naturally forms between the cells—a current which serves no useful purpose and wastes the active materials.

A number of similar cells connected in this way virtually becomes one cell of n times the size, where n is the number of cells in the battery; current is drawn simultaneously from each of them, uniting and dividing at the common positive and negative terminals respectively.

The E.M.F. of the combination *is only equal to that of one cell*, but the internal resistance of the battery is reduced to $\frac{1}{n}$th of the resistance of one cell.

Very little need be said here on the relative merits of joining cells in series or in parallel, but one or two leading principles may be mentioned. Generally the series arrangement is the best when the external resistance is high, the parallel method when the external resistance is low, compared in both cases to the resistance of a single cell.

A third method is also shown in Fig. 18 (c), a *series-parallel* arrangement. It is, as may be seen, a combination of the former ones, consisting of several rows of cells joined in series, the rows being subsequently joined in parallel. The method enables us to increase the E.M.F. of the battery, but at the same time to keep down the internal resistance. It is advisable to use similar cells, and ensure that an equal number are placed in each row, for reasons given above.

Uses of Cells.—Before finally leaving the cells, it will not be out of place to refer very briefly to some of their uses in connection with the electroplater's art.

The Daniell cell may be used for the deposition of copper on a small scale from an acid copper solution, and for small electrotyping work, such as medallions. The Bunsen is suitable for the deposition of nickel on small articles, or for gilding, while the Bichromate may be used for the preparation of small quantities of gilding solution by electrolytic methods. The Edison Lalande, although of low E.M.F., has a small internal resistance, and is capable of sending currents of the order of 10 to 15 amperes without much polarization for 10 to 20 hours, before the supply of materials is exhausted. It may be left standing on open circuit without appreciable waste. Such currents, however, can only be obtained with external circuits of low resistance.

Owing to the fact that accumulators may now be obtained in a large variety of designs and sizes at a reasonable price, and that in most towns means exist for having them recharged without much difficulty, they are, for many purposes, gradually taking the place previously occupied by primary cells. The modern accumulator is a very reliable article, and if properly looked after and used in a legitimate manner, will work satisfactorily for a number of years.

CHAPTER VI

THE DYNAMO

In Chap. III. it has in effect been shown that a dynamo is primarily a generator of E.M.F., and when at work maintains a P.D. across its terminals, and across the various portions of any external circuit to which it is connected.

In dealing therefore with this important piece of electrical apparatus, it will be advisable to explain those portions of it which are instrumental in the production of an E.M.F.; how the E.M.F. is set up; and then to develop our explanation into a practical machine.

Before doing so, however, it will be advantageous to introduce a few elementary magnetic and electro-magnetic principles.

Elementary Magnetic and Electro-Magnetic Principles.—Every one is more or less familiar with some of the very elementary and yet striking properties of a magnet. It is well known that either end of a magnetized bar will attract and pick up small iron objects, such as nails, and cause a compass needle to be violently deflected when brought into its vicinity. If the compass needle be pivoted in a horizontal position, its ends point respectively to the magnetic N. and S., and however much it may be disturbed from this position it will swing to and fro and gradually come to rest in precisely the same position as before. Further investigation leads to the conclusion that the neighbourhood surrounding a magnet is in a special condition different from the same space when the magnet is removed, inasmuch as there is manifested at every point in it a magnetic force.

The region or space in which magnetic force manifests itself is termed a *magnetic field*, and for purposes of explanation of magnetic and electro-magnetic phenomena, a magnetic field is regarded as being permeated with "*lines of force*"—lines along which magnetic force will act when another magnet is brought into the field. A graphical representation of the distribution of lines of force in one plane of a magnet, or of a combination of magnets, may be obtained by laying the magnet or magnets horizontally, placing on top a piece of stiff white paper, and then sprinkling the latter with some fine iron filings. On gently tapping the paper the filings will arrange themselves along definite lines and curves. Such a picture for a single bar magnet is shown in Fig. 19.

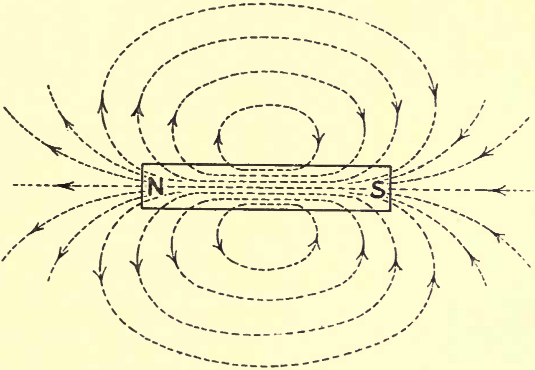


FIG. 19.—Magnetic lines of force of bar magnet.

The direction in which each filing arranges itself shows, very approximately, the direction along which the magnetic force at that point is acting.

Poles of a Magnet.—The magnetic lines of force about a magnet appear to emanate from two centres of maximum intensity, situated near to the ends of the magnet; these centres are called the *poles*, the one nearest the end which persistently points N. when pivoted horizontally is termed the "N.-seeking pole," the other the "S.-seeking pole";

usage, however, has now contracted these to "N. pole" and "S. pole" respectively. It is also a characteristic that the N. pole of one magnet will attract the S. pole of another, but repel the N. pole, hence the "first law of magnetism" states that "like poles repel, unlike poles attract."

Direction of Magnetic Lines of Force.—Lines of force are found to be circuital, *i.e.* to complete their circuit from pole to pole, and to have a definite direction in space. By a convention similar to that adopted with respect to the direction of flow of a current, this direction is taken to be the same as that in which a free N. pole * would move if placed so as to be acted on by the magnetic forces. Imagine, then, that such a pole is placed near to the N. pole of a magnet; then from the above law, it is obvious that the free N. pole would be repelled by the N. pole of the magnet and attracted by the S. pole, its motion being along a line of force. Consequently it may be said that the direction of these lines outside the magnet is from N. pole to S. pole and *vice versâ* inside.

Electromagnets.—If a wire be coiled up in the form of a long spiral around a rod of soft iron, and a current of electricity be passed through the wire, the iron for the time being is magnetized, and will exhibit properties similar to those described above. Such an arrangement is termed an *electromagnet*, and where strong magnetic fields are essential the electromagnet is the only practicable means of obtaining them. This arises from the fact that very soft iron and certain classes of steel may be temporarily magnetized by means of a current to a far higher degree than that to which hard steel can be magnetized permanently.

Polarity of Electromagnet.—The polarity of an electromagnet is dependent on the direction in which the

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* This is purely an imaginary pole, as the poles of a magnet are in reality inseparable. We cannot magnetize a piece of steel so that one portion exhibits N. polarity, without some other part exhibiting S. polarity.

current circulates spirally round it. Let Fig. 20 represent an iron bar overwound with a spiral of wire—hereafter called a "solenoid"—and traversed by a current in the direction indicated by the arrow-heads. Then the polarity will be as marked in the diagram, and as determined by the following rules:—

(1) Right-hand Rule.—Grasp the solenoid with the right hand so that the fingers point round it in the same direction as the current circulates, then the thumb outstretched at right angles to the fingers points towards the N. end.

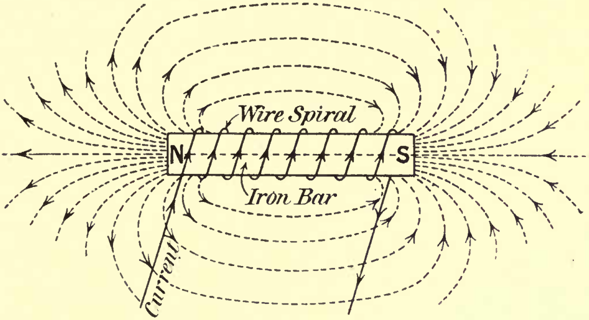

Fig. 20.—Magnetic lines of force of solenoid.

(2) Clockface Rule.—If when looking at the end of the solenoid the current circulates in the same direction as the hands of a clock rotate—*i.e.* clockwise—the end looked at is the S. pole. Conversely, if the current circulates counterclockwise, the end looked at is the N. pole.

The dotted lines in Fig. 20 indicate the general distribution of the lines of force, and it is seen that the distribution is similar to that of the simple bar magnet illustrated in Fig. 19.

The Field Magnet of a Dynamo is virtually a large electromagnet designed to produce a very large number of lines of force, and lead as many of them as possible through air gaps between the poles, within which the armature revolves.

Let us suppose that we take the electromagnet of Fig. 20 and bend it (the winding included) so that its poles come nearer together, as in Fig. 21 (*a*). Let also its pole ends be made curved, so forming a cylindrical cavity as shown. We then have a simple form of dynamo field-magnet with two poles, one N. pole, and one S. pole—a two-pole field, in fact.

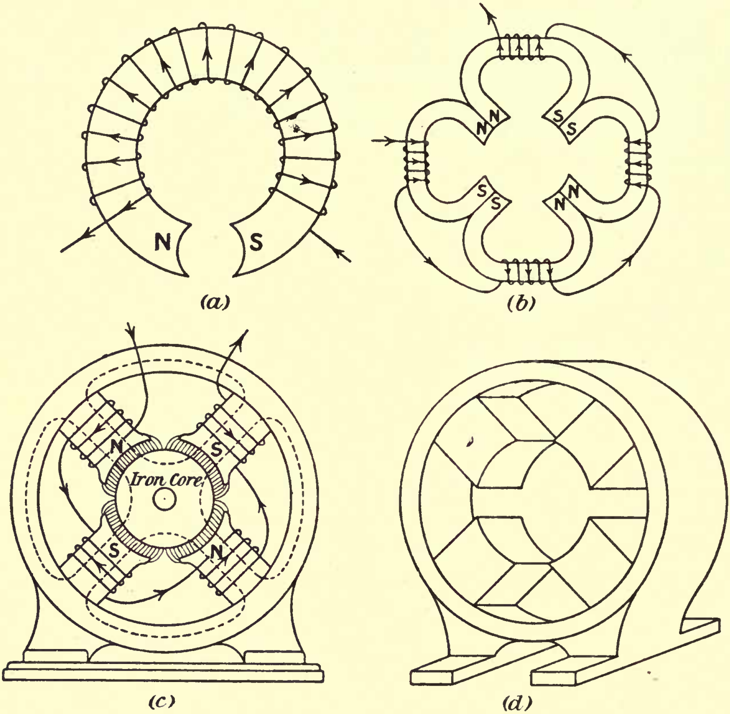

FIG. 21.—*a*. Two-pole magnet.
b. Four-pole field built up of 4 magnets.
c. Four-pole dynamo.
d. Four-pole field-magnet in perspective.

Two-pole dynamos, however, are now obsolete. All modern machines are built with multipolar fields having at least four poles. We shall therefore confine our subsequent explanation to a four-pole dynamo.

Let us now take four electromagnets like Fig. 20, bend them as described above, and arrange them as in Fig. 21 (*b*). Let the windings be joined as shown to virtually form one, taking care that the current circulates so as to produce the polarity shown in the figure. We have now eight separate poles, but owing to the fact that two adjacent poles are of like polarity, viz. two N. poles or two S. poles, these adjacent poles act as one, and we have in effect four poles arranged alternately N. and S.; in other words, a four-pole field.

But such a construction is unmechanical. There is no reason why the adjacent iron poles which, as already observed, are similarly magnetized, should not be combined, and the solenoids or magnetizing windings placed where they are most effective, *i.e.* near the poles. It is, therefore, an easy stage from Fig. 21 (*b*) to Fig. 21 (*c*), which represents the arrangement of a modern type of four-pole field magnet, while Fig. 21 (*d*) is the same, but shown in perspective; its outline is thus more clearly defined. The iron core in the figure is cylindrical, and it is on this that the armature winding is built up, as explained later.

Fig. 21 (*c*) also shows by fine full lines the approximate way in which the lines of force distribute themselves in the air gaps between the poles and the iron core, while the dotted lines indicate their mean path through the iron portion of the field magnet and core. We may note in particular that the direction of the lines in the air gaps are from the whole of the curved surface of each pole to the iron core, or *vice versâ*, depending on whether a N. pole or a S. pole is referred to. There is a "brush," so to speak, of lines of force crossing each air gap.

The Armature is that portion of the machine in which an E.M.F. is set up by rotating wires in the magnetic field produced by the field-magnet, and before considering the armature in detail the underlying principle must be considered.

Let a straight metal bar or wire be rigidly mounted on the periphery of the iron core or cylinder (from which it is insulated) in such a way that when the core is revolved between the poles of the field-magnet (Fig. 21 (*d*)), the bar moves parallel to the axis of rotation (Fig. 22). The bar or wire may be made of any metal, but copper is invariably used in practice, for reasons mentioned in a former chapter.

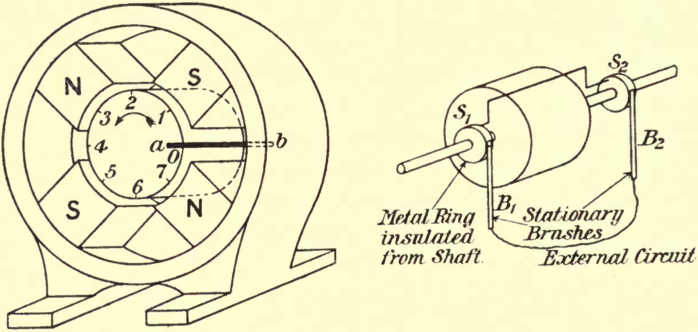

FIG. 22.—Single wire on armature of 4-pole dynamo.

Bearing in mind the way in which the lines of force cross the air gaps (Fig. 21 (*c*)), it is evident that as the wire revolves it *cuts* through the lines of force—its length being at right angles to them—during those periods when it is passing in front of a pole. Now, when lines of force are *cut* in the manner described, there is a P.D. set up between the ends of the wire, and thus the *cutting* of lines by the wire generates an E.M.F. in it.

The direction of the E.M.F. so produced may be determined by means of the following rule, due to Dr. Fleming :—

Hold the thumb, first, and second finger of the right hand at right angles to one another. Point the thumb in the direction of motion of the wire which cuts the lines, and the first finger in the direction of the lines; then the second finger points along the wire and indicates the direction of the E.M.F. set up.

Applying this rule to the above case, it is found that when the wire moves in front of a S. pole, the direction in which the E.M.F. acts along it is opposite to that generated in the wire when moving in front of a N. pole. For example, let the wire rotate in the direction shown by the arrow; then, when it moves in front of a N. pole, the E.M.F. acts from *b* to *a*, and *vice versâ* for a S. pole.

As these changes in the direction of the E.M.F. occur at regular and definite intervals of time, assuming the speed of rotation to be constant, it is termed an alternating E.M.F., and if for the purpose of obtaining a current in an external circuit we arrange matters as shown at the right hand of Fig. 22, the current in the circuit will be an alternating one, the brushes being alternately positive and negative. Further, the magnitude of the E.M.F. (or of the current) varies from instant to instant, as illustrated by the graph (Fig. 23).

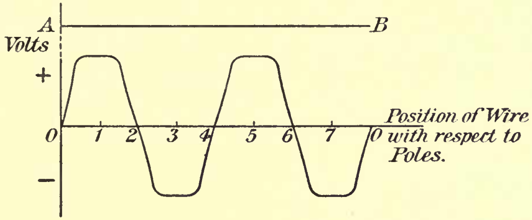

Fig. 23.—Change of voltage with position of wire relatively to the poles.

The above is the fundamental principle of most forms of dynamos, but for plating and other purposes the current must be direct—*i.e.* must flow only in one direction in the external circuit. One brush must therefore always be positive, the other always negative. In fact, for direct-current machines not only must the above condition be fulfilled, but also to be as perfect as possible the voltage across the brushes and the current flowing should be as constant as possible *at any moment during one revolution of the armature*, its graph approximating to the straight line AB (Fig. 23).

The former may be accomplished by making the brushes interchange their connections with the rings at those moments when reversals take place (wire in positions 0, 2, 4, 6), which is accomplished in effect by the device called the **commutator**.

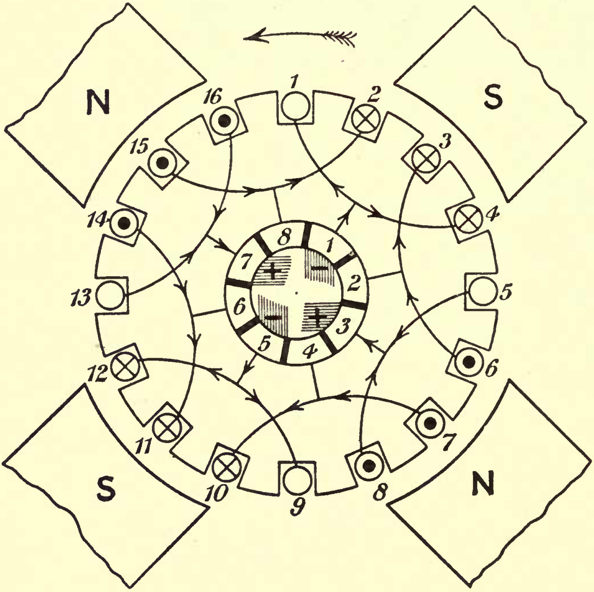

FIG. 24.—4-pole winding with 8-part commutator.

But the E.M.F. generated by one single wire of reasonable length revolving in a strong magnetic field, and at as high a speed as practicable, is very small; hence in all commercial dynamos there are a number of active wires out of which as component elements the armature winding is formed, as will be seen later. With an armature having a large number of active wires, we can add together the E.M.F.'s set up in two or more of the wires by joining them in series. Again, by distributing these wires uniformly around the core parallel to the original wire, and properly connecting them up to a commutator having a large number of segments, we can secure, almost absolutely, the second condition mentioned above, viz. constancy of voltage across the brushes at any instant during one revolution of the armature.

The method of connecting together the active wires constitutes the problem of armature winding. In modern practice only drum windings are employed, and although there are several distinctive varieties, armatures so wound are termed "drum" armatures.

Generally the active wires are embedded in slots (insulated) (Fig. 24) formed during the construction of the core. The iron core serves a double purpose—it not only concentrates the lines of force in the direction desired, but it also considerably reduces the "magnetic resistance" experienced by the lines in passing from pole to pole across the air gaps, and incidentally diminishes the energy required for exciting the field-magnet. The core is built up of a number of thin iron stampings lightly insulated from one another, suitably clamped and mounted to revolve with the shaft.

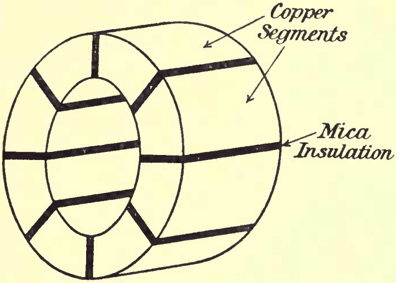

FIG. 25.—8-part commutator.

Let us now consider a more complete drum armature having sixteen active wires fixed in an equal number of slots in the iron core. Let the wires be joined together at the front and back end (the one remote from the commutator), and also to the commutator segments, as shown in Figs. 24 and 26.

The type of winding adopted is only a simple one for explanatory purposes, and it requires a commutator with eight segments, an outline of which is shown in Fig. 25, but we do not show it in great detail nor the manner in which it is mounted to revolve with the shaft. If the armature be rotated in the direction of the arrow, then at the moment when the active wires are as shown in the figures, the E.M.F. in all the wires under a N. pole will be directed towards the observer, or from back to front, while in those under S. poles it will be in the opposite direction, or from front to back. These directions are indicated by the points of arrows (·) and the tails of arrows (×) respectively. Wires numbered 1, 5, 9, 13, midway between two consecutive poles, are in the position of least action, and have little or no E.M.F. set up in them.

Fig. 26 is another diagram of the armature in question, supposed to be laid out flat, and likewise the commutator, from which we may more readily trace out what we require.

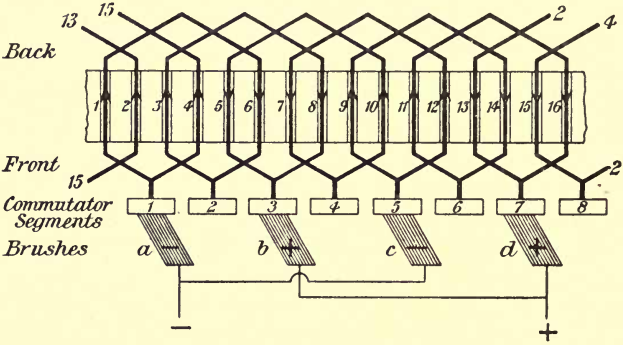

FIG. 26.—Development on the flat of preceding drum armature.

Now, an examination of the armature winding will reveal the fact that it may be divided up into four groups, each group consisting of the same number of wires in series; group A consists of wires numbered 1, 6, 3, 8; group B, wires 9, 14, 11, 16; group C, wires 5, 10, 7, 12; and group D, wires 4, 15, 2, 13. Suppose next we take each group separately and let its E.M.F. be represented by four cells in series, each cell having the same E.M.F. as that developed for the moment in the wire which it represents. Let also the ends of the combinations be joined to metal blocks figured to agree with those of the commutator segments, to which the ends of each group are connected. We then get a representation of the whole armature, as in Fig. 27, the straight arrows showing the direction of the respective E.M.F.'s of the groups, and as each group on the armature is situated at any moment in a similar position with respect to the field-magnet poles, the groups will have equal E.M.F.'s. It will now be seen that the blocks 3 and 7 are positive to those marked 1 and 5, the latter are therefore negative. Let the positive blocks be electrically connected to form a common positive, and similarly blocks 1 and 5, to form a common negative. We have then in reality the four groups

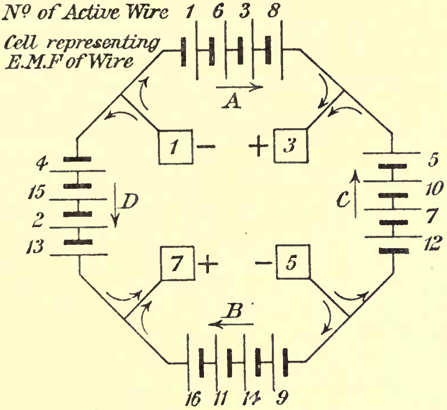

FIG. 27.—Analogous arrangement of cells.

joined in *parallel*, and any external circuit placed across the common pairs of terminals will receive a current from the arrangement as a whole.

Applying the above to the actual armature, segments 3 and 7 will be positive, segments 1 and 5 negative, and fixed brushes resting on these will collect the current from the armature. Consequently four brushes are required, which in their relative positions are alternately positive and negative, those of like polarity being joined electrically to form a common positive and negative respectively, to which the external circuit is connected.

But so far only the conditions at a particular moment have been discussed. Let, therefore, the whole armature, together with the commutator, move forward, the brushes of course remaining stationary, until segments 2, 4, 6, 8 are under the brushes. Then other wires occupy exactly the same positions as those in the diagram, but the direction of the E.M.F.'s will still be as shown, consequently brushes *b* and *d* will still be positive, *a* and *c* negative. The same reasoning holds as successive segments pass under the brushes. We see, then, that the direction of the current in the external circuit is always the same.

In actual practice the brushes always bridge more than one segment, for reasons which need not be entered upon here, and when the machine is loaded the best sparkless position is generally a little in advance of that shown in the diagram. It is found by trial, for which purpose the brushes of direct-current dynamos are always mounted on a rocker; they may thus be moved backward or forward while the machine is working.

Type of Dynamo for Plating Purposes.—Direct-current dynamos are usually "self-exciting," that is, they supply the necessary current for maintaining the magnetism of the field magnet, and according to the method adopted of electrically connecting together the field winding, armature, and external circuit, machines are spoken of as Series, Shunt, or Compound dynamos. The shunt machine is the only type suitable for electrolytic purposes, and the only one, therefore, that need concern us here. From Fig. 28 it will be seen that the "shunt" winding (field-magnet winding F) is connected across the brushes (neglecting the rheostat for the moment), and consequently a portion of the armature current—about 2 or 3 per cent.—is diverted through this winding and excites the field-magnet. The rheostat R is merely a variable resistance for varying the exciting current. An increase of excitation produces a larger number of lines of force, and augments the E.M.F. generated. An adjustment of this kind is very desirable, since the voltage of a shunt dynamo diminishes as more and more current is drawn from the machine.

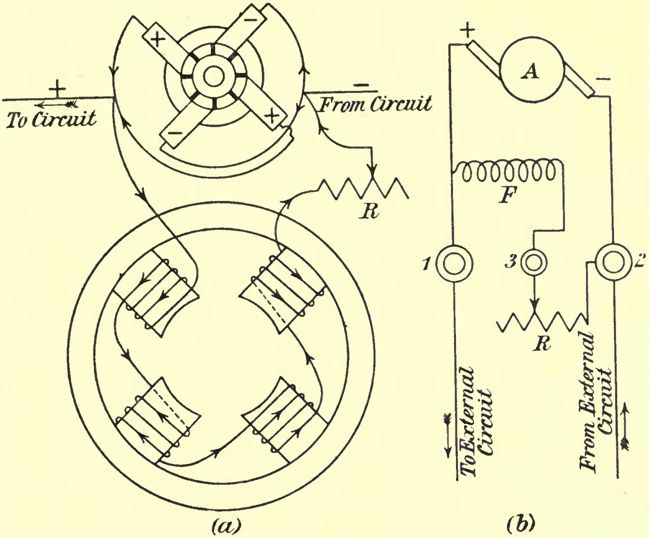

Fig. 28.—Diagram of connections of shunt-wound dynamo. *a*, armature supposed removed from field-magnet. *b*, conventional representation.

As the voltage required to effect the electrolysis of most plating solutions is only of the order of a few volts, and as the vats are usually supplied with current independently of one another, a low-voltage dynamo is all that is requisite from this point of view. The current, however, will depend on the number of vats to be supplied at one time, the kind and the amount of work put into them to receive deposits.

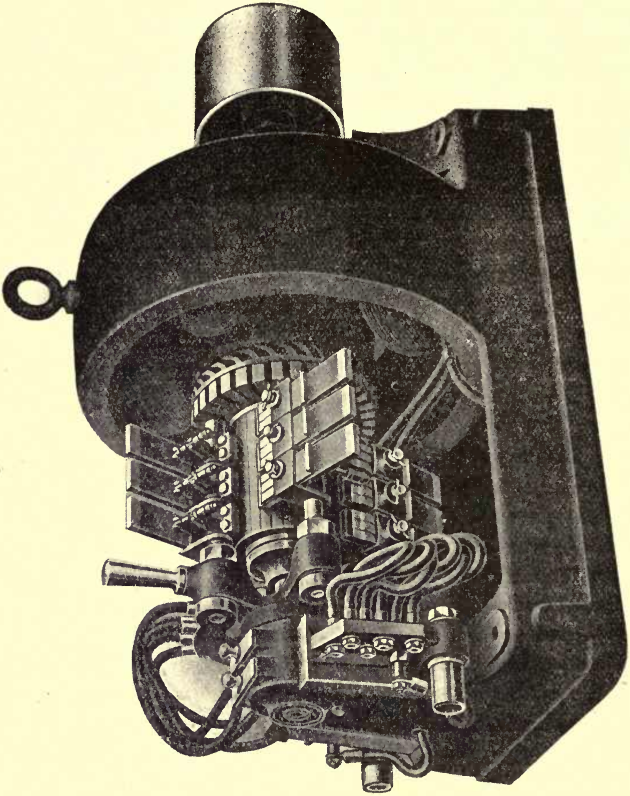

FIG. 29.—Four-pole plating dynamo.

Generally, then, plating dynamos are machines of low voltage and high amperage, and a typical modern form of four-pole machine is shown in Fig. 29.

Care and Management of a Dynamo.—When installing and in the subsequent management of a dynamo, special attention should be given to the following points:—

The machine should be fixed in a dry situation, with plenty of light, and with sufficient room for proper inspection, cleaning, etc. Remember that it is a vital part of a plating equipment, and frequently the whole of the plating is dependent on the good working of one machine.

Put it as near to its work as possible.

Bolt the machine firmly on a solid and level foundation, which for large machines should be made of concrete. Vibration is detrimental to the life of a dynamo, and may lead to chattering and sparking of the brushes when at work. Sparking will rapidly destroy both brushes and commutator.

If the machine is to be belt-driven from a line of shafting, see that the dynamo shaft is set parallel with the one driving it, and that the two pulleys are in line. In such a case it is a good plan to have a fast and loose pulley on the line shaft, so that the machine may be stopped independently of the main engine.

All parts of a dynamo should be kept scrupulously clean, free from dust, waste oil, and water; very special attention should be paid to the bearings, commutator, and brush gear.

Bearings.—Keep them well supplied with good oil. Most modern machines are constructed with oil ring lubrication, but even so they should be inspected periodically to see if the rings are working properly.

Commutator and Brushes.—These two parts require careful attention. A commutator in good condition presents a smooth polished surface of brownish copper, without evidence of scratches. A very little vaseline or a preparation called "comm bar" may be applied to the commutator surface occasionally as a lubricant.

The brushes should be adjusted by the tension springs to make a light but certain contact on the commutator, and when two or more brushes are on one spindle they should be exactly in line.

In a four-pole plating dynamo there will be four sets of brushes; these should be spaced so that the angular distance between successive sets is the same.

If the commutator becomes worn or uneven it may be filed with a smooth file and polished with fine glass cloth, but the only real remedy for a commutator out of truth is to take the armature out of the machine and turn up the commutator in a lathe.

Copper dust, which collects on various parts (chiefly the brush gear), due to the gradual wear of the brushes, should be removed as soon as it is in evidence. It is a good plan to use a pair of bellows occasionally, and blow out any dust which may have collected in cavities that cannot easily be cleaned; for example, the hollow spaces between the wires where they join the commutator segments.

Electrical Energy from Public Supply Mains.—No mention has yet been made of the best means of driving a dynamo, nor can this be definitely stated, as so much depends upon the particular case.

In most instances the method used would be one of the following:—

(1) Driving it from a counter-shaft, driven by the main engine supplying all the power requirements of the works.

(2) Running the dynamo by means of an engine reserved specially for the power requirements of the plating shop.

(3) Driving the machine by means of an electric motor, direct or belt coupled to the dynamo, the motor receiving energy from the private electric generating plant of the works, or from the supply mains of an outside power station.

Undoubtedly there is much in favour of the plating shop having under its control the prime mover for its power requirements, and electric motors offer many advantages. They are clean, run very steadily, and when coupled direct to the dynamo the combination occupies very little floor space, and both are under the supervision of the attendant.

The question of driving the motor from electric supply mains, if such are available, is worthy of attention, especially when extensions to existing plant are in contemplation. In most towns electrical energy for power purposes can be obtained at fairly cheap rates. The question of expense in this connection is really not of primary importance. It must of course be taken into consideration, but the total cost of supplying energy to plating vats is generally a comparatively small item compared with other factors in the cost of the deposited metal.

The intervention of the electric motor is necessary, because a private or public power plant is designed to deliver energy at voltages varying from 100 to 240 volts, or thereabouts, and such voltages cannot be applied directly to plating plants of large magnitude without a considerable waste of energy in resistance—a waste which would be very much greater than that represented by the inefficiency of the combined motor and generator. Besides, in the case of the supply being by means of alternating current, direct application is out of the question. The motor-generator is therefore essential for economical working, and a direct or an alternating current motor would be used, depending on the nature of the supply.

Horse-power of Motor-generator.—In estimating the horse-power of a motor to drive a given plating dynamo, it is necessary to remember that the whole of the mechanical energy used in driving the dynamo does not reappear as electrical energy; in other words, allowance must be made for the fact that the machine has not 100 per cent. efficiency.

Generally the efficiency of a plating dynamo fairly well loaded may be taken to be about 75 per cent., *i.e.* $\frac{3}{4}$ of the energy imparted to it reappears in the form desired. A machine, therefore, whose capacity is 2·4 kilowatts (8 volts 300 amperes) will require a motor capable of developing $\frac{8 \times 300}{746} \times \frac{100}{75} = 4{\cdot}3$ brake-horse-power approximately.

Again, the power to *drive the motor* will be greater than its brake-horse-power owing to the various losses in conversion. Taking an efficiency of 85 per cent., the 4·3 horse-power derived above must be increased by $\frac{100}{85}$ to arrive at the horse-power input to the motor. The input will therefore be $4·3 \times \frac{100}{85} = 5·06$ horse-power. Expressing this electrically, we get $\frac{5·06 \times 746}{1000} = 3·78$ kilowatts. This last figure represents the power taken from the supply mains under the conditions assumed, and it is this figure which should be used in estimating the cost of supplying energy to the vats when use is made of a motor-generator set.

Thus in the above case 3·78 kilowatt-hours (Board of Trade Units) of electrical energy would be used per hour, the cost of which works out to $3·78 \times 1·5 = 5·67$ pence per hour if the price per unit supplied, from whatever source, is $1\frac{1}{2}$ pence.

CHAPTER VII

PLANT USED IN ELECTROPLATING

In the preceding chapters details have been given of dynamos, accumulators, and other means of obtaining current for electro-deposition; the descriptions in the present chapter will therefore be confined to what may be termed general plant and apparatus required in electroplating establishments, and its arrangement.

Vats.—The construction of vats for electroplating varies according to the particular chemical properties of the solutions used. Welded or riveted wrought-iron tanks are the most generally useful, but it is obvious that acid solutions must not be placed in such tanks without some kind of protective coating. For cyanide and nearly all other alkaline solutions used in general electroplating an iron tank is, however, quite suitable, since iron is unaffected by any alkaline cyanide. For the deposition of silver particularly, therefore, iron vats are invariably used, usually with a lining inside of fine Portland cement in order to secure efficient insulation in making electrical connections. This lining is readily put on by a skilled plasterer, the inside surface of the tank being roughened to assist adhesion.

A welded iron tank $\frac{3}{8}$ inch in thickness with a cement lining of about $\frac{3}{4}$ to 1 inch is an ideal silver-plating vat. See illustration, Fig. 30.

These vats are, however, only suitable for cold solutions; for hot solutions the best vat is of enamelled iron. Care should be taken to see that the enamel is perfectly sound, Such vats are used for hot gilding solutions, brassing and alkaline copper solutions, and indeed any alkaline solution. Jacketted boilers with good enamelled linings are very useful for such solutions.

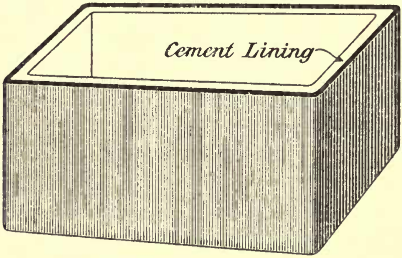

Fig. 30.—Welded Iron Vat. Section showing cement lining.

For acid solutions which are usually used cold the best class of vat is acid-proof earthenware, but if for reasons of size of work or expense this is impracticable, a strong wood vat with a fairly stout lead lining may be employed. Such vats are very popular and are made largely by manufacturers of plating plants, as shown in Fig. 31.

The joints of the lead lining must always be fused and *not soldered*, and wherever the solution contains free sulphuric acid the innermost lining of thin tongued and grooved boards is necessary. These vats are very largely used for nickel-plating and for acid-coppering.

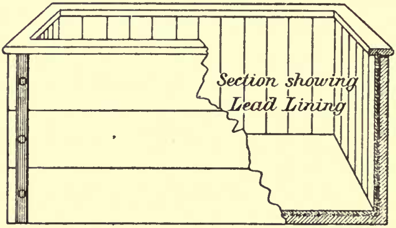

Fig. 31.—Wood Vat, *lead lined*, showing also an inner lining of thin match-boarding.

An excellent, though rather expensive, vat for nickel-plating is a welded iron tank lined inside with strong sheets of glass joined at the corners by means of marine glue or some similar acid-proof cement.

The only disadvantage of such a vat is the risk of fracture of the lining by accidentally dropping the articles to be plated when hanging them from the cathode rods. Slate is occasionally used as a material for lining in a similar fashion, and though not so clean in appearance has the advantage of being less liable to fracture than glass.

Vat Framework and Connections.—All plating vats should be fitted with a strong framework of well-varnished wood running round the top edge. Such a framework is usually constructed in two parts, the upper part carrying the cathode rods, and the lower the anode rods. The former is fitted with roller or ball bearings, so that by connection with an eccentric shaft the cathodes may be given a gentle swinging or "to and fro" motion in the vat.

The arrangement is illustrated in Fig. 32.

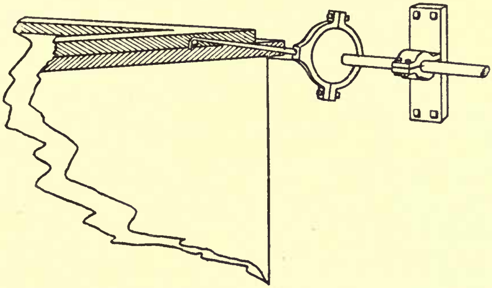

Fig. 32.—Cathode Motion Frame.

The movement of cathodes in electroplating is a matter of great practical importance, as by this means a greater current density can be used and consequently more work done, and at the same time a fine smooth deposit obtained.

These points will be intelligible when it is considered that such movements of cathodes in relation to the electrolyte continually gives to the surface of the deposit a slight friction, which to a small extent may be considered analogous to burnishing. In the electro-deposition of copper, Cowper-Coles has obtained some very striking results by means of an extended application of this principle.*

During recent years, many ingenious devices have been introduced in vat fittings with a view to securing agitation of

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* See *Journal Institution of Electrical Engineers*, vol. 29, pp. 264 *et seq.*

electrolytes as well as movement of cathodes. One of the oldest and most inexpensive of these is the simple mechanical agitator devised by von Hübl. It consists mainly of "beaters" or "paddles" rigidly attached to a shaft running along the top edge of the vat. This shaft is in turn connected to an eccentric wheel, and a slow reciprocating movement is thus imparted to it, and consequently to the "beaters." A diagram of the arrangement is shown in Fig. 33.

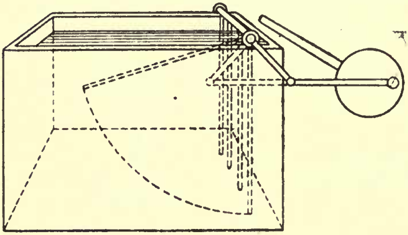

Fig. 33.—Von Hübl's Agitator.

Compressed air has also recently been applied to the agitation of electrolytes with considerable success. A very good agitator of this class is one designed and manufactured by Messrs. W. Canning & Co. of Birmingham, an illustration of which is by permission inserted opposite (Fig. 34).

The main advantage obtainable by the agitation of electrolytes is through the consequent continual renewal of the solution in the immediate vicinity of the cathodes. Under normal conditions of electrolysis, continuous deposition of metal from solution is made possible, owing to the principle of the migration of ions alluded to in a previous chapter. Positive ions in electrolytes constantly travel towards the cathode and negative ions to the anode; consequently as one set of ions is decomposed their places are taken by another set, which in their turn are decomposed, and so electro-deposition is continuous so long as current is passing. The natural rate of migration is, however, very slow. Lodge found, for example, that the rate of migration of hydrogen ions—the swiftest known—is only about 1·15 centimetres per minute. The normal tendency in electrolysis is, therefore, for the liquid round the anode to increase in concentration, and that round the cathode to decrease. Now, it will be readily understood that when a solution is agitated the normal rate of migration of ions is

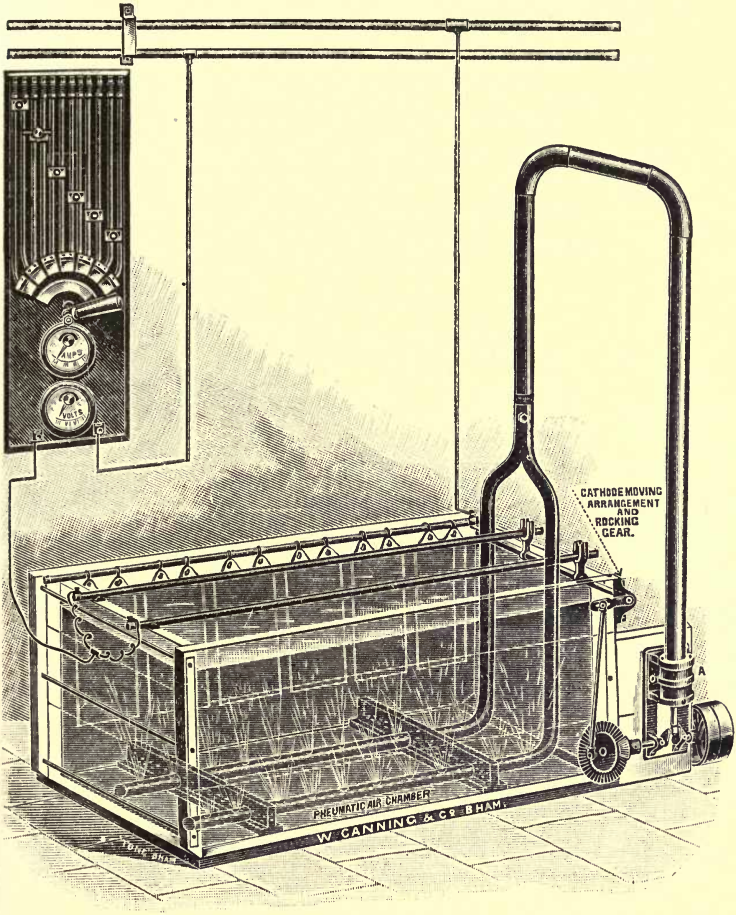

Fig. 34.—Patent Pneumatic Agitator. A, Air compressor.

considerably enhanced, and this tendency to unequal concentration neutralized, with the result that the conductivity of the solution is much increased, and a correspondingly higher current density made possible, which of course means an important saving of time.

In the consideration of vat connections, however, the greatest importance must be attached to the electrical arrangements. It is much to be regretted that in many plating establishments this point does not receive the attention it deserves. In commercial electroplating, where large vats are necessary, the anode and cathode connections are always on the parallel system (see Fig. 35), and in arranging these the ideal is attained when the arrangement permits the current to distribute itself equally in every part of the vat. To this end the main conducting bars should be carried along *all sides of the vat and not merely, as is so often the case, along one side only*. This applies to both anode and cathode rods. The distribution of current along conductors is exactly analogous to the distribution of water along a number of different channels. If equality of the distribution of water is required, then all the channels or waterways must not only be at the same level but of exactly the same size, and the same principle applies to the distribution of electricity, *i.e.* it must be made as easy for the current to flow along one set of conductors as along another. Where a number

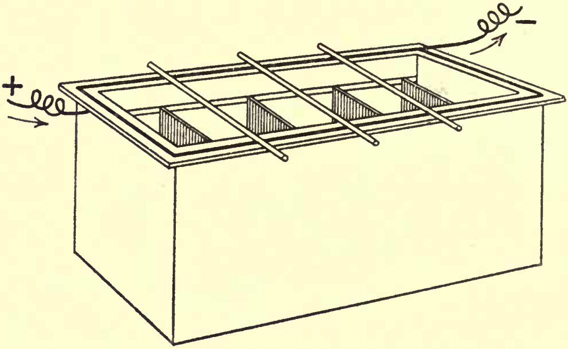

Fig. 35.—Method of connecting Anodes and Cathodes in plating vats.

of articles of one kind are being electroplated with any metal in one vat, it is manifestly to the advantage of the plater's reputation that all should receive an equal deposit, and this is impossible in a vat containing a number of parallel connections unless the current is evenly distributed.

The illustration of a quantity of spoons or forks being silverplated in one vat may be used to enforce this point. If these are all of one quality and size, as is often the case, the manufacturer's reputation depends upon each of them receiving an equal deposit, and so giving the same durability in subsequent use. If the current is not evenly distributed, then though the total weight of silver deposited may be quite correct, yet some will be overplated and others underplated, and this variation may in practice be from 5 per cent. to as high as 25 per cent.

To re-emphasize this point, therefore, the main connections of the vat *must run entirely round its edges*, and must have a cross-sectional area more than sufficient to carry the maximum current required (see Table of Solid Copper Conductors for information on this point, p. 394). In most vats, as has been observed, there is more than one pair of electrodes (anode and cathode); where this is the case the rods or conductors carrying these must be of the same sectional area, and they should be so arranged that the distance between each anode and cathode is as nearly equal as possible. Thus in the case of a vat six feet in length in which it is proposed to have six anodes, these should be placed twelve inches apart, and the respective cathode rods exactly midway between them. It is also advisable to make more than one connection between the main conductors of each vat and the main leads from the dynamo, *e.g.* one at each end of a vat, and in the case of long vats also at one intermediate point.

In large plating establishments where a number of vats are in use, the method of their arrangement is always, like the internal connections themselves, on the parallel system.

Figs. 35 and 36 show the method of connecting the anodes and cathodes in a vat, and the method of connecting a number of vats to the main leads from the dynamo or source of current.

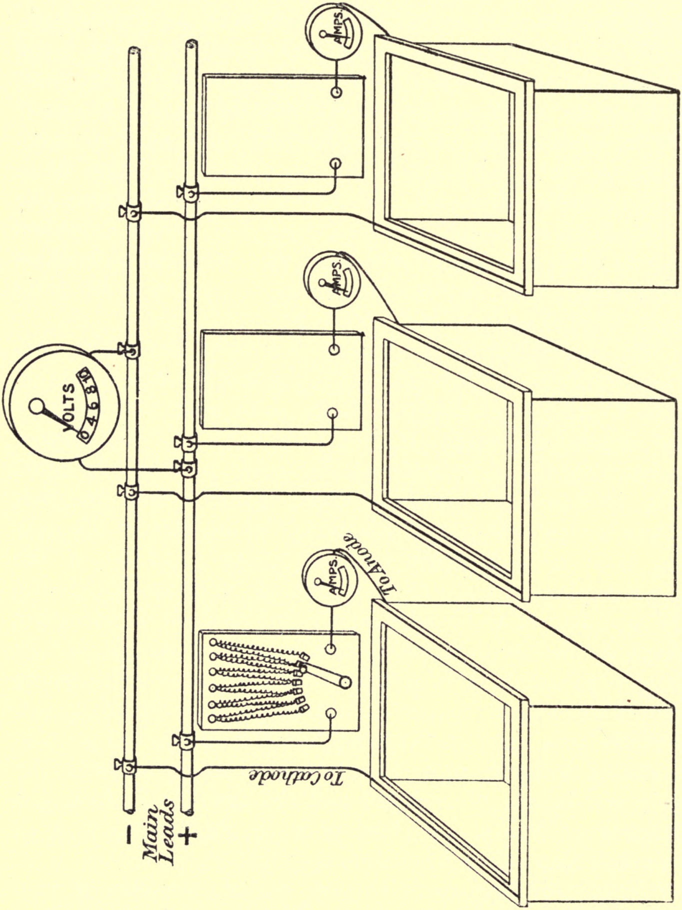

Fig. 36.—Method of connecting a number of vats to main dynamo leads.

The latter diagram also shows the method of arranging resistance frames (often called resistance boards in practice), ammeters and voltmeters, for the measurement of current, P.D., and the regulation of the current in the vat circuits. These very important adjuncts of a plating shop equipment will now be considered.

Resistance Frames, or Rheostats.—Rheostats used in electroplating shops for current regulation should be—

(1) simple in design and arrangement;

(2) strong and durable;

(3) constructed of wire of high resistivity, and of a material not readily attacked by fumes.

The "continuous switch" type of rheostat is the best, as the current may be regulated without breaking the continuity of the circuit, sparking being thereby avoided. Its arrangement should provide easy access to the contacts and general connections for cleaning purposes. Fig. 37 illustrates diagrammatically an arrangement in general use, and one which fulfils the above requirements. Fig. 38 shows the contacts and switch arm in detail.

The base of the rheostat should always be of slate, or similar insulating and incombustible material, and of sufficient strength and thickness to carry terminals, contacts, and connections, capable of conducting the maximum current used. A thickness of from $\frac{1}{2}''$ to $\frac{3}{4}''$ is usual.

Slate is used to a large extent. It is easily drilled and is a fairly good insulator, especially when enamelled. Enamelling, however, is a refinement which is not necessary for plating purposes, on account of the low voltages employed.

The resistances are frequently constructed from platinoid or German silver wire (an alloy of nickel, copper, and zinc) wound in open spirals. The authors have found, however, that some alloys of this description corrode badly in use under average workshop conditions. The best resistance wires they have tried hitherto for plating practice are those obtainable under the trade names "Eureka" and "Ferry." These are very pliable wires of high resistivity, and have been found to withstand the corrosive fumes and atmosphere of the plating shop better than many others.

The number of "contacts" or "stops" in a rheostat is usually about seven, but in the case of vats containing a larger number of pairs of electrodes than this, it will be found very convenient to have at least as many resistances as the number of pairs of electrodes in the vat itself. In this way the current can be regulated according to the number in use at one time.

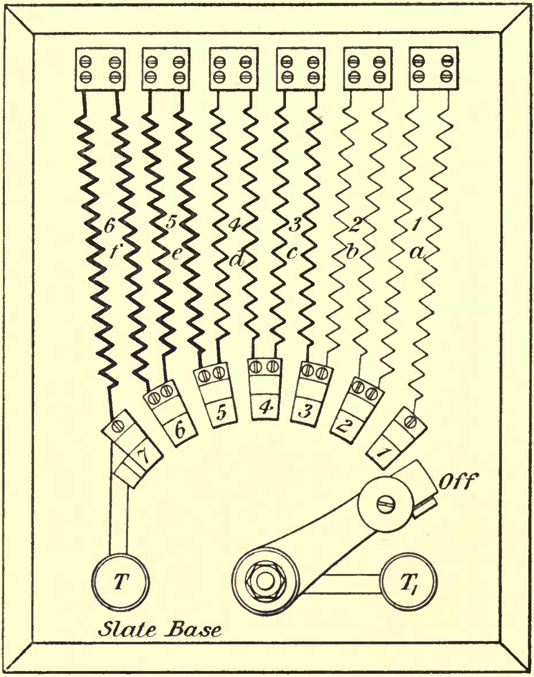

Fig. 37.—Resistance Frame.

Very few details respecting the precise number of steps advisable, the total resistance, and its subdivision between the various contacts can be given here, as so much depends upon individual requirements, but a few details of the design, electrical arrangement and size of wire to use may be useful.

As already mentioned, Fig. 37 illustrates a very common form which is adaptable for much of the ordinary routine work. It consists of a number of resistance coils arranged as shown, which are normally connected in series, when the switch arm is on contact 1, but which may be cut out of circuit one by one by moving the arm over the contacts from right to left. Thus with the switch arm on contact 3 the current enters, say, at terminal T_1, passes along the arm to contact 3, flows through resistance coils *c*, *d*, *e*, *f*, and out at terminal T; coils *a* and *b* are cut out, as there is no path *viâ* contact 3, through coils *b* and *a* after contact 1. When the arm is in the "OFF" position, it is obvious that the circuit is broken, and therefore *no current can flow*.

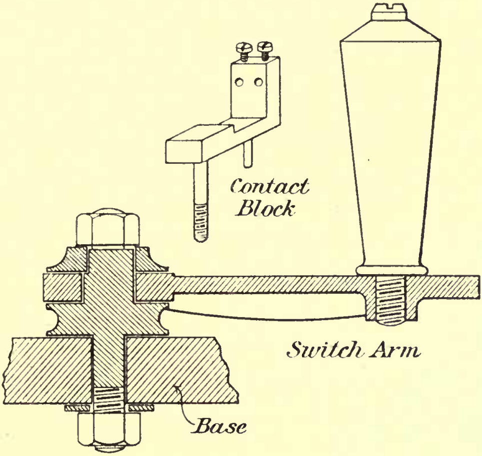

FIG. 38.—Details of contact block and switch arm.

In such a rheostat the resistance per step is often unequal, the first (*i.e.* *a*) being greater than the second, the second greater than the third, and so on. When all the coils are in circuit the current is smallest, but increases as the coils are cut out by the movement of the switch arm. Owing to the gradation of resistance required, coupled with the fact that the coils towards the left carry a greater current than those towards the right, several different gauges of wire are frequently used in the making of the coils, a thicker wire being employed for the smaller resistances, *i.e.* those which carry the larger currents.

In all cases when a current flows through a resistance, energy is dissipated in heating the material,—a fact which will have been gathered from a previous section,—and in consequence, the temperature of the substance is raised. The rate at which heat is generated in a given wire is according to Joule's Law proportional to the square of the current, and the temperature of the substance will go on increasing until the rate of generation of heat is balanced by the rate at which heat is lost by radiation, conduction, and convection. In brief, the rate at which the heat can be got rid of depends upon the radiating and other properties of the material, and upon its environment. It is therefore very desirable that wires of suitable size should be used for the coils of resistance frames, in order that no excessive temperature rise, with its risk of fire or fusion, should result.

By experiment it has been found that platinoid and eureka wire, exposed to the atmosphere in a horizontal position, attain the temperature of blood heat (98° F. or 36·6° C.) when carrying the approximate currents indicated in the following table:—

TABLE X.

Size.	*Current-carrying capacity in amperes.*		
S. W. G.	Platinoid.*	Eureka.*	Ferry †. (final temp. 100° C.).
8	37	30·6	33
10	25	20·37	23
12	15	12·23	16
14	10	8·15	9·4
16	6	4·89	6·1
18	3·3	2·72	4·4

Table XI. gives useful information respecting various kinds of resistance wire.

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* Compiled from the London Electric Wire Co.'s list.

† Compiled from the list of Henry Wiggin & Co., Ltd., Birmingham.

TABLE XI.

Size.		German Silver.*			Platinoid.*			Eureka.*			Ferry.†		
S.W.G.	Diam. inches.	Feet per ohm.	Ohms per 1000 yds.	Ohms per lb.	Feet per ohm.	Ohms per 1000 yds.	Ohms per lb.	Feet per ohm.	Ohms per 1000 yds.	Ohms per lb.	Feet per ohm.	Ohms per 1000 yds.	Ohms per lb.
8	0·160	188·4	15·93	0·068	104·0	28·85	0·124	89·5	33·5	0·144	83·8	35·8	0·152
10	0·128	120·5	24·89	0·160	66·6	45·08	0·303	57·4	52·3	0·352	53·7	55·8	0·370
12	0·104	79·6	37·70	0·384	43·9	68·29	0·696	37·8	79·3	0·807	35·4	84·7	0·847
14	0·080	47·1	63·72	1·090	26·0	115·42	1·987	21·0	133·9	2·304	20·9	143	2·430
16	0·064	30·15	99·56	2·670	16·5	180·34	4·852	14·3	209·4	5·620	13·4	224	5·960
18	0·048	16·94	177·0	8·460	9·37	320·6	15·33	8·07	371·8	17·80	7·5	400	18·87

* Compiled from the London Electric Wire Co.'s list.
† Compiled from the list of Henry Wiggin & Co., Ltd., Birmingham.

Ammeters and Voltmeters.—Instruments intended for the measurement of current are called *ammeters*, while those designed for the measurement of difference of potential are called *voltmeters.*

Fig. 39.—Ammeter.

The principle upon which a large number of these instruments work depends on the magnetic effect produced by the passage of a current through a fixed coil of wire, on a movable soft iron needle.

The chief advantages of moving iron instruments are undoubtedly their simple but sound mechanical construction and their comparative cheapness.

The Nalder gravity-control moving iron instrument is illustrated in Fig. 39. The essential features of its construction (Fig. 40) and operation are as follows :—

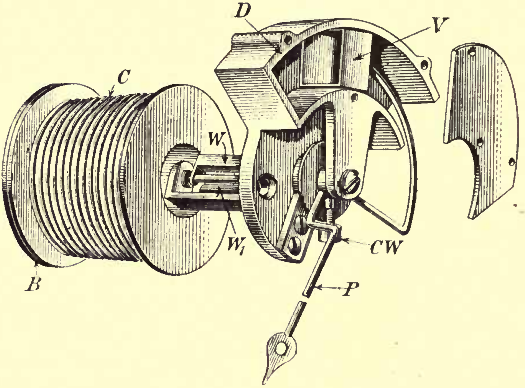

Fig. 40.—Interior of Ammeter with moving portion drawn forward to show working parts.

C is a coil of insulated wire wound spirally on a hollow brass bobbin B, fixed to the base plate of the instrument. The moving portion consists of a soft iron wire, or a small bundle of wires, W, attached to a steel spindle in such a way that the former moves concentrically with the latter and lies inside the coil parallel with its axis. The spindle is carried in jewel centres, and near one end is fastened the pointer P, the counterpoise or control weight CW, and the arm carrying the damping vane V, which moves with very little clearance inside a damping box D.

When no current passes round the coil, the control weight CW hangs vertically, the pointer stands at zero on the scale, and the moving piece of iron W lies close to and parallel with a rod of soft iron W_1 fixed to the framework carrying the spindle.

On passing a current through the coil the adjacent ends of the moving and fixed irons become similarly magnetized with, say, north polarity at the ends nearest the pointer and south polarity at those more remote. There are, therefore, two north poles near together at one end of the system, and two south poles at the other end; consequently since like poles repel one another, the moving iron W is repelled from the fixed iron W_1, with a force which is greater the larger the current. The moving iron, the control weight, and the pointer are therefore turned through an angle.

On the other hand, a diminution of the current reduces the force exerted between the iron pieces, and the action of gravity on the control weight brings the movement back and thus diminishes the angle of deflection. It is obvious then that the angular deflection of the pointer is dependent on the current, and thus it is a measure of the current flowing. The object of the damping box is to steady the movement and help the pointer to come to rest quickly.

Such an instrument may therefore have its scale graduated in amperes by passing definite known currents through its coil and marking the positions taken up by the pointer.

The "range" of an ammeter can be extended in many cases by the employment of a "shunt" placed in parallel across the terminals of the ammeter. The shunt is a strip of metal, of low resistance, which bears a certain definite relation to the resistance of the ammeter coil; by it a certain fixed proportion of the total current passing through the ammeter and shunt together is shunted past the ammeter. Its readings require, therefore, either to be multiplied by some factor or to be taken on an alternative scale dependent on the multiplying power of the shunt in use.

The principle of the instrument described may be adopted in the construction of either an ammeter or a voltmeter. It is essential, however, to point out and make clear the difference between them, and under what circumstances an instrument whose action depends on a *current*, may be used to measure a P.D. and thus become a voltmeter.

It may first be remarked that as the force causing the needle to deflect is proportional to the ampere-turns (current × number of turns) on the coil, it is possible to use a small number of turns through which passes a large current, or a large number of turns and a small current, and yet have the pointer deflected through the same angle.

We may note also that ammeters are always connected in series with the circuit (see Fig. 36), and (in the types outlined above) as the whole of the current to be measured passes round the coil only a few turns of wire are required. There is not much difficulty therefore in comprehending that the deflection of the pointer under these conditions is a measure of the current.

Again, the resistance of the coil of an ammeter should be as low as possible, otherwise there will be an excessive waste of energy in the instrument. For example, if $I =$ current passing through the instrument, and R its resistance, the energy dissipated in the instrument is I^2R joules per sec. (see page 52), and obviously as I is the current we desire to measure, the first factor (I^2) is fixed, hence the dissipation depends solely on R, and will be as small as possible when R

is as low as possible. A small number of turns is therefore an advantage from this point of view.

A voltmeter, however, is joined across or in parallel with the portion of the circuit the P.D. of which is required (see Fig. 36), and its resistance must be relatively large compared with that of the circuit across which it is placed. One consideration which determines this in the case of a voltmeter is that its introduction into the circuit should not materially alter the resistance between the two points of the circuit across which it is applied. Expressed in another way, a voltmeter ought not to divert through itself any appreciable current from the circuit. From either point of view the change which occurs is as small as possible when the voltmeter resistance is as high as possible.

The second consideration is that the power absorbed when working should be small, and since this may be expressed as $\frac{V^2}{R}$ (page 52), where $V =$ P.D. applied to the instrument, $R =$ its resistance, it follows that for a given value of V, the power absorbed diminishes as R is increased.

The winding of a voltmeter therefore consists of a large number of turns of fine wire, through which only a small current flows.

The current (I) which flows through the winding of a voltmeter is, according to Ohm's Law, $I = \frac{V}{R}$, V being the applied P.D. and R the resistance of the winding, from which $V = I \times R$, and it follows that a definite current and consequently a definite deflection will always be obtained for the same voltage, *providing that* (R) *the resistance of the instrument remains a constant.* It is on this ground that the scale may be graduated in volts. For example:—Suppose the pointer of an instrument whose resistance is 200 ohms to be deflected to a certain point on the scale by a current of $\frac{1}{10}$ amp. Then as $V = IR$ the P.D. across its terminals would be $\frac{1}{10} \times 200$, *i.e.* 20 volts, and this point may therefore be marked 20, and similarly for other points; the instrument will then read directly in volts, and hence be a voltmeter. Constancy of resistance is therefore important for ensuring the reliability of the instrument's indications.

Ampere-hour Meter for Electroplating.* — Until quite recently the only method of controlling or ascertaining the amount of metal deposited in a plating bath has been to note the average current-flow during any period, and the elapsed time. The product of these quantities gives the approximate ampere-hours of current passed, and from this it is possible to ascertain the amount of metal which has been deposited.

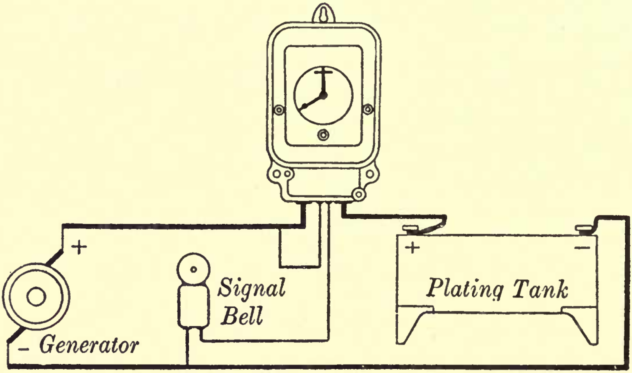

Fig. 41.—Diagram of ampere-hour meter and signal bell.

By the use of a special form of ampere-hour meter, illustrated in Fig. 41, the former method of watching a clock and ammeter is entirely done away with, remarkable accuracy being obtained simply from the record made by the ampere-hour meter. The standard meter as furnished for electroplating control has a dial reading in any desired unit weights of the metal with which the meter is to be used; for example, dwt. of silver, grains of gold, pounds of copper, etc. The meter is equipped with a movable pointer, operated by a knob in the middle of the glass window over the

* From *The Metal Industry*, May, 1912, by kind permission.

dial, so that the pointer can be set at the amount of metal desired for any particular plating operation. For example, if twelve dozen spoons are to be silver plated, and require 100 dwt. of silver, the indicating pointer would be set at 100 on the dial, after which the large moving hand, operated by the mechanism of the meter, would be set at the zero point. As current passes through the meter, the large hand moves in a clockwise direction around the dial until it reaches the pointer, in this case set at 100 dwt., when contact is made against a pin in the adjustable pointer, thus operating through auxiliary leads an electric light or bell, as a signal (Fig. 41).

While the ampere-hour meter has been furnished and is being successfully used with all kinds of plating baths, its widest application has been with silver and nickel. For control of gold plating a special arrangement using two meters is used, as the amount of gold ordinarily deposited in any operation is very small, a few grains only, in many cases.

The principle and construction of the meter were very completely described in *The Metal Industry*, April, 1909.

Cleansing and Dipping Tanks.—Tanks to contain hot caustic potash or soda solutions should always be of welded iron. Welded iron tanks are for the purpose much superior to either cast iron or riveted ones. The heating arrangements may be for Bunsen burners or steam coils. If steam is available the latter system is by far the most convenient. For electrolytic cleansing the vats should be fitted with a strong, well-varnished wood frame, in order to carry the anode and cathode rods and provide efficient insulation. As in this class of work fairly large currents are used, the authors have found it also advisable to mount the rod connections on porcelain insulators.

For acid dips and pickles well-glazed earthenware (Fig. 42) is undoubtedly the best material, except in very small work where glass can be employed. For a hot dilute sulphuric acid pickle the best vat is one of solid lead not less than

$\frac{3}{8}$-inch thick. This, however, must be heated by means of steam coils, also of lead, and all joints burnt or fused.

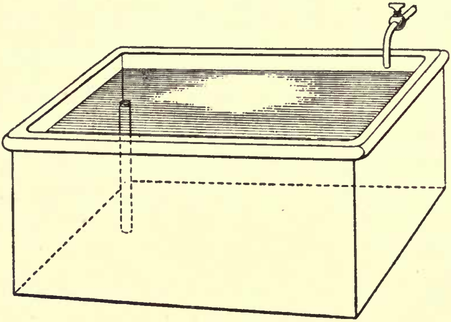

Fig. 42.—Earthenware Rinsing Tank.

Scratch-brush Lathes and Scratch-brushes.—Lathes for scratch-brushing are made in two types, single and double-ended. See illustrations, Figs. 43 and 44.

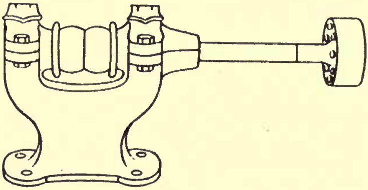

Fig. 43.—Single scratch-brush lathe.

Where a number of lathes are required the single-ended type is almost invariably adopted, so that all brushes rotate in one direction. As the operators must in scratch-brushing face the end of the spindle and not the side, it is obvious that a double-ended lathe presents one end

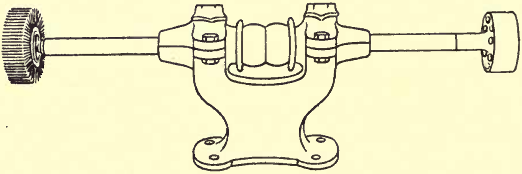

Fig. 44.—Double scratch-brush lathe.

where, as the operator holds it, the article is met by the brush at the right-hand side; at the other end it is met at the left-hand side. To the average worker this is very confusing. In small plants, however, a double-ended lathe is often used, and one end reserved for brushing the insides of hollow ware articles.

The illustrations in Fig. 45 show the type of brush generally used for flat work and the outsides of hollow articles.

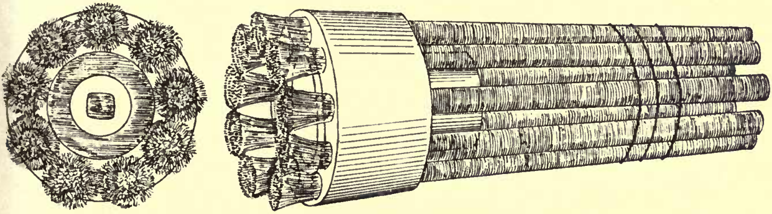

FIG. 45.—Scratch brush for flat work (about $\frac{1}{4}$ natural size).

The complete brush consists of 7 or 9 "knots," as they are called (Fig. 46), mounted on a brass chock, so arranged that as the ends wear they can be moved outwards until the stock is too short for any further adjustment. The knot itself is simply a bundle of perfectly straight lengths of very fine wire—from 38 to 43 B.W.G.—bound tightly together by means of thick copper wire closely coiled round it. The usual diameterof the knot is $\frac{1}{2}$ inch.

FIG. 46.—A "knot."

Other types of brushes for hollow work inside and other uses are shown in Fig. 47.

During use, these are simply screwed on to the pointed end of the lathe spindle.

An important point in connection with scratch-brushing is the speed of the lathes. They should not be run from the same shaft as polishing lathes, or if so steps must be taken to reduce their speed. The exact number of revolutions per minute depends largely on the class of work done and on the metal to be plated, but from 1200 to 1500 revolutions per minute may be taken as the average requirement. If the speed is too slow the brushing is ineffective; on the other hand, if it is too fast the articles are given a grained or frosted appearance which interferes considerably with the subsequent finishing and polishing processes.

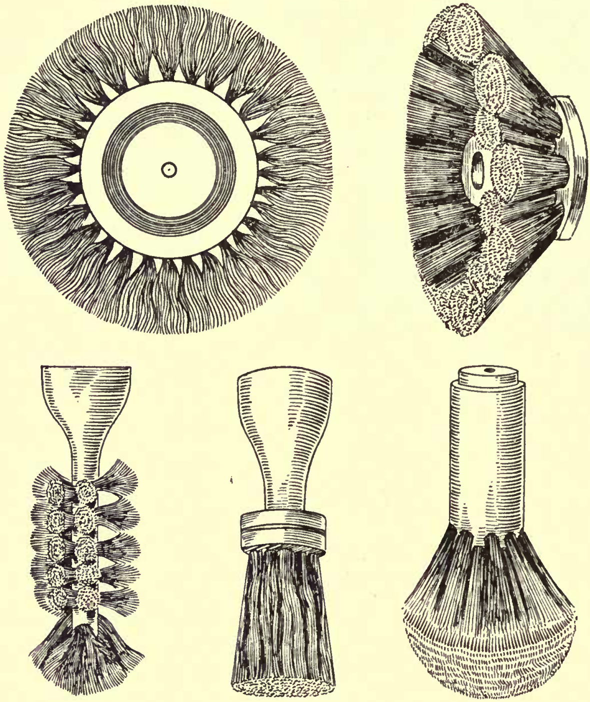

FIG. 47.—Types of scratch brushes for inside and special purposes.

Polishing Lathes.—Lathes for polishing are constructed on exactly the same principle as for scratch-brushing, except that usually only double-ended lathes are employed. As has been already intimated, their speed should be greater than the scratch-brushing lathes, generally 2000 revolutions per minute. Owing to the dusty nature of most polishing processes the lathes should always be installed in a shop, separate from the cleansing or plating shops, but in their immediate vicinity, as in many classes of plating, particularly nickel, polishing is closely identified with the other processes preparatory to plating.

Sand-blasting.—Another essential part of the plant of a thoroughly well-equipped electroplating establishment is an efficient apparatus for sand-blasting. Very many beautiful and artistic effects in the electro-deposition of metals can be simply and quickly obtained by a judicious use of such apparatus.

In addition, the sand-blast is a very efficient cleansing agent for many kinds of work. There is on the market at present a large variety of types of sand-blasting machines,

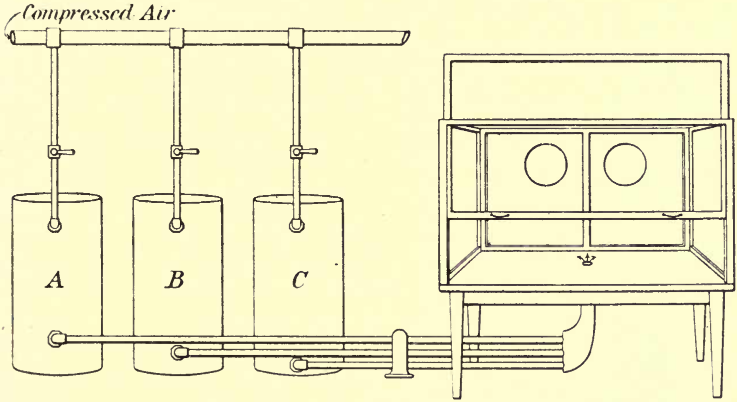

FIG. 48.—Sand-blasting apparatus.

A, Sand container, coarse.
B, " " fine.
C, Pumice.

but a number of these have been designed for use in cleansing and "fettling" large iron-castings for engineering work, and are not at all suitable for the average electroplater's purpose. They are usually worked either by steam or compressed air at very high pressures, and give on most metals a surface far too coarse for electroplating requirements. The accompanying illustrations (Figs. 48 and 49) show various types of machines adaptable for electroplaters. Fig. 49 is a Continental type of apparatus—very compact, and convenient for use in a limited floor space. It is however only suitable for small work such as cups, small bowls, cigarette cases, matchboxes, etc., though if confined to this class it is very efficient, and has the additional advantage of being comparatively inexpensive. For larger work, particularly when different grades of "matting" or "graining" are required, the type of machine illustrated in Fig. 48 is most

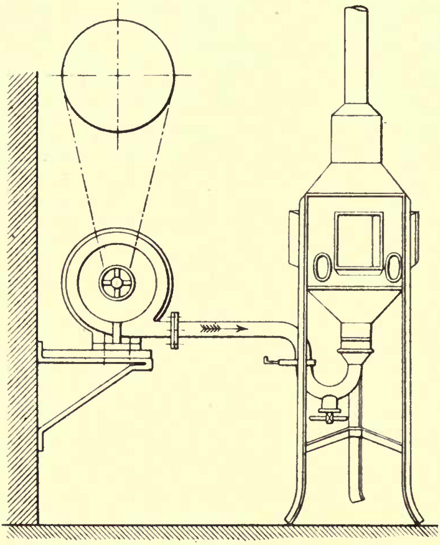

Fig. 49.—Sand-blasting apparatus.

generally convenient. Such types can be readily and conveniently adapted for a large range of work, and not only can the pressure be varied but different grades of material employed according to the requirements of the moment.

To obtain the necessary pressures either steam or compressed air may be employed, but for the classes of work with which the electroplater usually has to deal, the latter is by far the most convenient. For small jobbing work machines fitted with a foot bellows are used, but these have only a very limited application.

The modes of using sand-blasting apparatus and the classes of material employed will be described in the following chapter (on preparatory processes).

General Arrangements of Plant.—A properly designed plating shop should consist of at least three separate rooms or sections, each one distinct yet conveniently connecting to the others, so that work may pass from one to the other with a minimum loss of time. These rooms should also be if possible arranged on the ground floor, and be well lit and well ventilated. The two latter points are particularly important, not only from the point of view of securing successful work, but also of the health of the operators. Contrary to what appears to be popular opinion, none of the ordinary operations of electroplating are of themselves injurious to health, provided only that a thoroughly efficient system of ventilation is secured, and let it be said that this is also conducive to a high standard of work.

The principal room or section of the building should of course be the plating shop proper, containing the plating vats and, unless another small room is available, the dynamo and electrical instruments. The room immediately adjoining this should be reserved for cleansing operations, and should contain scratch-brushing lathes, scouring benches, sinks, potash and acid dipping tanks, and all solutions for processes immediately preparatory to plating proper.

The third room or section should contain the polishing or finishing lathes. Sand-blasting machines and apparatus may be placed either in this latter room or in that for preparatory processes; but in either case a wooden partition should be arranged, so that the sand or pumice powder which may escape may be confined to as small an area as possible, and not allowed to become objectionable in other processes.

Sometimes the dynamo is placed in a recess and partitioned off from the vat room, but it is better that the operator in charge of the vats should have this machine in sight so that any irregularity may be immediately detected. If, however, accumulators are used to any extent they should be enclosed in a separate room or compartment, since in charging they give off fumes which are very objectionable. In laying down a plating plant care should be taken to arrange the dynamo or sources of current as near to the plating vats as possible in order to avoid loss of energy in transmission, and also the expense of long lengths of cable or connecting wires. The vats themselves should be arranged along the sides of the room, sufficiently near to the walls to allow the latter to be used for the electrical leads and connections, and the eccentric shaft for movement of cathodes, or agitating arrangements. In planning the position of individual vats relatively to the dynamo regard should be paid to the voltages required, *e.g.* nickel vats requiring a high voltage should be nearer to the dynamo than the silver ones which only require a very low one. This point may be disregarded in small shops, but in very large establishments it is worthy of attention.

A suggested outline plan for general electroplating shops is sketched diagrammatically in Fig. 50.

We have previously mentioned that all electrical arrangements and connections for plating vats are connected "*in parallel*." The general method of wiring is to carry two main cables from the dynamo round the entire length of the shop, and if necessary on both sides. Sub-connections are then made by jointing short lengths of cable to the mains, and connecting these in turn to each vat and its resistance board and measuring instruments as shown in Fig. 50. Owing to the low voltages employed in electroplating, however, it is not at all essential that these main leads should be of insulated cable. They may be and often are plain bare copper wires solid drawn, of sufficient cross-sectional area to carry the required current, and so long as these wires are securely fixed on insulated brackets so that there is no danger of "short circuits" they are quite as effective as the much more costly cable and often more convenient, as by means of sliding binding screws the sub-connections may be taken off at any point with the minimum of trouble and inconvenience. In the sub-connections to vats and resistance boards it is always better to use insulated cable owing to the risk of the connections crossing, and so causing "short circuits."

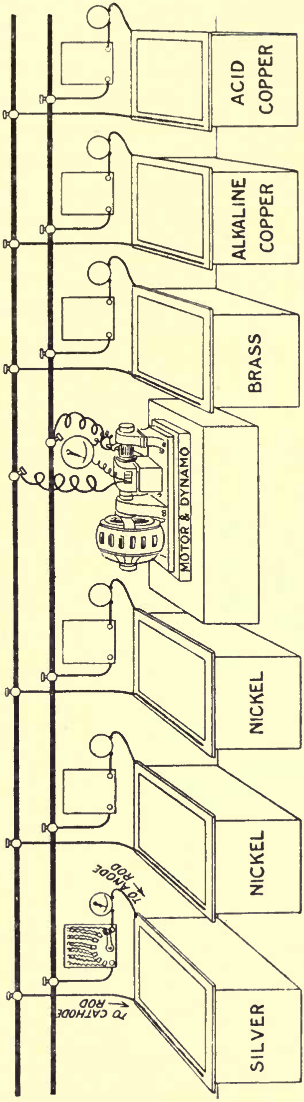

Fig. 50.—Plan of arrangement in general plating shop.

Working Dynamo and Accumulators in Parallel.—On p. 114 several ways were mentioned which are in use for driving the dynamo supplying current to the vats. Whatever method is adopted, it is an advantage to have the speed of the machine as steady as possible, since this tends to ensure steadiness of the current supplied. The steadiness or otherwise of the current is readily noticeable by glancing at the ammeter in the circuit. A steady current will produce a steady deflection on the instrument, the pointer remaining at rest, but one which is the reverse causes the pointer to oscillate to and fro. In cases however where a fluctuating current is traceable to an unsteady drive, a battery of large accumulators may be run in *parallel* with the dynamo, as shown in Fig. 51, but only when the dynamo is shunt wound or has its field-magnet winding supplied with current from another source.

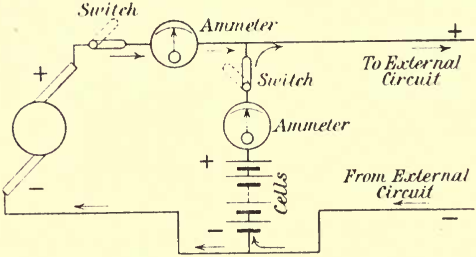

Fig. 51.—Connections for dynamo and accumulator run in parallel.

With this arrangement the fluctuations will almost if not entirely disappear, since in the event of the dynamo current diminishing, the cells will discharge a current approximately equal to the diminution, and so compensate for it, while any increase in the dynamo current will go (wholly or in part) as a charging current through the cells. Cells used in this way are said to be floating on the circuit.

The voltage of the accumulator must be the same as that at which the dynamo usually works, and as the P.D. of a single cell is two volts the number of cells to be joined in series for the purpose is easily found; an 8-volt dynamo would require 4 cells, a 10-volt dynamo 5 cells.

In connecting up care must be taken that the positive pole of the cells is connected to the positive main from the dynamo, and it is advisable to have a central-zero permanent magnet moving-coil ammeter, and also a switch in both dynamo and cell circuit as shown in the diagram. By means of the switches it is obvious that the dynamo and cells may be used separately for the supply of current to the circuit, or both together in parallel. In the latter case a larger current may be drawn from the combination than it would be safe to take from the dynamo or cells used alone. The type of ammeter mentioned enables us to observe not only the value of the current in amperes in the respective circuits in which the instruments are placed, but also the direction of the current; for if both are supplying the circuit the pointers will, say, deflect to the right of the zero mark, whereas if the current in either circuit for any reason reverses, the ammeter in that circuit will show a left deflection.

Again, in the section dealing with the deposition of alloys, it will be pointed out that the constancy of the P.D. acting in the circuit is a most important feature in such cases. And as an unsteady current resulting from imperfections in the driving arrangement is really caused by fluctuations in the value of the E.M.F. generated due to the varying speed of the machine, the benefit to be gained from the use of accumulators alone or in conjunction with a dynamo is obvious. Accumulators have an extremely steady and almost a constant P.D. during the major part of their discharge.

Another feature of this combination of dynamo and accumulator is the possibility of charging the cells from the dynamo, while the latter is also supplying current to the vats. Especially is this so when the current required for deposition is comparatively small and the dynamo only lightly loaded. For instance, suppose we have an 8 volt, 300 ampere machine and four large cells, and that the work in hand only requires 100 amperes. Under such conditions the dynamo is working at $\frac{1}{3}$ full load, and in general the efficiency of the machine would not be at its best. But by arranging the four cells in two sets of two in series, as in lower part of Fig. 18, and connecting them to the main leads from the dynamo as illustrated by the whole of Fig. 51, *i.e.* so that they form two branches across the leads, the cells could readily be charged with the 8 volts available. If each set were capable of being charged with 100 amperes (the current being adjusted to this value by the resistances) we should have 100 amperes in each cell circuit, and 100 amperes going to the vats, or 300 amperes in all. The dynamo would then be fully loaded, and working with increased efficiency, $\frac{2}{3}$ of the energy developed being stored as chemical energy in the cells, to be used subsequently.

After charging the cells in this way, it would only be a simple matter to arrange all four in series, and connect them in parallel with the dynamo as previously observed. More than 300 amperes if necessary could then be obtained, both cells and dynamo supplying current to the external circuit.

CHAPTER VIII

PREPARATORY PROCESSES

THE subject of the preparatory treatment of articles prior to actual electroplating is of the greatest possible importance. It is in the preliminary stages of treatment in the plating shop, that three-fourths of the troubles and difficulties incidental to electro-deposition have their rise; and in no section of the art do care, patience, and skill bring their reward so quickly and so completely as here.

"**Absolute cleanliness in all things**" should be the working motto of the electroplater, whether he deals with the noble metals like gold, silver, or platinum, or with the more ordinary copper, nickel, or brass. This motto, further, should be given a very wide application, not merely to the articles dealt with, themselves, but also to the shops through which they pass; the plant, the benches or tables, even the floors should be kept as rigidly clean as it is possible to keep them. The greatest care in removing grease and tarnish from a metallic surface is often completely nullified by a dirty scratch-brush lathe, or a little greasy matter on the edge of a vat or earthenware rinse-pot.

In the present chapter, general outlines of methods applicable to all metals will be given; special methods of treatment peculiar to one class of work only will be given in the chapters relating thereto.

Before dealing however with the processes belonging strictly to the plating department, it may be advisable to give a general description of methods employed to render surfaces perfectly smooth and regular so that the subsequent "finish" shall possess the smooth gloss and brilliant polish usually associated with finished electroplated work. Articles as they come from the manufacturers' hands, whether spoons or forks, cutlery, flat-ware or hollow-ware in any class of metal, and whether made by casting, forging, stamping, rolling, or by hand, usually retain the marks of the varied operations through which they have passed; and all such irregularities, file-marks, etc., must be buffed or polished off. This process is usually known as "**buffing**" or "**polishing.**" The operations vary according to the basis metal and class of work handled, but consist essentially of treating the articles with fine emery powder, pumice powder, Trent sand, rotten stone, etc., by means of emery wheels, leather or felt discs, bristle brushes, calico dollies and other hand or machine tools of a similar nature.

In the present book it is quite unnecessary to enter in detail into the manufacture of these tools or materials, as they can be readily and reasonably purchased from manufacturers who make a speciality of polishing reagents. A brief outline of the treatment of the principal metals in industrial use will therefore suffice in this connection.

Silver, *Copper*, *German Silver*, *Brass*, and similar metals and alloys, are buffed generally on lathes similar in type to Fig. 44, p. 136, by holding them firmly, and with an even pressure at all parts of their surface, against a leather or felt disc screwed on to the lathe spindle. The buffing material is in the first instance usually powdered pumice and finally finely sifted Trent sand thoroughly mixed with rape or some similar oil. The pumice or sand is allowed to "flow" between the article and buff. In the best practice and class of work the pumice powder is used for "grounding," *i.e.* smoothing out the coarser marks of the surface, and fine sand applied as a secondary or fining-off process. For many kinds of work fairly hard bristle brushes are used in a similar manner.

Britannia Metal, *Pewter*, and *Tin* alloys generally are given very much the same kind of treatment to the above except that only finely sieved sand mixed with oil is used. Pumice powder is much too keen and abrasive for use on the softer metals.

With regard to the respective use of pumice powder and sand in buffing processes, it should be observed that the former material has much greater "cutting" properties than the latter. It is therefore an exceedingly useful substance for clearing the surface roughness, or grain, of the harder metals, particularly nickel and copper alloys. If, however, as is often the case for the sake of cheapness, the article is not given further treatment the "cutting" marks of this material are always discernible, and it is impossible after plating—whatever metal be deposited—to give the work the fine mirror-like polish characteristic of really well-finished work.

For articles of any of the above-mentioned or similar metals, intended to be plated either with copper, brass, silver, gold, and most other metals, the treatment just described is sufficient. As, however, such goods always leave the fine sand with a surface which though quite smooth is yet dead or dull in appearance, they are not sufficiently prepared for deposits of nickel or cobalt. These two metals as deposited electrolytically possess such a high degree of hardness that unless the surfaces upon which they are deposited are not only perfectly smooth but possess a fairly high polish, it is impossible after plating to bring out to the fullest extent the brilliant colour and gloss of which they are both capable. The materials mainly used for this purpose are Sheffield lime, Vienna lime, Tripoli, rouge, crocus, and compositions mainly composed of these substances, applied by means of calico mops or dollies, the processes being practically a continuation of those previously described.

Iron and Steel Goods requiring a perfectly smooth and bright surface are prepared almost entirely by means of emery powder. This extremely useful substance—unrivalled as a polishing reagent for this class of work—is a natural product consisting almost entirely of the oxides of iron and aluminium.

In the first stages of preparation solid emery wheels are generally used, but in the later stages, leather buffs, treated with various grades of emery powder, are employed. These buffs are really wooden bobs or discs covered on the outer edge with leather, of a thickness of from $\frac{3}{8}$ to $\frac{5}{8}$ inch. The leather covering is secured to the disc by means of glue, and the operation must be carefully and skilfully performed, as accidents occasionally happen through the covering breaking away from its base, when in use on high-speed polishing lathes.

Before actually using these buffs they must be "dressed," as it is termed, with emery powder. This also is an operation demanding a little practice and experience; the outer surface of the leather is given a slight coating of thin glue spread equally over it. While the glue is still warm, the disc, which is held by means of a short rod passed through its centre, is rolled backwards and forwards regularly in a trough or shallow dish containing the emery powder of the grade required. Any irregularities of surface may subsequently be removed by fixing the buff on the lathe and while revolving, pressing firmly a piece of lump pumice at its face. A number of buffs are thus prepared using various grades of the powder, from say No. 60 (fairly coarse) for the earlier stages of polishing to No. 120 or 140 (very fine), for the final gloss. From time to time the buffs require redressing with emery powder, and opportunity should be taken at the same time to examine the security of the leather covering on the disc.

For small work and work having many irregularities or indentations in the surface, solid leather buffs are used. These can of course be turned to any diameter from 1 or 2 inches upwards and are thus convenient for use in polishing hollow articles.

The present writers have also found a good quality of felt, of corresponding thickness to the leather, suitable for the covering of wooden bobs for use in obtaining a very high polish with No. 140 emery in the *final stage of polishing.*

Very small articles are now often prepared for plating by means of what are termed "tumbling barrels" (Fig. 52).

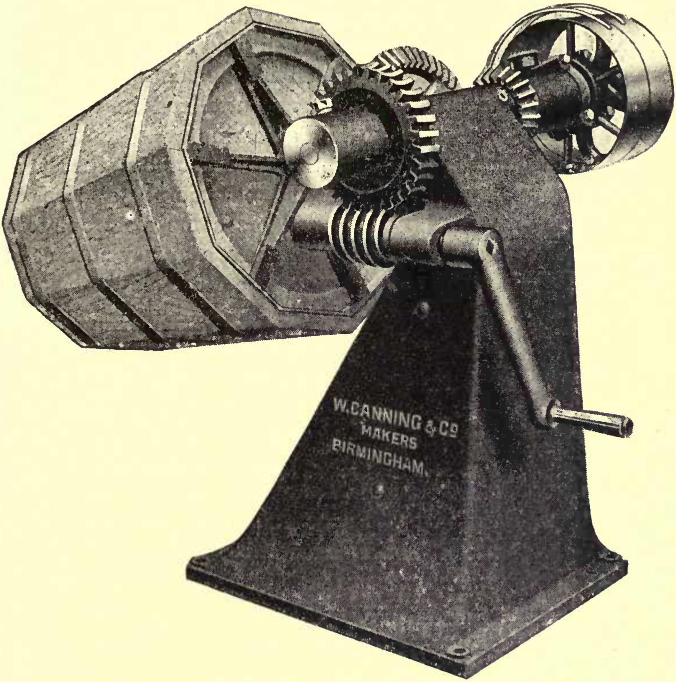

Fig. 52.—Tumbling Barrel.

Cleansing Processes.—After the preliminary treatment outlined above, the articles are ready for the processes which may be considered as essential parts of the plating operations proper. These are (1) cleansing from grease, and (2) cleansing from metallic oxides or tarnish.

(1) *Cleansing from grease.*—This is accomplished mainly by the use of boiling solutions of caustic soda or potash (strength ½ lb. per gallon). These substances have the property of converting fatty materials and greases, which ordinarily are insoluble in water, into a soap and glycerine,

both of which substances are readily soluble in water and may then be entirely removed from the surface of the article. The process in its chemical reaction is exactly analogous to the main operations in soap manufacture. In the latter case equivalent weights of caustic alkali and some form of vegetable or animal fat are placed in the soap-boiling pan, and both substances are entirely neutralized in the production of soap together with free glycerine.

It is of the utmost importance to remember that this operation is a *chemical* reaction and not simply a case of washing off grease in a hot liquid, as some electroplaters apparently believe. Each time, therefore, a greasy surface is immersed in the cleansing liquid a certain equivalent of caustic alkali is neutralized and the solution rendered correspondingly weaker. It is, further, important to note that the grease is not necessarily washed away even when this chemical action is complete. It is simply converted from an insoluble compound to a soluble one, which can be readily dissolved off in water. During the process therefore it is always advantageous to brush the work over from time to time to remove the soapy compounds and enable the potash to complete its work thoroughly.

Articles occasionally reach the electroplater which are covered with oily matter upon which potash has little or no action. This is the case, for example, where goods are coated with vaseline or any of the paraffin compounds in order to protect from atmospheric action. These substances, and indeed all mineral oils, are best removed by means of benzene, in which they are perfectly soluble. Articles should be well brushed with the benzene, and then scoured with whiting made into a thin paste with water, afterwards thoroughly rinsed under running water. This treatment will be found very effective in dealing with a class of work which sometimes gives a great deal of trouble.

The above processes are applicable to all ordinary metals and alloys dealt with by the electroplater. It must be observed however that tin and lead, and alloys containing large proportions of these metals, must not be allowed to remain in the potash tank any longer than is absolutely necessary to remove the grease, as these metals are attacked to some extent by strong alkaline solution. Aluminium also should be excluded from these liquids, or at most be given but a momentary immersion. The benzene treatment with subsequent scouring with lime or whiting will be found the best method of removing grease from surfaces of this metal.

2. *Cleansing from oxides or tarnish—dipping and pickling.*—After the removal of grease in the potash boil there still remains, in the case of most of the metallic surfaces treated for plating, a film of oxide or other stain which must be completely removed before the article can be given a perfectly adherent coating of deposited metal. This is accomplished by means of acid dips or pickles, the composition of which varies according to the kind of metal to be treated.

For copper, brass, German silver, and similar alloys, one of the best dips is made up as follows:—

		*Metric.**
Sulphuric acid . .	10 imperial gallons	50 litres
Nitric acid . . .	2 ,, ,,	10 ,,
Water	10 ,, ,,	50 ,,
Common salt . .	4 ozs.†	125 gr.

The sulphuric acid is slowly added to the water in an acid-proof earthenware vessel, and the nitric acid and salt added when the mixture has cooled. The whole is thoroughly stirred before use.

Sometimes it is desired to bring articles from the dip with a decided dead or dull effect. This may readily be

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* Where metric alternatives are added for convenience, it will be seen and must be borne in mind by the reader that they are *not* necessarily strict equivalents (unless an = sign is employed), but merely give the requisite *relative* proportions, which is all that is necessary for the plater's purpose.

† In all cases, unless otherwise stated, the avoirdupois ounce and pound are used. Troy weight is only used in the case of silver and gold and certain of their compounds in Chaps. IX. and X.

done by using a dip composed of equal parts of sulphuric acid and water to which about a quarter of its bulk of nitric acid is added and a small proportion of zinc sulphate (from 1 to 3 ozs. per imperial gallon, or say from 6 to 18 grams per litre).

A good *pickle* for these metals is composed of dilute sulphuric acid (one of acid to twelve of water). This is generally used, prior to dipping, for articles which are badly stained.

A preliminary immersion in a pickle enables the dipping acid to act more quickly and effectually.

Iron and steel goods, particularly those with bright surfaces, must not be dipped in strong acids; these articles are usually pickled in dilute sulphuric or dilute hydrochloric acids. A pickle for this purpose, recommended by Langbein, which gives excellent results, is made up as follows:—Add 28 ozs. of strong sulphuric acid to 2½ imperial (or 3 U.S.A.) gallons of water, dissolve in the mixture 2 ozs. granulated zinc, and finally add 12 ozs. nitric acid. Stir thoroughly and put aside to cool. Dilute nitric acid itself (1 in 20) is also a useful pickle for bright steel goods.

In the case of the softer metals such as zinc, lead, tin, and alloys consisting mainly of these, oxides and stains are best removed by scouring with powdered pumice or whiting and scratch-brushing; but in many instances a dip consisting of a strong solution of potassium cyanide (1 lb. per imperial gallon or 100 grams per litre) will be found extremely useful.

A similar dip is sometimes used for treating polished surfaces of copper or brass which might be injured in strong acids.

If however the cyanide dip is used for polished surfaces which are to be *nickel-plated*, a precaution which must be most carefully observed is to rinse thoroughly in clean running water in order to avoid contaminating the nickel bath with traces of the cyanide liquids. The method of procedure which we have found most satisfactory after the cyanide dip is to rinse well in water, afterwards to immerse the articles for a few seconds in very dilute sulphuric acid (1 in 20), again to rinse quickly, and place immediately in the nickel vat.

Electrolytic Cleansing.—This is a modern development which will doubtless ultimately replace the older methods of cleansing by simple immersion in potash or soda liquids as described above. The fundamental principle of this method is to attack and remove the grease or oxide from metallic surfaces by means of chemical reactions which are made to occur electrolytically. The reader will by this be familiar with the fact that whenever an electric current is passed through an electrolyte, chemical substances are produced and chemical action occurs both at the anode and the cathode. It will therefore be readily understood that, given a suitable electrolyte, products may be generated at the surface of the electrodes which strongly attack either grease or oxides, or both.

A considerable number of particular methods and solutions for electrolytic cleansing have been published, but the literature of the subject is as yet in a somewhat unsatisfactory condition, and much investigation remains to be made relative to the exact nature of the reactions which occur and the conditions essential to the most efficient results.

Some of the earlier experiments in electrolytic methods of cleansing appear to have been made by Mr. Cowper Coles mainly in the direction of "pickling" iron preparatory to electro-zincing, the method adopted being to make the articles alternately the anode and cathode in dilute sulphuric or dilute hydrochloric acid as the electrolyte. This method was very successful in removing both grease and scale from such surfaces.

In 1899 a process was patented on the Continent for electrolytic cleansing by means of aqueous solutions of alkaline salts. In working this method also the articles to be cleaned may be made either the anode or cathode or both alternately. For the preparation of iron plates it was directed to use a 20 per cent. aqueous solution of sodium sulphate. In the electrolysis of this solution sulphuric acid is formed in the vicinity of the anodes and, on the other hand, caustic alkali (sodium hydrate) is formed at the cathode. For removing oxides and scales, therefore, the plate to be treated forms the anode, and for cleansing from grease, the cathode, the opposite electrode in each case being also sheet iron. This process is said to be operated on a very large scale on the Continent, and is both efficient and economical.

For non-ferrous metals and alloys generally, and also brightly polished iron and steel goods in preparation for electroplating, the following and similar solutions have been strongly recommended :—

		*Metric.**
Caustic soda	½ lb.	250 gr.
Carbonate of soda (crystals) . .	½ lb.	250 ,,
Sodium cyanide	½ lb.	250 ,,
Water	one imp. gall. or 1⅕ U.S. ,,	5 litres

The solution is contained in an iron vat, and may be used either hot or cold. The electrical connections include a resistance board for current regulation and a reversing switch. In this way the current density can be varied, and the article made either anode or cathode at will. On immersion the articles are first made cathodes and a strong current passed for a few minutes, the anodes being usually iron or carbon plates. This action neutralizes grease, but sometimes produces stains which a brief reversal of the current, making the articles the anodes, will completely remove, and the goods are brought from the vat clean and bright.

The methods of electrolytic cleansing which the present writers have found most efficient are as follows :—

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* Throughout in the case of such formulæ as the above for solutions, the basis for the metric alternative has been taken as 5 litres (instead of 4·54, the strict equivalent of 1 imp. gallon), but the quantities of the ingredients are adjusted to agree therewith.

1. For removing scale and oxide from average cast or wrought iron goods, make up as an electrolyte a solution of one part strong sulphuric acid to from twelve to fifteen parts of water. The articles to be treated are made the cathodes, and the anodes consist of strong plates of sheet lead or carbon. The voltage used should be not less than 4 volts with a current density sufficiently strong to generate gas freely at the cathode surface. From 10 to 15 minutes will usually suffice to remove all oxide from an average class of work.

A most important saving of time is thus effected, since often in ordinary pickling an immersion of several hours is required to loosen the scale adhering to these goods.

2. For German silver, brass, cupro-nickel, and all such alloys as well as copper, the electrolyte is made up of a simple solution of caustic soda in water. Commercially pure caustic soda should contain 78 per cent. of sodium hydrate, $NaOH$, and this should be used in the proportion of about $\frac{3}{4}$ lb. per imperial gallon of water (or 75 grams per litre). The solution should be worked hot in order to assist in a complete saponification of the grease. The articles are made the cathodes, and anodes may be of carbon or sheet iron (we prefer the latter).

A voltage of 4 or 5 volts is sufficient for ordinary work, with a current density of not less than about 12 amperes per square foot. The higher the current density, the quicker the removal of grease.

As will be readily understood, the electro-chemical action resulting in this case is the rapid liberation at every point of the entire cathode area, of nascent hydrogen and sodium; the former assists in the reduction of oxides, the latter, attacking the water, forms anew sodium hydrate, which immediately neutralizes the grease in the vicinity of its formation, and as fresh sodium hydrate is continually being formed by the current at every part, even in the deepest recesses, of the immersed surface, this reaction is extremely rapid and effective.

No one who has given this method a thorough trial will for one moment doubt its immense superiority to the old method of simple immersion in caustic soda or potash with a periodical scrubbing of the greasy surfaces with the potash or scouring brush.

At the discretion of the operator, the acid dip may be omitted in the case of metallic surfaces treated electrolytically, but as it is only a momentary process, and therefore involves practically no loss of time, it is advisable in most cases to give the articles this treatment as a safeguard.

With regard to the electrolytic cleansing or pickling of iron or steel goods in acid solutions, an interesting point has been observed by several experimentalists which deserves mention here. This class of work is very often called upon to conform to certain physical or mechanical tests, and while before electrolytic treatment they have been found to possess the qualities corresponding to these requirements, they have been found afterwards to be appreciably changed, and occasionally have lost some rather important properties.

The most probable explanation of this unfortunate phenomenon is that the iron has occluded some proportion of the hydrogen gas which is always liberated very freely in all electrolytic actions of the nature described above. If porous castings particularly are allowed to remain for any considerable length of time in contact with hydrogen, in what is undoubtedly at the moment of liberation a nascent condition, it is in the highest degree likely that sufficient may be occluded to affect appreciably its composition and constitution, and therefore mechanical properties. Sand-blasting (see later, p. 160) has been suggested as an alternative method of cleansing surfaces of articles in regard to which this difficulty is liable to arise.

Scouring and Scratch-brushing.—These processes are very largely adopted, not only in the treatment of articles preparatory to plating, but often during plating itself, particularly in building up thick deposits, in order to obtain perfectly regular and even coatings. Scouring and scratch-brushing are operations having the same ultimate effect, and are used as supplementary to the cleansing methods described in the foregoing paragraphs. As the term implies, scouring consists of scrubbing the surfaces to be plated by means of fine sand, lime, whiting, or precipitated chalk, with either bristle brushes or pads of calico flannel, or swansdown. Scratch-brushing, on the other hand, consists in brushing, usually by machine power, with very fine hard brass or German silver wire brushes, using some liquid lubricant having organic matter in solution, *e.g.* stale beer, malt, bran, or oatmeal water, or solution of soapwort, dilute vinegar, etc., etc. A very dilute decoction of fine pea-meal in water will be found effective.

The apparatus for scratch-brushing has already been described (see page 136), as also various types of brushes. It must be noted that the wire used in making up these brushes must be harder than the metal undergoing treatment, but not sufficiently so to scratch or otherwise injure the surfaces treated.

It will be understood that scratch-brushing is much more severe in its effects than scouring, and consequently for highly glazed or polished surfaces the latter operation is almost invariably substituted, the scouring material being lime or whiting. Scouring must also be resorted to usually in treating deep recesses or parts which cannot well be got at in lathe scratch-brushing.

Since both these processes are usually the last through which an article passes before immersion in the plating liquid, or, in the case of silver deposition, the quicking bath, it is of the greatest importance that the fingers be kept absolutely clean in handling goods. In the case of work for nickel-plating for which scouring is often adopted, a good plan is, after thoroughly washing the hands, to rub over them a little dry whiting or fine pumice powder, and to repeat this occasionally during scouring operations.

While on the subject of scratch-brushing it may be well to recur to the fact previously mentioned, that this process is often resorted to during plating, in building up thick deposits, particularly of copper, silver, or brass. In the case of silver, for example, when the deposited metal has obtained a thickness of from 0·0025 to 0·003 inch (0·065 to 0·075 mm.), however smooth the basis metal surface may have been originally, the "grainy" crystalline nature of the deposit causes a definite irregularity on the surface of the plating which if allowed to go on would ultimately render it impossible to obtain a perfect polish during finishing operations. An extreme illustration of this point may be observed on the backs of electrotypes or the surfaces of electrolytically refined copper plates ("electrolytic cathodes").

A thorough scratch-brushing of the surfaces at the stage named will, however, by flattening or grinding off the projecting points of these minute crystals of which the deposit is composed, render the surface almost as smooth as the original basis; and so enable the operator to proceed to build up a further deposit of equal thickness without fear of obtaining a final surface too rough for finishing.

It is often advisable, and, indeed, where soft-soldered articles are concerned, necessary, to give work a preliminary film of deposit—often termed a "striking" or "starting" deposit—and then scratch-brush, before placing in the vat for the full deposit. Starting or striking deposits are usually given with a current stronger than the normal, and the effect of this is to force the deposit of metal over parts of surfaces, such as soft soldered seams or joints, which are less conductive than the main surface. Scratch-brushing at this stage has the effect of testing the adhesion of the deposit generally and remedying any roughness which the strong current may have caused at edges or projecting corners.

For many classes of work, particularly flatware, this process is unnecessary.

Sandblasting.—Amongst processes preparatory to electroplating in any of its branches *sandblasting* must now be considered of increasing importance, inasmuch as it provides almost ideal means of producing in the preliminary stages of treatment effects which, in the finished product of the electroplater's art, are often exceedingly beautiful and artistic. It is now indeed a process not merely of a preparatory nature, but is, in a large number of instances, used in the finishing stages. This latter application will however be touched upon in Chapter XVIII., so that only the former need be treated here.

The apparatus required for this process has already (in the previous chapter) been fully described, and it only remains to be stated in this connection that the type of apparatus chosen will be determined by the size and class of work to be done.

It is, of course, well known that sandblasting consists essentially in forcing under strong pressure (usually compressed air) currents of sand or similar abrasive material against metallic or other surfaces undergoing treatment; the effect being to give to these surfaces a character varying from an extremely slight dull or dead appearance to a very coarse-grained or crystalline frosted effect. Whatever grade of result is obtained, however, the characteristic nature of sandblasting is the perfect regularity of texture and consequently also uniformity of colour imparted to the surface treated.

In attempting any description of the details of sandblasting processes it should be plainly stated that actual figures given with regard to pressures and classes of material must be taken, not as exact values, but rather as guides to those who may be to a large extent unacquainted with the possibilities of these methods. Requirements, as well as conditions, vary so greatly that it is impossible to do more than give approximate numbers derived from the experience of operators having considerable knowledge of the ordinary needs of the trade.

A brief survey of the possibilities of the types of machines previously referred to will show that, broadly speaking, there are two methods by which differential treatment may be applied, (1) by variation of pressure, and (2) by variation of material. In one or other of these directions an almost infinite variety of results can be obtained. In the first case, the *depth* of the blasting effect is regulated. In the second, it is mainly the grain or texture which is influenced. But both these factors are so interdependent on each other that this distinction can only be taken as applying approximately.

It will be fairly obvious that different metals require widely differing treatments to obtain even similar effects. Iron and steel goods, for example, may be subjected to a much higher pressure and coarser material than the soft tin or zinc alloys which occasionally have to be treated. The former class are usually sandblasted at pressures of from 20 to 24 lbs. per square inch, the abrasive material being generally a medium or coarse grain of Calais sand. The latter can rarely be subjected to a higher pressure than from 3 to 5 lbs. per square inch, and only the finer grades of sand employed.

In electro-zincing iron and steel this treatment is now often resorted to, instead of dipping, scouring, or scratch-brushing. The articles are cleansed from grease in benzene, or caustic potash in the usual manner, rinsed in hot water, dried, then sandblasted, and after thorough rinsing to remove all traces of sand are ready for plating.

Silver, which perhaps more than any other single metal is required to undergo this treatment, is now to a large extent treated with pumice powder of various grades, instead of sand; particularly in preparation for "oxidizing" or gilding. A finely frosted matte finish, for example, is given to silver or electro-silver-plated goods which are intended for subsequent colouring or gilding, by blasting with finely divided pumice, say No. 60 at a pressure of about 8 lbs. per square inch.

A few special modes of treating silver, copper, brass, and German silver for particular effects are detailed in the following Table XII.

TABLE XII.

Sandblasting. Silver, Copper, Brass, and German Silver.

Material.	*Pressure.*	*Effect.*
No. 54 Calais sand	12 to 15 lbs. per sq. inch	Rather coarse satin-like surfaces. Usually termed frosting effects.
Powdered pumice, No. 60	8 to 12 lbs. per sq. inch	Satin-like surfaces, finer than above.
Powdered pumice, No. 90	6 to 8 lbs. per sq. inch	Dull, exceedingly fine matted surface.
Powdered glass	6 to 8 lbs. per sq. inch	Similar matte to above, but *bright*.
Coarse Calais sand, about No. 18	15 lbs. per sq. inch (momentary pressure only)	Ice-like crystalline surface, similar to moulded glass.

Partial Frosting.—By this term is meant some treatment which will leave part of the surface of an article with a frosted or satin-like appearance while the remaining part is normal. As would naturally suggest itself to any one acquainted with the sandblasting of glass, this may be done by means of stencils cut from ordinary writing-paper. These paper stencils are cut so as to reveal the parts to be frosted, and then pasted with glue on to the surface of the article. After thoroughly drying, the work is submitted to sandblasting, and all parts left uncovered receive the frosted effects. The glued paper can be readily removed subsequently by immersing in hot water.

A sandblasting apparatus fitted with a very small nozzle is often very useful in ordinary cleansing operations for treating deep recesses in hollow-ware articles which are difficult to clean properly otherwise either by scratch-brushing or by scouring; particularly is this the case where soft solder has been used in such recesses.

Preparation of Aluminium and its Alloys.—The problem of electroplating aluminium with any other metal has for long attracted the attention of electroplaters, but complete success in this direction does not yet appear to have been attained. One of the principal difficulties is the great affinity of this metal for oxygen. Even when most careful precautions are taken effectively to cleanse the surface and remove every trace of oxide, the slightest exposure to a moist atmosphere and even an immersion in an aqueous electrolyte is sufficient to form a fine film of aluminium oxide and so to prevent that perfect cohesion of the basis metal and its deposited coating which is essential. Repeatedly has it been found, when this metal has been given what appeared to be a thoroughly sound coating of copper or silver which indeed has stood the test of burnishing (see p. 359), that sooner or later, on standing, small blisters have appeared here and there over the surface of the article, and the deposit rendered absolutely valueless.

There seems also very good reason to believe that the liberation of hydrogen, which always occurs to a greater or lesser degree in electrolysis of aqueous solutions, is another very serious obstacle to obtaining the perfect adhesion of an electro-deposited metal on aluminium. This point however requires further investigation.

Directions for the preparation of this metal for plating can only therefore be considered as suggestive for further experiments and research.

A slight acquaintance with the chemical properties of aluminium will suggest the necessity of avoiding strong alkalies in preparatory treatment. If the surface is very greasy, benzene should be used in the first place, and subsequently after rinsing in clean water the articles should be passed through a hot solution of cyanide of potassium—this being the safest alkali to use in this connection, with or without the addition of a little ammonia. For removal of oxide, dipping in hydrochloric acid of various strengths is usually resorted to.

It should be said however that the successful plating of aluminium depends to a considerable degree on the composition of the electrolyte, probably quite as much or more than on the particular preparatory process adopted.

Preparation of Non-metallic Surfaces for Plating.—In addition to the well-known metals and metallic alloys used in the arts, the expert electroplater is often called upon to give deposits of copper, silver, or gold to articles of glass, china, wood, vegetable growths, and other substances which are non-conductors, and therefore must be rendered conductive before any electrolytic deposit can be imparted to them.

The principles adopted in dealing with this class of work may be described under two heads, (*a*) chemical, (*b*) mechanical.

Under the former principle the method usually adopted is to treat the surface in question with some solution or series of solutions which by chemical action will precipitate a metallic powder or film, and so give the article superficially the conductive property of a metal.

Under the latter principle surfaces are either brushed over with fine plumbago or a mixture of plumbago with a very finely divided metallic powder, or "metallized"—as the process is termed—by brushing with finely divided silver, copper, or tin powders, after preliminary treatment with some solution which will give an adherent base. Examples of the plumbago method are found in the treatment of gutta-percha moulds for electrotypy (see p. 268), and of the metallizing process in the treatment of wood by first applying a coating of thin varnish or lacquer, and then, while this is still plastic, brushing the entire surface with a plentiful supply of copper bronze powder.

Many different methods have been tried and used with more or less success in both the chemical and mechanical processes of treatment, but it should be said that success depends quite as much on the experience and skill of the operator as on the particular method chosen.

(*a*) In the great majority of cases the method of chemical treatment adopted is to precipitate finely divided metallic *silver* on the surfaces to be treated. The reason for the choice of silver as a metallizing agent is fairly obvious in view of the highly conductive property of this metal.

One of the best modes of procedure is carried out as follows, and is particularly applicable to gelatine moulds for electrotypes, vegetable and organic substances, such as grass, leaves, flowers, fruit, lace or cotton fabrics, etc.

The surfaces to be treated should first of all be thoroughly washed with alcohol or benzene to remove all dirt and greasy matter, then sprayed with fine jets of water, especially in all recesses or undercut portions, and the excess water drained off. Then while the surface is just damp, carefully pour, over every part required to be metallized, a saturated alcoholic solution of silver nitrate. This should be previously prepared by dissolving in pure alcohol as much silver nitrate as the liquid will absorb—the solution of the crystals can be assisted by immersing the containing vessel in a hot-water bath. Now set the article aside to drain off and dry, and when quite dry repeat the operation until it is certain that not the smallest portion of the surface has failed to receive the silver solution. The next step is to reduce the silver in the film of solution, so that the silver as the result adheres to the prepared surface, either in the metallic or some other form which shall be electrically conductive. This may be accomplished in two ways, either by treatment with phosphorus or some similar substance which will reduce the silver nitrate to finely divided metallic silver, or by exposing to the fumes of sulphuretted hydrogen * (H_2S), which reduces the nitrate to sulphide of silver, a compound which is a fairly good conductor of electricity.

If the above operations are carefully and completely carried out, the article treated now possesses a surface which will conduct the current and is capable of receiving an electrolytic deposit.

For glass, china, and earthenware, silver is also used as

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* This gas is readily generated by placing on a shallow dish a few small pieces of iron sulphide and covering them with dilute hydrochloric or sulphuric acid. The operation must be performed in a draught cupboard.

a metallizer, but the method of treatment is somewhat different. The articles are first thoroughly cleansed from grease in potash or benzene, then immersed for a short time in a dilute solution of hydrofluoric acid—the containing vessel for this acid must be of gutta-percha, since it will attack and ultimately dissolve glass—rinsed in clean distilled water, momentarily redipped in the acid, rinsed again, and are then ready for the silver treatment.

For this purpose two solutions are necessary:—

(1) Dissolve 90 grams of sugar candy in distilled water, add 4 c.c. of nitric acid of a specific gravity of 1·22, and 175 c.c. of alcohol. Make up the bulk to 1 litre by adding distilled water.

(2) Dissolve 1·8 grams silver nitrate in 180 c.c. distilled water, add ammonia drop by drop until the precipitate which forms is *nearly* redissolved, then add 0·9 gram potassium hydroxide (KOH) dissolved in a little water, and again *nearly* redissolve the precipitate by the addition of a few drops of ammonia.

The article being now ready for immersion, take 10 c.c. of No. 1 solution and 180 c.c. No. 2 solution, mix together, and *immediately* immerse the whole surface to be silvered. The amount of the two solutions must of course be increased proportionately if the articles are too large for this quantity of liquid. The result of the operation is that a film of metallic silver is thrown down by the reaction of the organic compound in No. 1 solution with the silver salts n No. 2. The preliminary treatment in hydrofluoric acid having slightly roughened the surface of the prepared article, this film of silver is quite adhesive and forms an efficient conducting coating, on which a further deposit may be built up electrolytically.

It should be observed that it is advisable to line the containing vessel for the above operation with a thin coating of white wax, or some similar substance, to prevent as far as possible deposition of the silver on this vessel as well as on the article immersed.

Q. Marino has recently taken out several patents for the metallization of glass and china and similar surfaces preparatory to electroplating, the novel feature of which is principally the use of a mixture of cuprous oxide and silver nitrate as the metallizing solution. A brief description of this inventor's method is given in the following.

The surfaces to be treated are first rendered slightly rough or given a "matte" by dipping in hydrofluoric acid or by sandblasting. A cold solution is prepared by introducing cuprous oxide into a solution of nitrate of silver whereby is formed a grey substance consisting of nitra-tetra-cuprate of silver; this substance is dissolved in hydrofluoric acid and applied to the surface of the article to be metallized by means of a brush. While the surface is still wet, an intimate mixture of finely divided copper and zinc powder or copper with some more electro-positive metal is dusted over the damp surface.

In this way the silver-copper compound is reduced by electro-chemical action to the metallic form, and the surface of the article thus rendered conductive. The inventor however prefers to rub this conducting film briskly when dry with a brush until it presents a polished and uniform appearance, thereby facilitating the passage of the current.

Instead of silver, or, as in the foregoing paragraph, silver-copper, copper alone may be used as a conducting film, as described by F. D. Chattaway, F.R.S., in a paper read before the Royal Society (Nov. 21, 1907), from which the following is abstracted. The method is based on the discovery of a reagent for the precipitation of copper in a thin reflecting metallic film in the same manner as silver may be thrown down by organic and some other compounds. The reagent found to be successful with copper is phenylhydrazine.

The following procedure, which resembles that employed in silvering glass, gives a uniformly excellent result. Heat a mixture of one part of freshly distilled phenylhydrazine and two parts of water till a clear solution is obtained. To this add about half its bulk of a warm saturated solution of cupric hydroxide in strong ammonia. Add next a hot 10 per cent. solution of potassium hydroxide (KOH) until a slight permanent precipitate of cuprous hydroxide is produced. The prepared glass or china surface should now be immersed and the liquid, which should be colourless or pale yellow, heated cautiously, when a fine thin coherent, perfectly reflecting lamina of metallic copper will be deposited. The article should be left in contact with the solution for an hour or so before removal; it should then be washed with distilled water and transferred to the electrolytic bath for further deposition.

(*b*) Articles principally treated by mechanical methods are mainly of gutta-percha, vulcanite, wood, and similar substances. The former are generally washed with alcohol and benzene, sprayed with clean water, dried, then thoroughly brushed over either with fine plumbago powder or with an intimate mixture of 2 parts by weight of plumbago and 1 part of tin powder. Occasionally finely divided silver is used in place of tin. The brushing must be very thoroughly done, and continued until the whole surface has a smooth metallic lustre.

Wood should be made thoroughly smooth and cleansed by rubbing well with methylated spirit. A thin slow-drying varnish (copal varnish) should now be applied to every part of the surface to be plated, and, after drying, a second coat. When the last coating is not quite dry, but in the condition technically known as "tacky," fine copper bronze powder should be thinly spread over the varnished surface and thoroughly brushed until a smooth coherent metallic film is obtained. The bronze powder should be repeatedly applied until it is certain that every part is covered.

A very reliable method of varnishing is first to prepare a thin varnish by dissolving ½ ounce of orange shellac in 1 imperial pint of denatured alcohol (or 12·5 gr. in 500 c.c.). Give the wood one or two coats of this, and afterwards a coating of copal varnish, brushing on the metallic powder before the latter is quite dry.

The principal difficulty in plating wood is that the surface is apt to contain pin-holes. This can only be overcome by care and thoroughness in the bronze powder treatment.

P. Marino has recently taken out a patent (Pat. No. 20,012, Sept. 1911) for the preparation of wood, gypsum, paper, etc., for electrolytic deposition, of which the following is a summary. The article is coated with a solution of an alkali silicate, allowed to dry, then painted with a solution of 60 parts silver chloride, and 100 parts of ammonium fluoride in a saturated solution of potassium cyanide. It is then treated with a saturated solution of 100 parts of hydrazine sulphate and 60 parts of sodium hydroxide. The effect of the latter treatment is to reduce the silver contained in the silver solution to the metallic form, the article being as a consequence covered with a thin film of finely divided metallic silver. The film thus produced is made into a coherent deposit by friction such as vigorous brushing.

It will be noted that the principle of the foregoing method is also based on the reduction of a silver salt by means of an organic reagent, the novelty of the process lying almost entirely in the particular reagent chosen.

"Wiring" Articles for Plating.—This is a matter of some considerable importance to electroplaters. Some very unsatisfactory specimens of electroplating have in our experience been traceable to bad electrical contact during immersion in the plating vat. Objectionable marks are also often observed in the finished article through carelessness in this respect.

The variety and divergences of size of the goods dealt with make it impossible to give detailed directions to meet all requirements; but a few general principles may be laid down.

(1) It is *generally* advisable to use copper wire of various gauges for this purpose. Copper is not only a very good conductor of electricity but is very malleable and ductile

and can be bent and twisted into almost any shape required without breaking. In the case of wire which has once been used, particularly when it has received a deposit of another metal and been afterwards stripped, it should be well annealed; otherwise annoyance will be caused through its becoming brittle.

(2) It is the best practice to make as many contacts for the cathode rod as is reasonably possible. An article of any appreciable size is not as a rule satisfactorily plated, that is, with an equal distribution of current, with only one contact wire. For example, a tea or coffee pot should have at least three points of contact: one, say, at the bottom of the handle or socket, another wire passed down the spout, then upward through the cover opening and secured outside; and the third point of contact, either by a separate wire or connection to the first, to the cover. The attachment of the cover to the body of the pot by means of the joint is often an unsatisfactory one from the electrical point of view. With wires thus arranged the whole article is in good electrical contact when hung from the cathode rod. Obviously the method of wiring must vary according to the shape of the article, but the foregoing will serve to illustrate the principle.

(3) On flat ware and plain surfaces where points of contact are likely to show marks, the wires must be carefully moved from time to time during deposition, especially when thick deposits are being given.

In many cases copper or brass springs, hooks, skeleton frames, or racks for small work are in use, but advantage is now generally taken of plating barrels and other mechanical arrangements for small work which is to be plated in large quantities. Details of these are given in the catalogues of dealers in platers' supplies.

CHAPTER IX

DEPOSITION OF SILVER

THIS is probably the most important branch of the electroplater's art, not only from the widespread nature of the applications of silver deposition, but also from the beauty and perfection of results now obtainable and the intrinsic value of the metal itself.

Properties of Silver.—Silver is a beautifully white metal capable of taking a brilliant polish. It is very malleable and ductile, being excelled in this respect only by gold, than which however it is harder and more tenacious. It is unaffected by oxygen at ordinary temperatures, but when exposed to air, especially that of towns, it becomes discoloured by means of the small traces of sulphuretted hydrogen which are ordinarily found in the atmosphere, silver being extremely susceptible to the action of sulphur compounds. It is readily dissolved by nitric acid and more slowly by hot concentrated sulphuric acid, but it is scarcely acted upon by hydrochloric acid at any temperature. Silver excels all other metals in its power of conducting heat and electricity, and is also the most generally useful of all metals as a protective coating for metallic articles of domestic use owing to its non-liability to attack by organic substances such as fruit and vegetable juices.

Solution for Deposition.—The solution now invariably used for electro silverplating is that of the double cyanide of silver and potassium in water (formula, $KAg(CN)_2$), though for its electro-deposition in refining operations a simple solution of silver nitrate ($AgNO_3$) in water is used.

Materials Used—Quality and Tests.—Before describing in detail the methods of making an electro-silver-plating bath it will be advisable to deal with the important question of the materials used, particularly that of **cyanide of potassium.** This substance is of very great importance to the electroplater, entering as it does into the composition of so many of the solutions with which he has continually to deal. Many attempts have been made to replace it by some other reagent less poisonous and offensive in general properties, but up to the present without success. It is still unrivalled as the principal chemical reagent in the practice of electroplating. The question of its purity or otherwise assumes therefore first-rate importance.

Commercial Cyanide of Potassium is usually obtained as fused cakes or blocks. In its purest form it is colourless or nearly so, but the ordinary product is greyish white. It has a characteristic smell, closely resembling that of bitter almonds. It is perfectly soluble in water, giving an alkaline reaction, and very slightly soluble in absolute alcohol. It is deliquescent and decomposes rapidly when exposed to the atmosphere into potassium hydroxide, potassium carbonate, and ammonia. It also decomposes to some extent if dissolved in *hot* water; in making solutions of potassium cyanide therefore *cold* water should invariably be used. In its decomposition hydrocyanic acid gas (HCN) is also slowly given off, and as this is extremely poisonous care should be observed not to inhale deeply when using cyanides. It should be stored in a dry, cool place in air-tight cannisters or jars.

For use by the electroplater, potassium cyanide is commonly prepared by fusing together in an iron vessel yellow prussiate of potash, more correctly named potassium ferrocyanide, having the formula $K_4FeC_6N_6 . 3H_2O$, and potassium carbonate (K_2CO_3). The reaction of these substances in fused mass results in the formation of potassium cyanide (KCN), potassium cyanate (KCNO), carbonic acid gas (CO_2), and metallic iron (Fe), the latter being deposited.

In actual manufacture steps are usually taken to de-oxidize the potassium cyanate formed, so as to obtain a higher percentage of pure KCN.

The practical details of the process of the manufacture of cyanide are as follows: About 25 lbs. of the prussiate of potash, which has been previously finely ground and dried at or just over the temperature of boiling water (100° C.), are melted together with 8 lbs. of potassium carbonate in a sufficiently large iron pan fitted into a coke-fired furnace having a good draught, and so arranged that the heat reaches every part of the pan as evenly as possible. In the bottom of the pan a taper hole is bored, through which is inserted an iron rod whose upper end is shaped into a ring for convenience of extracting. After the charge is placed in the pan it is covered over to exclude the atmosphere, and the heat applied. In a short time, depending on the temperature, the greenish colour of the melt changes to a porcelain white (the colour is judged by removing a small portion and allowing it to solidify); then a further 39 lbs. of the prussiate salt are weighed out and added in quantities of about 4 lbs. at a time, waiting until the green colour given by one addition is discharged before adding another lot. When the final addition has been made and the colour of the melt is to the liking of the operator, the pan is removed from the furnace, the taper rod withdrawn, and the molten contents allowed to run into the casting pan in the form of cakes or slabs. Care must be observed in running the material that as little as possible of the finely divided iron is carried out by the stream of molten cyanide. Immediately the substance has solidified, it is broken up and packed in air-tight jars or tins.

Owing to its extreme liability to decompose both in the molten and solid state, it is almost impossible to obtain an average quality of over 96 per cent., but if the operation has been carefully carried out the percentage of purity should in no case be below 92. It will be evident however that the purity of the final product is largely dependent on the purity of the original materials used, as well as on the efficiency of the methods adopted for deoxidizing the cyanate of potassium which, as has previously been stated, is always formed. On this latter point a good deal of uncertainty exists, some of the methods employed, such as adding small quantities of finely divided metallic tin, being of very doubtful efficiency.

Other methods * for the manufacture of potassium cyanide are:—

(1) To heat the completely dehydrated ferrocyanide with metallic sodium, thus obtaining a cyanide of higher strength, consisting of a mixture of potassium and sodium cyanides:—

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe.$$

Such a product is known commercially as "double salt cyanide."

(2) Beilby's process, in which a fused mixture of potassium carbonate and charcoal is treated with ammonia, the product being a very pure molten cyanide which is filtered from the small amount of insoluble matter present and is then cast into moulds yielding crystalline cakes of pure white cyanide.

The following are the principal impurities found on analysis in commercial potassium cyanide, and usually some, if not all, are present in the purest specimens of the salt, viz. potassium cyanate, potassium thiocyanate, potassium ferrocyanide, potassium sulphate, potassium sulphide, potassium carbonate, potassium silicate, potassium formate, and the corresponding sodium salts, and often in addition calcium and aluminium compounds. None of these impurities are of any value to the electroplater, and some are very deleterious. If however the sample used is found to contain from 92 to 95 per cent. of pure KCN, then the total amount of impurities present is sufficiently low to be disregarded. It is, therefore, essential for good work that the percentage composition of commercial potassium cyanide be

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* See Roscoe and Schorlemmers' *Treatise on Chemistry*, vol. ii., "The Metals," pp. 352–3.

determined before it is used for making up an electro-silver-plating solution.

The assay of cyanide of potassium.—A thoroughly reliable method of assaying a sample of commercial cyanide to ascertain the percentage of pure potassium cyanide present, known as Liebig's method, is outlined in the following *:—

The theory of the method depends on the fact that when a solution of potassium cyanide is added to one of silver nitrate, the first reaction which ensues is the formation of silver cyanide according to the following equation:—

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

This occurs in the proportion of their respective molecular weights, viz.

$$AgNO_3\ (\mathbf{170}) \propto KCN\ (\mathbf{65}).$$

If however the addition of potassium cyanide is continued after the precipitation of the whole of the silver, a second reaction begins and the silver cyanide which is quite insoluble in water is slowly re-dissolved in the excess potassium cyanide until the whole of it is held in solution, this further action being

$$AgCN + KCN = KAg(CN)_2.$$

These reactions, upon which a silver-plating solution itself depends, will be more fully explained later. It will be evident however, from a study of the foregoing, that if a few drops of silver nitrate solution *are added to* a solution of potassium cyanide, a precipitate results which at the very moment of formation re-dissolves in the excess of potassium cyanide present, and that this will occur on further additions of silver nitrate until the whole of the pure cyanide present has been taken up. On this principle depends the method which will now be given for the assay of cyanide of potassium for the percentage of real cyanide.

The apparatus required is a fairly delicate assay balance,

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* Extracted from a pamphlet on *The Assay of Commercial Cyanide of Potassium*, by A. H. Allen, late Public Analyst of Sheffield.

one turning to one milligram or less, preferably 0·01 mg. (gram weights should be used), a 100 c.c. burette and stand (see Fig. 53), and a flask holding 500 c.c.

The sample of cyanide, which should weigh not less than 3 to 4 ounces (say 100 grams), and be a fair representation of the bulk, is first of all thoroughly powdered in a mortar, and if the assay cannot be immediately proceeded with, it must be transferred to a perfectly dry air-tight bottle or at least kept as completely as possible from exposure to the atmosphere. Now by means of the assay balance weigh out with extreme care 6·5 grams of the powdered cyanide—if the balance is not provided with glass pans a watch-glass must be counterpoised and the cyanide placed in this, as it must not be allowed to come into contact with a metal pan. Carefully transfer the weighed powder to the 500-c.c. flask by means of a glass funnel placed in the mouth of the flask. With a small quantity of distilled water now wash every particle of the powder into the flask and add a further quantity of water sufficient to dissolve it completely. When the solution of the powdered cyanide is complete—but not before—fill up the flask with distilled water, carefully observing to fill up just to the mark indicating 500 c.c. on the neck of the flask. During the filling of the flask the contents must be thoroughly shaken or stirred in order to ensure a solution of equal strength throughout. In a similar manner a standard solution of silver nitrate must now be made, by weighing out exactly 8·5 grams of pure re-crystallized silver nitrate, dissolving in distilled water and diluting to 500 c.c. of solution just as described for the standard cyanide solution.

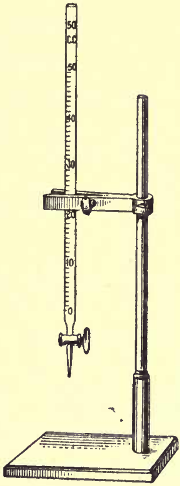

Fig. 53.—Burette and Stand.

The molecular weight of $AgNO_3$ being 170 and of KCN 65, it will be noted that the weighed amounts of both the potassium and the silver salts bear a simple ratio to their molecular weights :—

$$AgNO_3 + 2KCN = KAg(CN)_2 + KNO_3$$

$$\therefore 170(AgNO_3) \propto 130(KCN)$$

$$\text{or} \quad 17 \propto 13$$

$$\text{or} \quad 8{\cdot}5 \propto 6{\cdot}5.$$

The next step is to remove from the solution of cyanide any impurities which would interfere with the clearness of the reaction between silver nitrate and potassium cyanide solutions. Fortunately only one of the impurities previously mentioned has any effect in this direction, namely potassium sulphide, and since this is readily removed it is always advisable to assume its presence and proceed accordingly. Take a small quantity of pure white lead (lead carbonate) in fine powder, about as much as would cover a sixpence, insert this powder into the flask containing the cyanide solution and thoroughly agitate the liquid ; this will effect the conversion of potassium sulphide, if present, into the black insoluble sulphide of lead, which will thus be precipitated and may subsequently be filtered off. If no black precipitate appears, the sample may be considered free from sulphides and the filtering process of course omitted. The presence of the slight amount of white lead will not in the least interfere with the remaining processes.

The actual estimation may now be proceeded with by measuring out exactly 100 c.c. from each of the two standard solutions. The silver solution is measured by pouring it into the burette, just filling to a little above the zero mark, and taking care also that the jet below the top is quite filled and free from air-bubbles; the tap at the bottom is then turned, a few drops allowed to escape, and the level of the liquid thus brought exactly to zero. The cyanide solution may be measured by means of a 100-c.c. pipette and then poured into a small conical flask, the pipette being rinsed out with a little water which is afterwards added to the solution in the flask. This flask, containing the cyanide, is then brought under the tap of the burette, and the silver solution allowed to drop into it very slowly. It will be now observed that as each drop of silver solution enters the cyanide a slight milkiness is produced, which however immediately disappears on shaking or stirring with a glass rod. As the addition of silver solution continues, this milkiness disappears with greater difficulty until towards the end of the reaction vigorous stirring is required to clarify the liquid. This is an indication that the cyanide is nearly exhausted. The silver nitrate must now be added only one drop at a time, and at the moment when a permanent milkiness is produced it must be stopped. A little practice is necessary to determine this point exactly, but a careful worker will have little difficulty in the operation. It is advantageous to place a disc of black paper under the flask.

The point at which the solution in the burette now stands must be carefully read off, and will indicate directly without further calculation the percentage of real cyanide in the sample. Thus supposing it is observed that exactly 90 c.c. of silver solution have been added, then the sample tested is of 90 per cent. purity. It is advisable however to repeat the experiment at least twice, and if any divergence of results is observed the process should be repeated until two readings are obtained with not more than 1 per cent. difference. With careful attention to details a much closer agreement can be obtained.

The quantitative meaning of the process will be made clear by a further consideration of the equation given above.

$$\underset{170}{AgNO_3} + \underset{2(65)}{2KCN} = KAg(CN)_2 \text{ (a soluble compound)} + KNO$$

relative weights

Therefore 170 $AgNO_3$ corresponds to 130 KCN
and 1·7 ,, ,, ,, 1·3 ,,

In the standard solutions used in the above operations it will be noted that 100 c.c. of silver nitrate solution contain 1·7 grams $AgNO_3$ and 100 c.c. of potassium cyanide solution should contain 1·3 grams KCN if it were pure.

If then the cyanide solution is of 100 per cent. purity the two solutions will be chemically equivalent, and 100 c.c. of silver solution will be required to combine with 100 c.c. of KCN solution exactly. The lesser number which the latter amount actually does require is consequently the measure of its percentage purity.

It must however be pointed out that the figures and calculations of the foregoing method of assay of potassium cyanide are all based upon the assumption that the salt under examination is potassium and *not* sodium cyanide. If the latter is present in any appreciable quantity, the results of the assay will be high, owing to the fact that the atomic weight of sodium is only 23 compared with potassium 39. Under these circumstances the results of an assay may show a strength of cyanide over 100 per cent. Such a result is still of value, in making up a plating solution, as an indication of the proportion of CN in a specific amount of the salt. On the other hand, however, it is no criterion of the amount of impurity present. If the sample under test is presumably sodium cyanide alone the amount taken for the standard solution for testing must correspond to the molecular weight of NaCN (49) instead of KCN (65).

Silver, "Standard" and "Fine."—With regard to the only other essential constituent of a silver-plating bath, viz. silver, little need be said further than that it is always advisable to use "fine" silver which is practically of 100 per cent. purity in preference to the ordinary "standard" silver which is only 92½ per cent. pure. The plating solution may be made either from sheet silver by electro-chemical processes or from grain silver or a salt of silver by chemical methods. Where the latter methods are used and grain silver is employed, the silver is first converted into silver nitrate by dissolving in dilute nitric acid, and here it will be advisable to point out that at present silver nitrate of the highest possible purity may be purchased at a price only very slightly higher than the market price of the actual content of silver in the salt. Many operators therefore prefer to buy silver nitrate rather than metallic silver, and thus save the considerable amount of labour and possible loss incurred in conversion. This course is strongly advised by the present writers.

The amount of silver in silver nitrate is as 108 is to 170, thus $\frac{170}{108} = 1{\cdot}574$ ounces of silver nitrate contain 1 ounce of silver.

Tests for silver.—The following rough tests which may readily be performed in the workshop will be found interesting and useful.

1. Dissolve a small fragment of the metal to be tested in dilute nitric acid. Add a few drops of dilute hydrochloric acid or of a solution of common salt; a curdy white precipitate of silver chloride is instantly formed. To confirm, add a little strong ammonia and shake vigorously: the precipitate is dissolved. If copper or nickel is present, the nitric acid solution will be blue in colour, which the addition of ammonia will intensify.

2. A very convenient and approximately reliable method of distinguishing between "standard" and "fine" silver depends upon the fact that when alloys of silver and copper are heated over a Bunsen flame or on a muffle, superficial oxidation and consequent discoloration occur, and by this means some indication may be obtained as to the proportion of copper in certain of these alloys.

The alloy if not already in the form of sheet should be rolled or hammered flat and then *very slightly* heated until discoloration takes place. Too high a temperature must be avoided, since that would give different results.

Table XIII. on the next page gives a classification of the colour changes obtained in various alloys.*

In distinguishing between fine silver and the richer silver alloys the test is quite unmistakable, but the method ceases to be applicable in the case of alloys containing more than 160 parts by weight of copper per 1000 of the alloy.

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* See also J. Percy, *Metallurgy of Silver*, p. 157.

TABLE XIII.

Silver in 1000 *parts of the alloy.*	*Characters of the surface after heating.*
1000 (*i.e.* pure silver)	Dull, but quite white.
950	Uniform grey-white.
925	Dull grey-white, pinkish-black fillet at edges.
900	Dull grey-white, black fillet at edges.
880	Grey, almost black.
860	do.
840	Quite black.

To distinguish silver from other white metals and alloys.—Make up a test solution by dissolving 30 grains of silver nitrate in 1 oz. of distilled water (or 2 grams to 29 grams of water) and add a few drops of nitric acid. A drop or two of this solution when placed on base metals such as German silver and other white alloys instantly gives a brown or black stain due to the precipitation of the silver in solution. The surface of the metal must be quite clean or the test will be ineffective. No stain is produced with fine silver or standard silver. Silver alloys containing more copper than standard silver give a faint brown stain which increases in intensity as the proportion of base metal increases.

Another very beautiful and delicate test for the same purpose is made by dissolving in water in a test tube a sufficient quantity of potassium chromate crystals to make a strong or saturated solution. Make this solution fairly acid by adding a drop or two of strong nitric or sulphuric acid. By means of a glass stirring rod, apply one drop of this solution to the *clean* surface of the metal to be tested. If the metal is fine or standard silver a bright red stain (silver chromate) will be instantly produced. Other metals and alloys give either a very faint dirty coloration or none at all.

This test is extremely useful for distinguishing between silver and nickel deposits—sometimes rather a difficult task without some such acid.

Test for silver nitrate.—If silver nitrate is used, the following is a good method of testing its purity. Dissolve one gram of the salt in 30 c.c. of distilled water, and add 1 c.c. of pure hydrochloric acid. Heat to boiling point and filter off the precipitate, which will contain the whole of the silver contents (as AgCl). Then evaporate the remaining liquid, the filtrate, to dryness. If the sample tested is perfectly pure, there will be no residue or at most one weighing less than half a milligram.

Methods of preparing Depositing Solutions.—The methods of preparing silver-plating solutions may, as previously indicated, be described under two heads. (A) Electrolytic Methods. (B) Chemical Methods. Very many different formulæ have been published under both these headings, but only those will be described here whose value has been tested thoroughly in actual practice.

(A) *Electrolytic Methods.*—These methods, though quite applicable to many metals other than silver, have been far more largely applied to the preparation of silver-depositing solutions than to those for the deposition of any other metal. This is doubtless due in great measure to the fact that there is no possibility of loss of metal in the actual making of the solution by these methods.

The principle involved may be explained thus. When two electrodes are placed in an *electrolyte* and a current is passed through it, the anode, if a soluble one, is always attacked and dissolved. Consequently the electrolyte gradually acquires a considerable metallic content due entirely to the solvent action of the products of electrolytic decomposition at the surface of the anode. In this way an electrolyte which originally contained none of the metal of which the anode is composed may become so thoroughly charged with this metal as to form a solution from which it may be readily deposited.

The actual method of preparation is as follows: Suppose that it is desired to prepare 100 imperial (120 U.S.) gallons of solution. To form the electrolyte dissolve in a sufficiency of cold water 500 ozs. of potassium cyanide of not less than 95 per cent. purity. When the whole of the cyanide is dissolved, pass the resulting solution through a strong calico filter of fine mesh. The best method of making and using such a filter is to obtain a square wooden frame of the same inside measurement as the vat in which it is proposed to make and use the solution. Fasten by means of strong tacks two thicknesses of strong calico so as to stretch across the frame, then filter the cyanide solution directly into the vat. When filtered make the solution up to the required

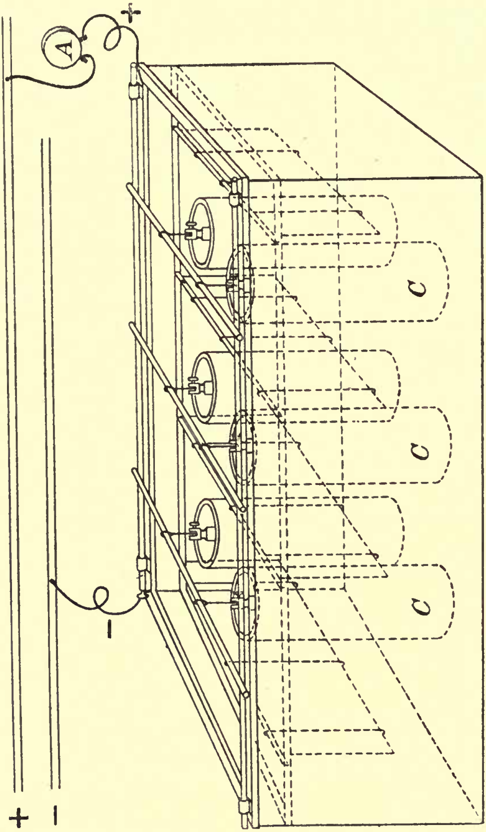

FIG. 54.—Electrolytic method of preparing silver-depositing solution.

bulk, 100 imperial gallons, by adding clean cold water, preferably distilled water. Then arrange the vat for electrolysis as shown in Fig. 54.

The anodes are of course fine silver, and should be arranged along the vat at intervals of about 12 ins. as illustrated; they should be rolled to as large an area as the size of the vat will allow so as to obtain the greatest possible efficiency in electro-chemical action at the anode surfaces. On the other hand, the cathodes which may consist of copper, German silver, or iron sheet, must be small enough to be contained in the porous cells (C) (Fig. 54). The liquid in these cells should be potassium cyanide solution of similar strength to that contained in the vat itself. The electrical connections are made as shown in the diagram, an ammeter (A) being placed in the circuits in order to enable the plater to form an idea of the progress of the operation. When the connections are completed, current is allowed to pass through the vat and continued until 200 ozs. (Troy) of silver have been dissolved. This may be ascertained both from the ammeter readings and by weighing the anodes before and after electrolysis.

The action taking place on the passage of the current may be briefly and simply described as follows:—

The electrolyte contains potassium (K) and cyanogen (CN) ions, forming respectively cations and anions. On electrolysis therefore potassium ions are liberated at the cathode. Immediately on liberation, however, potassium attacks the water present, forming potassium hydroxide and setting free hydrogen, thus:

$$2K + 2H_2O = 2KHO + H_2.$$

The products of electrolysis at the cathodes are therefore potassium hydroxide or caustic potash (KHO) and hydrogen gas (H_2), and as these are enclosed in the porous cell (C, C), they are to some extent at least prevented from diffusing through the bulk of the electrolyte.

On the other hand, the anion liberated at the anode is cyanogen (CN), which immediately combines with the metal constituting the anode, forming silver cyanide (AgCN). This compound is insoluble in water, but readily soluble in potassium cyanide; so long therefore as the electrolyte contains a considerable excess of uncombined potassium cyanide, this anode product is immediately dissolved to form the double cyanide of silver and potassium [$KAg(CN)_2$], which of course constitutes the required depositing solution.

The complete reaction taking place may be thus expressed:—

$$2Ag + 4KCN + 2H_2O = 2KAg(CN)_2 + 2KHO + H_2$$

It will be obvious therefore that the resulting bath contains a considerable proportion of potassium hydroxide, even if the liquid in the porous cell is thrown away. As the solution is worked however this is speedily converted, by the action of the atmosphere and by other secondary actions, into potassium carbonate.

The advantages of this method of making silver-plating solutions are mainly:—

1. The avoidance of risk of loss of silver.

2. Its comparative simplicity and the fact that it does not require chemical experience on the part of the operator.

The method has however several disadvantages which claim consideration, viz.:—

1. It is more costly than chemical methods in that it necessitates the expenditure of a considerable amount of electrical energy.

(This point assumes great importance where large quantities of solution are concerned.)

2. The composition of the bath is not under such exact control as is desirable, particularly in regard to the proportion of free cyanide present.

(B) *Chemical Methods.*—SOLUTION I.—The first solution to be described under this heading and one of the most widely used is made up from the following formula:—

For 100 gallons of solution :—

Fine silver	200 ozs. (Troy)	6·85 kg.
Or silver nitrate[*]	315 ,, ,,	10·8 ,,
Potassium cyanide	Q.S.[†]	
Water	100 imp. galls. or 120 U.S. ,,	500 litres

If metallic silver is used it should be in the form of grain and must be converted into silver nitrate as follows :—Place the silver in a sufficiently large acid-proof jar, preferably of porcelain or earthenware. Arrangements must be made to heat this by means of a water bath so as to obtain a temperature nearly equal to boiling water. Pour on to the silver pure nitric acid which has previously been diluted to twice its bulk with distilled water. As the solution becomes warm, a violent chemical action sets in and dense brown fumes of nitrogen peroxide are evolved with the formation of silver nitrate. The resulting reaction is

$$6Ag + 8HNO_3 = 6AgNO_3 + 2NO + 4H_2O.$$

The amount of nitric acid required may be readily calculated[‡] from this equation, if the strength of the acid be known, but it is advisable to add only half the required quantity at first, and when this is exhausted, which will be observed by the cessation of chemical action, the liquid should be poured off and set aside for crystallization, and the second portion of acid added. When the whole of the silver is dissolved, the resulting liquid is poured into a porcelain evaporating dish and heated at about 100° C. until the liquid shows signs of thickening and gives evidence of the formation of crystals on the edge. At this point allow to cool and a quantity of crystals of $AgNO_3$ will be obtained. The remaining liquid

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[*] For convenience, the weight of silver nitrate here and in similar cases is given in troy ozs., but in commerce silver nitrate is sold by the avoirdupois oz., and this must be taken into account when ordering.

[†] Q.S. = a sufficient quantity.

[‡] 200 ozs. of silver require 85 to 90 fluid ozs. of pure concentrated HNO_3 (sp. gr. 1·43).

must be poured off and still further evaporated, and a similar process repeated until the whole is crystallized.

It must however be emphasized that it is not now advisable for electroplaters to attempt the preparation of silver nitrate themselves. This salt is now manufactured on such a large scale and so economically by silver refiners and manufacturing chemists that in the case of any reasonably large quantity (100 ozs. or upwards) it can be purchased for very slightly more than the value of the metallic silver contents; the margin is indeed so small as to scarcely more than cover the cost of the nitric acid required, leaving out all considerations of time and cost of apparatus on the part of the electroplater.

Having now obtained the silver in the form of silver nitrate the operations involved in the making of a silver-plating solution may be summed up under three headings.

(1) The conversion of silver nitrate ($AgNO_3$) into silver cyanide ($AgCN$).

(2) The conversion of silver cyanide ($AgCN$) into the double cyanide ($KAg(CN)_2$).

(3) The addition of a further quantity of KCN to provide free cyanide.

These operations will now be explained seriatim.

(1) *The conversion of silver nitrate into silver cyanide.*—This is done by precipitating the silver from the solution of nitrate in water as silver cyanide by means of a solution of potassium cyanide. The reaction is

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

Now according to this equation one molecule of silver nitrate requires one molecule of potassium cyanide in order to convert it entirely into silver cyanide. If then the two salts are combined in the exact ratio of their molecular weights, the operation will be exactly complete. This point is extremely important, since owing to the fact that silver cyanide is soluble in potassium cyanide there is great risk of loss in the operation (in subsequent washing) by the possibility of adding an excess of cyanide solution over that required for precipitation of silver cyanide only. From the above equation, however, the amount of cyanide required may be exactly calculated and the danger entirely averted. Taking the molecular weight of the two substances, it is observed that 170 parts by weight of silver nitrate require 65 parts of potassium cyanide in order to precipitate the whole of the silver as silver cyanide. In the solution under consideration the weight of the silver nitrate is 315 ozs.; then

$$170 : 65 :: 315 : x$$

x being the weight of pure KCN necessary to convert 315 ozs. of silver nitrate into cyanide.

Calculating out thus,

$$x = \frac{315 \times 65}{170} = 120{\cdot}5 \text{ (nearly).}$$

It must be remembered however that the figure so obtained applies only to potassium cyanide of 100 per cent. purity. As it is impossible for such to be the case, a correction must be made to allow for the percentage of impurities. If the sample in use by the operator has been examined as previously directed, this correction is easily made, for the percentage of purity will be known.

Suppose it to be 95 per cent., then

$$95 : 100 :: 120{\cdot}5 : y$$

y being the actual weight of impure cyanide required.

Calculating out, we have

$$y = \frac{120{\cdot}5 \times 100}{95} = 127 \text{ Troy ozs. (nearly)}$$

(on the metric alternative of p. 187 the amount = 4·35 kg). This weight of potassium cyanide is then dissolved in sufficient cold water and added with vigorous stirring to the silver nitrate which itself has been dissolved in distilled water. In this way the first operation may be conducted with confidence and with little or no loss of silver. When precipitation is complete the precipitate is allowed to settle, and the top liquid, which it will be noted is simple potassium nitrate (KNO_3), is carefully syphoned off and set aside for recovery of the small trace of silver which may possibly be present. The precipitate is then thoroughly washed by pouring in clean hot water, stirring vigorously, and allowing to settle and then syphoning off. The washing should be repeated two or three times in order to get rid of all traces of the original liquid and leave nothing but the pure silver cyanide and a little water.

The next step is—

(2) *The conversion of silver cyanide* ($AgCN$) *into the double cyanide of silver and potassium,* $KAg(CN)_2$. For this purpose weigh out a further quantity of potassium cyanide of about 250 ozs. (say 7 kg.). Dissolve this in cold water so as to form a solution containing from 10 to 15 ozs. per gallon (68·5 to 103 grams per litre), and add slowly with constant stirring to the silver cyanide precipitate until it is just dissolved. Some little difficulty is sometimes found in determining this point owing to the fact that usually a certain quantity of insoluble matter is formed, due to impurities in the cyanide. A short experience will however enable the operator to judge when the solution is complete, and if by any chance some particles of silver cyanide remain undissolved at this stage they will be brought completely into solution in the next stage.

The final step is—

(3) *The addition of a quantity of potassium cyanide to form "Free Cyanide."* The exact amount of "free cyanide" required in a silver-plating solution is a point upon which expert opinion is still very undecided, and the matter will be further discussed later in the present chapter. In making a new solution however the safest rule is to add as free cyanide an amount of potassium cyanide *equal to that used to precipitate the silver in stage* (1).

In the particular instance now under illustration therefore 127 ozs. (Troy) of potassium cyanide must be added to the solution obtained at the end of stage (2).

The solution must now be filtered and afterwards made up to the required bulk, 100 imp. gallons, by the addition of water. Advantage should be taken of this addition of water to wash the filter through in order to carry into the vat any soluble matter which may be held in the deposited substances on the filter. The solution is then ready for use.

Solution II.—The solution now to be described was introduced by one of the authors a few years ago and is one which has been tried on a very large scale commercially with excellent results.

The formula is as follows :—

Silver nitrate	315 ozs. (Troy)	10·8 kg.
Pure anhydrous sodium carbonate	8 lbs. (av.)	4 „
Potassium cyanide	Q.S.	
Water	100 imp. galls. or 120 U.S. „	500 litres

The silver nitrate is dissolved in about 15 imp. gallons, (75 litres) of distilled or filtered rain-water and the sodium carbonate in a similar quantity in a separate vessel. When both salts are completely dissolved, the two solutions are added together and vigorously stirred. The resulting reaction is the precipitation of the whole of the silver as silver carbonate (Ag_2CO_3). The precipitate after some continuous stirring is allowed to settle, the top liquid poured off and then thoroughly washed in the manner directed in Solution I. After the last washings have been poured off, with as little loss of time as possible since the precipitate is very susceptible to the action of light and air, a solution of potassium cyanide is added slowly with stirring until the whole of the silver carbonate is dissolved.

A similar difficulty with regard to the presence of impurities in the cyanide will be observed as in the case of the dissolving of silver cyanide in potassium cyanide, but these insoluble impurities do not interfere with the reactions, and by close observation the operator will learn to distinguish the point at which complete solution is attained.

A similar weight of potassium cyanide must be added as free cyanide as in Solution I., viz. 127 ozs. (Troy), or 4·35 kg. on the metric alternative.

The solution is then filtered and water added to bring up the bulk to 100 imp. gallons (or 500 litres).

So far as simplicity in making is concerned, this solution has obvious advantages over No. I., and, as already observed, it has proved a very satisfactory solution in actual workshop practice. From a theoretical point of view an objection can be urged that a bath so made must contain a considerable quantity of potassium carbonate, as is indeed evident from the chemical reactions involved which are these—

$$(1)\ 2AgNO_3 + Na_2CO_3 = Ag_2CO_3 + 2NaNO_3$$
(washed away).

$$(2)\ Ag_2CO_3 + 4KCN = 2KAg(CN)_2 + K_2CO_3$$
(retained in bath).

The presence of potassium carbonate however in a silver-plating solution is not at all an objectionable feature. Indeed, all commercial silver-plating baths contain large proportions of this salt, particularly those which have been in use a number of years, and in the course of a long experience in the electro-deposition of silver we have observed that these old solutions (in use 25 years and upwards) give results in rapidity of working and quality of deposit which certainly cannot be obtained from freshly-made solutions prepared in the usual manner, in spite of the fact that the latter are made from cyanide of potassium of a much higher degree of purity than was obtainable a generation ago, and it is at least interesting and suggestive that the only notable difference which can be found after most exhaustive examinations is in the relatively far larger content of potassium carbonate that is possessed by the older solutions. In this connection the following typical analyses of old silver-plating liquids may be found interesting:—

Contents.	*Solution I.* *in use approx.* 30 *years.* *Ounces per gallon.*	*Solution II.* *in use approx.* 10 *years.* *Ounces per gallon.*
Metallic silver	3·15	3·48
,, copper	0·50	0·17
Double cyanide of silver and potassium (estimated as $KAg(CN)_2$)	5·80	6·42
Double cyanide of copper and potassium (estimated as $KCu(CN)_2$)	1·21	0·41
Potassium cyanate, KCNO	0·35	0·30
,, carbonate, K_2CO_3	13·05	11·49
,, sulphate, K_2SO_4	0·16	0·23
,, chloride, KCl	0·17	nil
,, cyanide, KCN (free)	2·17	1·43

It will be noted that the content of potassium carbonate in solution is in both instances extremely high, and in the case of the older liquid more than double that of the most important constituent ($KAg(CN)_2$). Both these solutions, it may be remarked, are in daily use and give completely satisfactory results.

It must be pointed out, however, that in all probability nothing like these proportions of potassium carbonate were present originally, the baths having acquired them in process of working by the reactions of electrolysis and exposure to the atmosphere. Evidently, however, this substance is not deleterious, and as the solution described in the foregoing (No. II.) approximates very closely to an old solution in its working properties even when freshly made, it is reasonable to suppose that this may be due at least in some measure to the presence of the potassium carbonate acquired in making. In all probability the latter acts as a conducting salt.

It occasionally happens—generally owing to the constant use of an excessive proportion of free cyanide in a silver vat—that in the course of years the amount of potassium carbonate present becomes so great as to render the solution very dense, and as a consequence sluggish and unworkable. (This is explained by the tendency of potassium cyanide, on exposure to the atmosphere, to become converted into potassium carbonate. Obviously, therefore, the more cyanide used, the greater the quantity of the latter formed.)

When this is the case, the difficulty may be overcome by adding to the bath a few pounds of barium cyanide dissolved in water. The resulting action is the precipitation of a proportionate quantity of potassium carbonate as barium carbonate and a corresponding formation of potassium cyanide, thus—

$$Ba(CN)_2 + K_2CO_3 = \underset{\text{(insoluble pptate.)}}{BaCO_3} + 2KCN$$

This treatment, which is really the conversion of the excess potassium carbonate into potassium cyanide, should be continued until the bath is restored to a satisfactory working condition.

Solution III.—The third solution to be described under the head of chemical methods is one very largely used in the United States. It is—

Silver nitrate . . .	315 ozs. (Troy)	10·8 kg.
Hydrochloric acid.	Q.S.	
Potassium cyanide	Q.S.	
Water	100 imp. galls. or 120 U.S. ,,	500 litres

The mode of preparing this solution is very similar to that described in the case of Solution II. The silver is precipitated from a solution of the silver nitrate in water, by means of hydrochloric acid, as silver chloride, thus—

$$AgNO_3 + HCl = AgCl + HNO_3$$

The silver nitrate is weighed out and dissolved in about ten to fifteen gallons of distilled or filtered rain water, and hydrochloric acid diluted by the addition of an equal bulk of water is added carefully until no further precipitate is produced. It is advisable to stir the solution vigorously from time to time during precipitation; when this is complete allow it to settle, and test the clear liquid by adding a further few drops of HCl to determine whether the whole of the silver is precipitated. The top liquid is then carefully syphoned off, and the silver chloride thoroughly washed by means of clean hot water.

A solution of potassium cyanide, prepared by dissolving from 200 to 250 Troy ounces in about 20 gallons of water (say, 6·85 to 8·55 kg. in 100 litres), is then added to the washed silver chloride until the whole of it is dissolved. (The same remarks in reference to impurities apply at this point as in the case of Solutions I. and II.)

The amount of free cyanide added in the case of this solution is usually rather larger than in the former solutions described, and varies from 150 to 170 ozs. Troy, according to the percentage of the cyanide used. When this addition has been made the liquid is then filtered in the usual way, and the bulk made up to 100 imp. gallons (or 500 litres) by the addition of water, which is also passed through the filter in order thoroughly to wash it.

General Remarks on making Silver Solutions.—It will have been observed that in giving the details of all the solutions described under the heading of "Chemical Methods," the exact amounts of potassium cyanide required for dissolving the respective silver salts—cyanide, carbonate, and chloride—have not been stated, but have been left to the operator to determine by actual experiment in making the solution itself. The reason for this is that this amount is variable, and in practice is never exactly that required by theory.

This point is particularly exemplified in the case of silver cyanide. According to theory the amount required to re-dissolve this salt is exactly equivalent to the amount which precipitated it from the solution of silver nitrate. In actual practice, however, *more* than this amount is always required; the extent of difference being greater in proportion to the extent of impurity in the sample of potassium cyanide used and also in proportion to the time occupied in the operation. The former factor is important in view of the fact that the impurities in potassium cyanide usually consist of salts like the carbonate or chloride which give a corresponding precipitate of the silver salt, and as will be shown presently such salts if present require a double proportion of potassium cyanide to re-dissolve them. The latter factor enters into consideration owing to the susceptibility of silver salts to the action of light. This may be explained by an example. Suppose that 134 grams of pure silver cyanide are to be dissolved in potassium cyanide, the normal action would be—

$$\underset{(134)}{\mathrm{AgCN}} + \underset{(65)}{\mathrm{KCN}} = \mathrm{KAg(CN)_2}$$

Therefore 65 grams of KCN should be required, but supposing that this pure silver salt had been left a few hours exposed to the action of light and the atmosphere, then part of the silver cyanide would have become decomposed into some other sub-salt of silver, and *before* that portion could be dissolved in potassium cyanide it would need re-converting into silver cyanide. Thus part of the 65 grams of potassium cyanide would be taken up for this requirement, leaving insufficient to complete the solution and consequently a further quantity would be necessary.

It must therefore be clearly pointed out that whatever salt of silver is used for the early stages of making solutions, if that salt is not cyanide, the action of dissolving in potassium cyanide occurs in two parts. In the first part the particular salt is converted into the single cyanide of silver, AgCN, and in the second part this is converted into the soluble *double* cyanide of silver and potassium. Thus in the case of silver chloride the reactions may be represented as taking place as follows—

$$\left.\begin{array}{l}(1)\ \mathrm{AgCl} + \mathrm{KCN} = \mathrm{AgCN} + \mathrm{KCl} \\ (2)\ \mathrm{AgCN} + \mathrm{KCN} = \mathrm{KAg(CN)_2}\end{array}\right\}$$

the results of the reactions being bracketed, since from their nature the operator has no means of distinguishing between them.

It may be of interest here to observe that during recent years silver cyanide has been placed on the market by reputable manufacturing chemists, and the operator may now, therefore, if he prefers, make a solution direct from this salt as bought, by simply dissolving in a solution of potassium cyanide.

It is not advisable to attempt to use a silver solution containing a *lower* proportion of silver per gallon than the weight recommended in the foregoing solutions. Many workers prefer a greater proportion, but it should be borne in mind that the amount of silver in a plating solution is equivalent to so much "capital" invested, and it is contrary to sound commercial principles to increase capital invested unless there is a reasonable prospect of a proportionate increase in the returns on capital, and it by no means follows that if the proportion of silver in solution in a plating establishment is increased, say, from 2 oz. to 3 oz. (Troy) per imperial gallon (or 1⅔ to 2½ oz. per U.S. gallon) there will be an increase in returns of 50 per cent. Indeed, it is impossible to obtain such an increase. Richer solutions do certainly—within limits—work more quickly than poorer ones, *i.e.* have a higher conductivity if all other conditions are equal, but not in anything like the proportions corresponding to the increased capital expenditure. In fact, it is no uncommon experience in practice to find a solution containing only 2 or 2½ oz. (Troy) of silver per imperial gallon conducting better and consequently working more rapidly than one containing double this proportion of metal. Some explanation of this, at first sight, rather perplexing phenomenon is found in the now generally accepted theory of electrolytic dissociation (see p. 23). As the effects of electrolysis are obtained by means of the dissociation into ions of the molecules forming the electrolyte, it follows that one of the main factors in the conductivity of a solution is the degree of dissociation of the dissolved substance. Now it may be stated as a general principle of electro-chemistry that while the *actual* conductivity of a solution falls off when it is diluted, yet the *equivalent* or the molecular conductivity increases with its dilution.* In other words, the extent to which an electrolyte splits up into ions (which alone are concerned in carrying the current) increases as the solution becomes more dilute *up to a certain point.* When dissociation is complete, however, the molecular conductivity is at its highest value. Each solution, therefore, has a point of maximum conductivity, and this point falls off with concentration on the one hand or dilution on the other. This, in bare outline, is one of the results of modern research into the question of the conductivity of electrolytes. The possibility, therefore, will be readily understood that, in a solution very rich in silver, a large proportion of the molecules of the silver salt remain undissociated and consequently take no part in the conductance of the current. As a matter of fact the presence or addition of *other* substances in the electrolyte may play a much greater part in the actual conductivity of the plating solution than an increase of the silver compound. This is borne out by practical experience.

To make the matter clearer it may be advisable to emphasize the point that electrical conduction is a phenomenon distinct from that of electrolytic decomposition. The two things must not be confounded. *All the dissociated ions present in an electrolyte take part in conducting the current, but by no means are they all necessarily deposited or liberated at the electrodes.*

In the case of electrolytes like that of a solution of the double cyanide of silver and potassium, where the actual metallic deposit is due to a secondary action (see p. 200) and not to a primary one, these principles assume paramount importance. The really essential point is that, given a solution of high conductivity, there shall be a sufficiency of silver salt in the vicinity of the cathodes to provide material for the secondary actions to complete themselves. The presence of silver beyond this is valueless and means

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* See R. A. Lehfeldt, *Electro-chemistry* (Longmans), p. 59.

commercially "unremunerative capital." The seriousness of the matter is obvious in cases where the electroplating of silver is carried out on a large scale, necessitating the use of several thousand gallons of solution.

Anodes.—The anodes used in silver-plating should always be of "fine" silver rolled into sheets approximately 0·03 inch ($\frac{3}{4}$ mm.) in thickness. Each sheet should be annealed at a dull red heat, and before placing in the vat it is advisable to rinse well in the potash boil in order to remove any dirt or greasy film which may adhere to them.

Management of Solutions.—The good management of solutions is one of the most important factors in the successful electro-deposition of silver. A silver-plating solution properly made and continuously well managed will give good results for a very long period. Some solutions which are in use to-day in the large plating establishments of the principal trade centres have been continuously used for upwards of thirty and even forty years. The two main points to be emphasized are—

1. The continual and regular adjustments of the proportion of "free cyanide" present, and
2. The arrangement of anode surfaces so that the superficial area of the anode surface presented to electrolytic action is approximately equal to that of the cathode surface.

The first point, the proportion of free cyanide, is one upon which, as previously indicated, considerable difference of opinion prevails, but the experience of the present authors after considerable experiment is that in all cases where the silver content is not less than 2 oz. nor more than 4 oz. (Troy) per imperial gallon ($1\frac{2}{3}$ to $3\frac{1}{3}$ oz. per U.S. gallon), the proportion of *free* cyanide present should be between 50 and 80 per cent. of the *combined* cyanide. *E.g.* suppose a vat to contain 108 oz. (Troy) of silver in solution; then, from the equation previously given, we know that that amount of silver will have required $2 \times 65 = 130$ oz. of potassium cyanide in order to convert it into the double cyanide of silver and potassium. The proportion of free cyanide present in such a vat should therefore be between 50 and 80 per cent. of 130 oz. In other words, to find the minimum of free cyanide

$$100 : 130 :: 50 : x$$
$$\text{or } x = 65$$

and to find the maximum

$$100 : 130 :: 80 : x_1$$
$$\text{or } x_1 = 104$$

i.e. 65 oz. and 104 oz. respectively.

It will be observed that the margin allowed between the minimum and the maximum points is fairly wide, as the exact amount from which the best results can be obtained varies somewhat according to local conditions. But it may be taken as a safe rule that in the case of a new solution the lowest figure should be adopted, and then as the solution ages the amount increased until the maximum is reached.

The necessity for the presence of free cyanide in a plating solution may be best explained by a consideration of the reactions which occur in the electrolysis of the double cyanide of silver and potassium. These are as follows :—

Primarily the electrolyte $KAg(CN)_2$ is decomposed at the electrodes thus—

$Ag(CN)_2$ liberated at anode.
K ,, ,, cathode.

The CN of the compound ion AgCN.CN combines with the silver of the anode, and forms AgCN, so that the complete reaction at the anode may be expressed thus—

$$AgCN.CN + Ag = 2AgCN.$$

At the anode therefore an excess of the insoluble substance silver cyanide is formed.

At the cathode, the simple ion K at the moment of liberation attacks the surrounding electrolyte $KAg(CN)_2$, and the deposit of metallic silver on the cathode is the result of the reaction ; thus—

$$KAg(CN)_2 + K = 2KCN + Ag \text{ (liberated).}$$

The actual deposit on the cathode therefore is really a secondary and not a primary effect of electrolysis.

As a result of the above reactions it will be observed that the liquid round the cathode is denuded of its silver contents, and on the other hand the anode is rapidly encrusted with insoluble silver cyanide. It is owing to the latter effect that the presence of a fairly large quantity of "free" cyanide is necessary, in order to dissolve the AgCN as quickly as it is formed, and so preserve the anode surface clear and metallic. A deficiency of free cyanide always results in the anodes becoming dirty and slimy, and consequently in an increase of the resistance of the circuit.

2. With regard to the second point in solution management, that of the arrangement of anode surface, little need be said further than that if a large amount of work is to be done and it is not desired to have a heavy weight of silver in stock in the vats as anode, the required surface may readily be obtained by rolling the silver sheets as thin as is necessary to give the maximum of superficial area required, and exposing the whole of the sheet to the action of the electrolyte: this can be done by fitting it into a skeleton frame of purest iron wire somewhat after the style shown in Fig. 55.

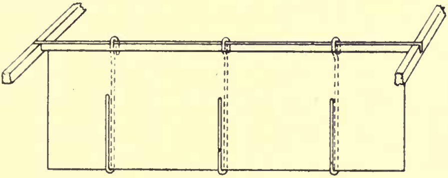

Fig. 55.—Framework for holding silver anodes.

The frame is in electrical contact with the + pole of the dynamo and is entirely submerged in the electrolyte. As iron is insoluble in cyanide solutions even when conducting the current, such a frame will last many years and introduce no impurity into the bath.

With careful attention to these two main points, the regular addition of water to make up for loss by evaporation and the maintenance of the temperature at from 18° to 20° C., uniformly good results will be obtained, and it will be found quite possible to work a solution so that its silver content scarcely varies more than a few dwts. from year to year. It must, however, further be observed that it is absolutely necessary to stir the solution thoroughly at least once in two days to prevent its separation into layers of varying density, and to secure evenness of deposit on the cathode surfaces.

Electrical Conditions in Silver Deposition.—The voltage required in the deposition of silver from a cyanide solution is very low; and under average conditions of conductivity of solutions and distance between electrodes, should not exceed $1\frac{1}{2}$ volts at the vat terminals. The current density generally employed is from $2\frac{1}{2}$ to 4 amperes per square foot of cathode surface, but the higher figure can only be employed when the cathodes are given a gentle swinging motion in the vat (see page 119); otherwise the deposit will become rough and granular, particularly on the edges.

Special Treatment of Metals for Silver-plating.—The general methods of preparation of articles for plating have been given in Chapter V., but the following special points require enumeration.

(1) *Copper*, *Brass*, *and German Silver*.—Practical experience in depositing silver on these metals has demonstrated that the adhesion of the deposit is considerably enhanced by coating them with a film of mercury after the usual cleansing operations, and before immersion in the silver bath. The principal reason for this is that copper and its alloys are extremely susceptible to the action of the atmosphere and oxidize so rapidly that it is almost impossible to complete the cleansing processes and transfer to the silver vat without having formed during conveyance to the vat a film of oxide which would prevent perfect adhesion. The preliminary deposition by a simple immersion process of a

thin film of mercury prevents this trouble, and incidentally, as mercury is more electro-negative than silver, prevents any "simple immersion" deposit of silver which it is not advisable to have. Hence the process known as *Quicking.* The term "quicking" is applied to the immersion of a metal in a solution containing mercury, during which a thin film of mercury is deposited by simple electro-chemical exchange. The solution generally used is made up as follows :—

Mercuric oxide (red oxide of mercury) .	1 oz.	31·2 gr.
Potassium cyanide	1 lb.	0·5 kg.
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. „	5 litres

The potassium cyanide is first dissolved in the water, then the mercuric oxide added, and the solution vigorously stirred. A black deposit usually occurs which remains undissolved, but this will quickly settle to the bottom of the vessel and may be disregarded. The working qualities of the solution should be tested by immersing in it a piece of clean, freshly "dipped" copper or brass for two or three seconds, when it should become completely covered with a clear bright film of metallic mercury. If the deposit is not clear and bright, add a little more potassium cyanide.

It is usually supposed and it is also reasonably probable that "Quicking" has the effect of strengthening the adhesion of the silver deposit owing to the well-known amalgamating properties of mercury, it being said that the latter first amalgamates with the basis metal and afterwards with the silver deposit on its surface. In other words, that it forms a kind of "cement" between the deposit and its basis metal. Some investigation upon this point, however, remains to be made.*

(2) *"Britannia Metal" and Alloys of Tin, Lead, or Zinc.*— Britannia metal is an alloy containing usually about 90 per cent. tin, the remaining 10 per cent. being copper and

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* See *Journal of the Institute of Metals*, No. 1, 1911, vol. v. p. 222.

antimony in varying proportions. The recommendations for the preparatory treatment of this alloy for plating will serve equally well for similar alloys containing lead or zinc. Successful electro-silver-plating of these metals requires considerable care and experience, and the various points in the directions which follow must be carefully attended to in order to ensure good results in the adhesion of the deposit.

Many text-books recommend a preliminary coating of copper, but there is no necessity for this, and in practice it is rarely if ever resorted to. For preliminary treatment, *i.e.* cleansing from grease, etc., the ordinary caustic potash boil is the most effective agent. Sometimes the boil is made up of a weaker strength than that for German silver and other copper alloys, but the best practice is to use a fairly strong solution—one containing at least ½ lb. caustic potash or soda per gallon—and to shorten the time of immersion. These metals are rather susceptible to the action of strong alkalies, and therefore a prolonged immersion in potash would tend to injure seriously the articles; but practical experience in handling these metals has proved that it is better in this respect to use a strong boil with consequently a shorter immersion than a weak boil which obviously will necessitate a longer one. The method of electrolytic cleansing is very useful in this connection.

When the articles are free from grease they are usually scratch-brushed thoroughly on a soft brush, then rapidly passed through another strong potash boil (reserved for this purpose), and *without rinsing* transferred to a "striking" or "starting" bath. This bath is an ordinary plating solution containing a comparatively small proportion* of metallic silver and a large proportion of free cyanide, and in addition to the usual anode sheets and cathode connecting rods the containing vat is usually fitted at one end with a shelf covered with a thin sheet of fine silver or copper connected with the cathode or negative rod. A strong current is used, and immediately the article is completely covered with a

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* From 10 to 15 dwts. per imp. gallon.

thin film of silver it is taken out, and if of flat work (dishes, etc.) is transferred to the ordinary plating vat and the deposit built up in the usual manner. Hollow articles, however, like teapots, are without being emptied of the starting solution, first placed on the silver-lined shelf, and while thus in contact with the negative pole, a cylindrical piece of sheet silver attached to the positive pole is held inside for a few minutes until the inside is as perfectly coated as the outside. They are then transferred to the ordinary plating vat as in the former case.

A difficulty often arises in the electro-silver-plating of Britannia metal owing to the "cutting" of the surface of this soft metal in scratch-brushing. Even the softest scratch-brush leaves marks on these surfaces which interfere with the subsequent finishing processes. This may be obviated by adopting the following method. After cleansing from grease, instead of scratch-brushing brush the article over by means of a soft bristle jewel brush, with a thin paste made up of precipitated chalk or whiting, and water. Rinse thoroughly in clean water, pass through strong potash to the starting vat, and proceed as before directed.

3. *Iron and its alloys.*—Iron and steel goods are, after cleansing from grease, immersed in an acid dip or pickle of 25 per cent. hydrochloric acid or 10 per cent. sulphuric acid, and then usually coated with a film of copper in an alkaline solution (see Chapter XI.) before immersion in the silver vat; English operators adopt this method generally as tending to give the most reliable results.

In the United States, however, the following is the generally adopted treatment of steel goods, coppering being omitted. After the ordinary cleansing treatment in hot potash and acid pickles the articles are rapidly passed successively through two "striking" baths. The first of these is made up by dissolving about 8 oz. of potassium cyanide in 1 imperial (or $1\frac{1}{5}$ U.S.) gallon of water (50 grams per litre) without any silver content whatever. The articles are immersed in this and connected to the negative pole of the dynamo, the positive pole being connected to anodes consisting of small sheets of silver and copper alternately. No appreciable deposit of course results from such a bath, but it has the effect of removing every trace of oxide which may remain on the surface of the articles. The second striking bath to which the articles are immediately transferred should contain from 6 to 8 dwts. of metallic silver per gallon and a large excess of free cyanide, and may be prepared by simply dissolving ½ oz. (=14·17 grams) of silver chloride in potassium cyanide solution of a strength of about 6 oz. per gallon (37·5 grams per litre). Silver anodes are used or a large copper and small silver anode alternately. After the goods are completely covered with a slight film of silver they are transferred without further treatment to the ordinary silver-plating baths for the deposit required.

Very successful results can also be obtained in the silver-plating of steel goods by giving them a preliminary film of brass from the brassing solution described on page 350 instead of coppering.

A further method of silver-plating iron and steel which is recommended, and appears to be used to some extent on the Continent, but was originally introduced in England, consists in depositing by separate current a preliminary coating of mercury on these surfaces before immersion in the plating vat.

The article is cleaned and pickled in the usual manner, then made the cathode for a few seconds in a bath consisting of a solution of the oxide or nitrate of mercury in dilute nitric acid. The liquid should contain from 1 to 2 oz. of the metal per gallon, and sheets of carbon are used as the anodes.

Bright Plating.—In 1847, not long after the introduction and use on a commercial scale of the cyanide solution for silver deposition, Millward accidentally discovered that the presence of a small trace of carbon bisulphide (CS_2) in the plating vat exercised a great influence on the character and appearance of the deposit. Usually the deposit of silver from an ordinary plating vat is of a dead pearly white appearance and somewhat coarse-looking in texture; the addition of carbon bisulphide, however, produces a bright lustrous deposit of very pleasing appearance and of a close smooth texture. It is difficult to assign any reason for this, and curiously enough successful results in "bright" plating depend as much on suitable electric current conditions as on the correct proportion of CS_2 present. The smaller the amount of carbon bisulphide which can be added to secure the desired result the better.

It is usual in silver-plating establishments to reserve one vat only for this treatment (unless a large amount of work is required) and to add the brightening liquid to this in extremely small proportions each day. One of the best methods of procedure is to mix together thoroughly, 4 British fluid ounces (=113·4 c.c.) of carbon bisulphide and 5 British fluid ounces (=141·7 c.c.) of ether, and store this solution in a well-stoppered bottle. Now, for a vat containing approximately 180 tc 200 imperial gallons, take $\frac{1}{2}$ oz. of this liquid, pour it into a Winchester quart bottle, and fill the bottle up with plating solution taken from the vat to be "brightened." Shake the contents vigorously for a short time so as to obtain a thorough mixture, and then add the whole of this solution to that in the vat and stir the vat contents up thoroughly. The operation is best performed at the end of the day's work, so that the vat may be ready for the following day. It is also an advantage to have two Winchester bottles and use them alternately; the $\frac{1}{2}$ oz. of ether solution of CS_2 may thus be in contact with the plating solution 24 hours before being added to the vat, and so assist the operator in securing the thorough mixture of carbon bisulphide with the plating solution, which is absolutely essential.

The current conditions required for the "bright" vat vary according to local circumstances, but it may be taken as a general principle in bright plating that a higher E.M.F. should be used than in ordinary silver deposition.

Except in the case of very thin films of silver it is not advisable to put the whole of the deposit on an article in the bright vat. The usual procedure is to put on the major portion of the required silver deposit in an ordinary vat and transfer to the bright for the last 10 or 15 minutes of deposition.

The problem as to what exactly are the reactions taking place in a "bright" vat is an extremely interesting one; but up to the present no very satisfactory solution is forthcoming. Carbon bisulphide, though only very slightly soluble in potassium cyanide solutions, certainly dissolves in the small proportion in which it is present in the ordinary bright plating liquid. It does not, however, appear to combine chemically with the solution, but remains in it simply as a dissolved body. Its decomposition, therefore (if such takes place), is due to secondary reactions, and a theory tentatively put forward is that it may become decomposed at the cathode surfaces only by the liberation of the ion K, which it will be remembered is the primary product of the electrolysis of silver cyanide solutions. That it may be decomposed, with the liberation of sulphur at the cathode, is apparently borne out by Gore's statement that he found the deposited silver of the bright-plating solution to contain traces of sulphur. Also that sulphur plays some part in the brightening effect seems very probable, as some experimenters have obtained good bright deposits by adding to the plating solution various compounds containing sulphur, other than carbon bisulphide. Another possible explanation is that it may act in a manner analogous to that of an addition agent, such as glue, etc. (see Deposition of Copper, Chapter XI., p. 248), and alter the character of the deposits, and consequently the colour, by affecting the size of the crystals.

A practical point of great importance to the electroplater is, however, the comparatively evanescent nature of the effects of CS_2. This the authors, after considerable observation, believe to be due not so much to decomposition as to evaporation. This substance is extremely volatile (its boiling point is 46° C.), consequently bright vats which happen by any chance to be exposed to a higher temperature than normal require more frequent addition of brightening liquid; on the other hand, where the working temperature of a vat is fairly low it is often found advisable to make additions only once in two or three days. It should be noted, however, that bright vats do not work satisfactorily at very low temperatures.

An important question often raised in practice refers to the best method of treating a bright vat which has acquired an excess of "bright" liquid; and a plan sometimes resorted to is to work the vat with silver sheets as cathodes with the idea that CS_2 would be decomposed and deposited out with the silver. This latter is an uncertain point, however, and in any case the plan is very inefficient and unsatisfactory. A far better method is to either boil the solution or heat it above 50° C. for a few hours; in this way CS_2, ether, and other volatile substances are expelled, and a "bright" vat which has been spoilt is restored to perfectly satisfactory working as a "bright" or even, if required, re-converted into an ordinary "dead"-plating solution.

The Assay of Silver and Free Cyanide in Solution.—It is essential to the efficient management of silver-plating solutions that the operator should be able from time to time to ascertain at least approximately the amount of silver and free cyanide contents respectively of a silver bath. The following methods are the most suitable for workshop practice, requiring the minimum of apparatus and being capable of yielding results of a fair degree of accuracy.

(A) *The Assay of Silver in Solution.*—Take an exactly measured quantity of the solution, say 100 c.c., or 5 fluid ounces, transfer to a beaker, and dilute by adding an equal bulk of water. Now add a considerable excess of strong hydrochloric acid, with the object of precipitating the silver from solution as silver chloride ($AgCl$). If only a small amount of HCl is added the precipitate produced will be silver cyanide, the effect of the acid being simply to neutralize the KCN in which AgCN is dissolved, so throwing down the latter, which is of course insoluble in water. Since it is better to get the precipitate as AgCl it is therefore advisable to add at least twice as much HCl as that which appears to complete precipitation. Owing to the fumes of hydrocyanic acid liberated the process should be conducted in a fume cupboard or where a good draught of air is available. Now place the beaker and its contents on a hot plate or sand-bath and warm gently. This will ensure the solution of any copper which may be present, and also assist the precipitate to settle. Dilute by adding cold water, pour off the top liquid cautiously and wash the precipitate once or twice by decantation; then empty it on to a filter paper folded

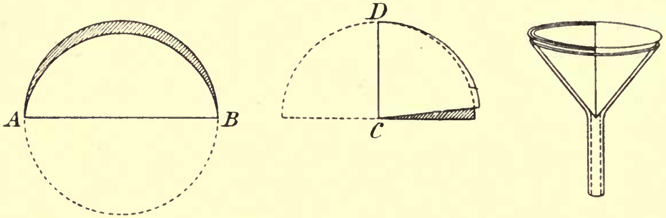

Fig. 56.—Method of folding filter paper.

and fitted into a glass funnel as shown in Fig. 56. The precipitate can then be thoroughly washed on the filter by pouring hot water on to it; this is done most conveniently by means of a wash bottle, the stream of water being directed so as to collect the precipitate to the apex of the filter. At this point the silver chloride may be dried, collected into a porcelain capsule (previously weighed), then fused, allowed to cool, the capsule reweighed, and the silver content thus estimated from the weight of silver chloride (AgCl) obtained, but some considerable experience and skill in chemical operations are required for this method. The plater will find it much more convenient to obtain the silver in metallic form before weighing. Several methods are available for this purpose, but certainly one of the best is the following, which was suggested to the authors by their friend Mr. F. C. Robinson (Chief Assayer to the Sheffield Smelting Co., Ltd.).

The precipitate on the filter is thoroughly dried, preferably in a steam oven, and transferred to a crucible, the bulk by gently squeezing the cone together, and the remainder by flattening the paper and gently rubbing one side against the other until every particle is detached. The paper itself is bound up lightly with a little thin platinum wire and burnt so that the ash may be collected and added to the contents of the crucible. An amount of dry powdered potassium cyanide of about equal bulk to the silver chloride is then mixed with the latter and a still further equal amount added on the top as a cover. The crucible, covered by a lid, is now placed in a muffle or injector furnace and gradually heated to a bright red heat. A Fletcher Russell concentric jet furnace with a foot-blower is very convenient for this purpose if a muffle is not available. Failing either, the silver may be reduced by means of a large silversmith's blowpipe as used for hard-soldering.

In this way the whole of the silver in the crucible contents is reduced to the metallic state and is found at the bottom of the crucible as a beautifully bright button of silver along with clean slag. Before weighing, the button or beads should be cleaned in boiling water, dried, and slightly flattened. With a little practice assays of an accuracy well within 1 per cent. may be obtained by this method. For other methods of the assay of silver, see Appendix.

(B) *The Assay of free Cyanide.*—This is carried out in a very similar manner to that directed for the assay of commercial potassium cyanide (see page 176), the principle of the method being the same. Take in a beaker 100 c.c. of the plating solution, and, in order to provide a larger bulk so that the reaction may be more easily observed, dilute with an equal bulk of water. Filter, and by means of the burette add standard silver nitrate solution (containing 17 grams $AgNO_3$ per litre) drop by drop until just a faint milkiness persists in the solution. At this point take the burette reading, and the amount in grams of free cyanide in the sample tested is this figure multiplied by 0·013 (the cyanide equivalent of 1 c.c. standard silver nitrate).

The following is an actual experiment :—

Amount of solution tested, 100 c.c.
Standard silver nitrate added, 93 c.c.
∴ amount of free cyanide = 93 × 0·013 = 1·209 grams.

It will be found very helpful to tabulate regularly the results of the above tests on plating solutions somewhat after the following fashion :—

No. of vat tested.	*Weight of silver.*	*Amount of combined KCN calculated on the formula $KAg(CN)_2$.**	*Amount of free cyanide.*	*Percentage of free cyanide to combined cyanide.*	*Remarks.*
15	2·15	2·59	1·209	47	

A convenient quantity of solution to take for examination is 100 c.c., and the figures in the above table are obtained from such a quantity. If it is desired to know the respective weights per gallon, these figures must be multiplied by 45·4 (4540 c.c. = 1 imperial gallon), and if further the weight is required in Troy ounces instead of grams, the result must be divided by 31·1 (the number of grams in 1 oz. Troy).

To take an example from the above table, let the weight of silver per imperial gallon be required in oz. Troy.

Then $$\frac{2{\cdot}15 \times 45{\cdot}4}{31{\cdot}1} = 3{\cdot}14$$

∴ solution contains 3·14 oz. per imperial gallon or 2·62 oz. per U.S. gallon.

Stripping of old Silver Deposits.—The silver coating

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* This calculation is based on the fact that 130 parts of potassium cyanide exactly combine with 108 parts of silver to form the double cyanide. Therefore multiply column 2 by 130/108 = 1·204.

on old copper, brass, or German silver goods may be dissolved off by immersing in the following :—

Concentrated sulphuric acid . .	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres
Powdered potassium nitrate (saltpetre) .	3 oz.	93·75 gr.

The acid is placed in an acid-proof earthenware jar which is arranged in a hot-water tank so that the temperature of the acid can be raised to 70° or 80° C. When the acid is warm add the saltpetre, which should be powdered as finely as possible, and stir well with a glass rod. In this way by chemical action a small amount of nitric acid is liberated in the solution. Such a liquid dissolves a silver deposit readily and is without action on basis metals composed of copper or its alloys. Great care must be taken, however, to exclude water or even moisture as far as possible, since in that case the basis metal *is* attacked and its surface considerably injured.

Silver coatings on iron and steel, Britannia metal goods, or zinc and tin and their alloys generally are best removed by making the article the anode in a solution of potassium cyanide of 8 oz. per imp. gallon and passing the current through by means of small carbon cathodes. The basis metal if iron or steel is not attacked in the least, and in the case of the other metals only slightly, and if care is exercised scarcely at all. Such a solution may be used until the potassium cyanide is almost exhausted, as will be evidenced by increasing density and sluggish working; it must then be put aside for the recovery of its metal and a new one made up.

Recovery of Silver from Stripping Solutions.—From the *acid* solution above described the silver is recovered by first diluting the stripping liquid by pouring it into a large earthenware tank which contains two or three times as much water as the bulk of the "strip" (the latter must of course be added to the water and not the water to the acid), and then precipitating the silver by (*a*) adding a considerable quantity of common salt (NaCl), in which case the silver is precipitated as silver chloride ($AgCl$), or (*b*) suspending in the liquid strips of scrap iron or zinc, thus by electrochemical exchange precipitating the silver as finely divided metallic silver on the surfaces of the suspended metal; from which it may be readily removed by simply washing them well with a stream of hot water. In either case the silver contents of the strip are entirely recovered in a convenient form, and if not required for use in the plating shop itself may be sold to silver refiners.

To obtain the silver contents from the cyanide solution different methods must be adopted, and by far the best, if a dynamo or accumulator is available, is to extract the silver electrolytically. This may be done quite easily and conveniently by means of anodes of sheet-iron or carbon, preferably the latter, and cathodes composed of very thin sheets of silver, about equal in area to the anodes, but as thin as practicable. The E.M.F. of the current used should be from 0·75 to 1·25 volts, and a current density of about 6 amperes per square foot will be most satisfactory. The silver recovered in this way will be found to have a high degree of purity and if not required for use may be sold to the refiners on assay results.

An alternative method to the above is to evaporate the solution down to as small a bulk as makes it convenient to manipulate and add an excess of hydrochloric acid, thus precipitating the silver as silver chloride. The operation should be performed in the open air so as to lessen the evil effects of hydrocyanic acid gas which is evolved. When precipitation is complete wash the precipitate by pouring into it a large volume of hot water. Stir vigorously, allow the chloride to settle, and syphon off the clear liquid. This process should be repeated at least twice. Silver chloride obtained in this way is quite pure, and may well be used to make up a new plating solution by dissolving in potassium cyanide as described on pages 194 and 195.

Silver Deposition by Simple Immersion Processes.—These processes, though not coming strictly within the range of electroplating as commonly understood, yet merit, in the case of silver at least, a certain amount of attention owing to their fairly wide commercial application for superficially coating small articles, such as buttons, pins, hooks and eyes, and small springs, with silver.

The solutions used for this purpose are almost invariably cyanide solutions made up in a very similar fashion to those for electrolysis by separate current, but containing a much smaller proportion of silver.

Either of the methods previously described may accordingly be used in the preparation of solutions for this purpose, but the amount of silver present should not be greater than ½ oz. (Troy) per imperial gallon (3·9 gr. per litre), and for most purposes a lesser amount will be found to work more satisfactorily.

One of the best solutions is made up as follows :—

Silver nitrate	½ oz.	15·6 gr.
Common salt (sodium chloride) .	¼ ,,	7·8 ,,
Potassium cyanide	1½ oz.	46·8 ,,
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

Dissolve the silver nitrate in about half a pint of water (0·31 litre for the above metric values) and the common salt in a similar quantity. Mix the two solutions and stir vigorously. Then in the remaining seven pints (4·38 litres) of water dissolve the potassium cyanide and mix the whole together, stirring meanwhile. The resulting solution after boiling for a short time is ready for use, and may be used either cold or lukewarm, say 90° or 100° Fahr. At the latter temperature it will work more rapidly than in the cold.

The articles to be treated should be thoroughly cleansed from grease and oxide as if for ordinary electroplating. Brass and copper goods may be coated directly, but iron and steel articles must be given a preliminary film of copper or brass in a separate current alkaline bath. Immediately before immersion in the silvering solution all work should be rinsed through a strong solution of potassium cyanide. Small articles are enclosed in a perforated basket so that when they are immersed they may be thoroughly shaken or agitated in order to expose every piece to the action of the solution. When a satisfactory colour has been obtained the goods must be well rinsed in cold water, then passed through boiling water and dried out on hot box-wood sawdust.

For certain classes of work silvering pastes are used; the paste being rubbed over the surface of the work to be plated by hand with a piece of chamois leather or swansdown. A good formula for a paste for this purpose is:—

Silver chloride	1 part by weight
Cream of tartar	2 parts ,, ,,
Common salt	2 ,, ,, ,,

Mix together well and add sufficient water to form a stiff paste.

This process is useless if the surface of the article to be treated is not absolutely free from the slightest trace of grease or tarnish; otherwise the deposit is quite patchy and of a bad colour.

CHAPTER X

DEPOSITION OF GOLD

ALTHOUGH by no means of such widespread commercial importance as the deposition of silver or nickel, the electrodeposition of gold is nevertheless a very valuable branch of the electroplating industry, and, by reason of the great variety of artistic effects which may be obtained, a very fascinating one too. Its application also is not altogether confined to ornamental purposes, but, of recent years particularly, has been extended to the provision of protective coatings to the commoner metals in cases where protection from acid and other corrosive influences is required.

Properties of Gold.—Gold is a very soft, yellow metal, capable of taking a brilliant and pleasing polish. It is the most malleable and ductile metal known, and is also a very good conductor of heat and electricity, ranking inferior in this respect only to copper and silver. It is not acted upon by air or oxygen at any temperature, and is therefore particularly suited to withstanding atmospheric influences. With the exception of selenic acid no single acid is capable of attacking or dissolving it, this property being also a very valuable one. It is, however, readily dissolved in the mixture of hydrochloric and nitric acids known as *aqua regia*, and it is also to some extent soluble in an aqueous solution of potassium cyanide.

In its uses in the arts, gold is usually alloyed with some other metal, principally silver or copper, in order to give it a measure of hardness and strength which it lacks in its pure state. With certain exceptions which will be explained later the pure metal only should be used for electrogilding.

As will be observed by its position in the order of the electro-chemical series, gold is a very negative element, and consequently is most easily reduced from its combinations by almost every other metal.

The principal salt of gold is its chloride, $AuCl_3$, formed by dissolving the metal in *aqua regia* (HCl 3 parts, HNO_3 1 part), and from this salt in the first instance all solutions of gold for electrogilding are made except those prepared by electrolytic methods.

As in the case of silver, the best solution for the electrodeposition of gold is the double cyanide of gold and potassium in water, and this must be prepared either from fine gold or from pure gold chloride. The latter salt, like silver nitrate, is manufactured on a fairly large scale, and may therefore be readily purchased of a high degree of purity.

Compounds of Gold.—The only salts of gold calling for mention here are the chloride and the cyanides. A description of gold chloride, together with instructions for testing, will be given later. With regard to the combination with cyanogen to form cyanides, gold, like silver, readily combines with the alkaline cyanides to form double salts. Unlike silver, however, *two* series of double cyanides are known, viz. the *auro* and the *auri* salts. With potassium, *e.g.*, we may have potassium aurocyanide and potassium auricyanide, the respective formulæ being :—

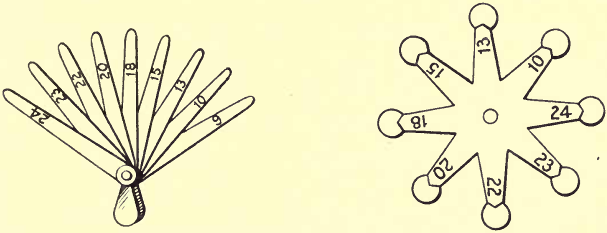
Auro . . $KAu(CN)_2$.
Auri . . $2KAu(CN)_4.3H_2O$.

Under ordinary conditions of making gold-depositing solutions the former salt is formed, but the latter can be made and used for electrogilding, as will be explained.

Tests of Materials.—(*A*) *Gold.* The exact assay of gold and its alloys is an operation demanding considerable training and experience ; but as it is often very necessary for the electrogilder to be able to make rough or approximate tests for gold, it is hoped that the following hints will be of service. Colour alone is misleading in judging the quality of a gold alloy, since by careful adjustment of the proportions of copper and silver present alloys of low quality are often made to bear a close resemblance to those of higher quality. The alloys of high and low quality can, however, be usually distinguished from each other by using the following "test" acids recommended by Wigley, *i.e.* nitric acid 4 oz., hydrochloric acid $\frac{1}{2}$ oz., water 3 oz.

This "acid" with alloys rich in copper gives a green solution and copious evolution of gas bubbles, while with alloys of high carat the action (if any) amounts only to a coloration. The most common of the rough tests for gold is the *touchstone* method. For the following description of this method the authors are indebted to Mr. E. A. Smith, of the Sheffield Assay Office.

The method consists in rubbing the alloy to be tested on a small block of hard, smooth, dark stone, resembling slate, called a *touchstone*, and comparing the appearance and colour of the streak thus produced with those made by a series of small bars of carefully prepared alloys of definite composition known as "touch-needles" (Figs. 57 and 58). The effect of the action of a drop of nitric acid and of dilute *aqua regia* on these streaks is also noted; the streak from the less pure alloy will be more readily acted upon, with the production of a more or less green colour, according to the



Figs. 57 and 58.—Touch needles.

proportion of copper present. Several series of touch-needles are usually employed, consisting of alloys of gold and copper, gold and silver, and gold, silver, and copper, either corresponding to legal standards or in series in which the proportion of gold increases by carats or half-carats.

The valuation of an alloy is made by determining to which of the touch-needles the streak it produces most nearly corresponds. In order to get correctly the streak of the alloy to be tested the surface of the metal should first be slightly filed away, as this may have been made somewhat richer than the bulk of the alloy by boiling with acid to remove the base or inferior metal from the surface—a method often resorted to by goldsmiths to get a "colour" on gold articles.

(*B*) *Gold Chloride.*—The formula for this salt is generally stated as $AuCl_3$; the commercial salt in its crystallized form, however, whether purchased or made in the workshop, contains excess hydrochloric acid and water, and is more correctly described by the formula, $AuCl_3.HCl.4H_2O$. According to this formula the percentage of metallic gold in the salt is 48, but sometimes a slightly higher proportion is found owing to a small loss of HCl and water which occurs in drying the crystals.

To test for percentage of gold, dissolve $\frac{1}{2}$ gram of the salt in 25 c.c. of distilled water. Add to this pure potassium hydroxide (a solution in water) until the gold solution is distinctly alkaline (test with litmus paper); now add 5 c.c. of a 10-volume hydrogen peroxide solution, and heat at the temperature of boiling water for about an hour. The precipitate produced is finely divided metallic gold, which should be washed with water rendered slightly acid with hydrochloric acid. It must then be collected in a porcelain crucible, dried, and carefully ignited.

The resulting product should weigh not less than 0·24 gram.

To test for foreign metals, the filtrate from the above should be treated by passing sulphuretted hydrogen gas through it or by adding strong ammonia and afterwards ammonium sulphide. No coloration or precipitate should be obtained.

Varieties of gold chloride containing sodium chloride are now largely sold for photographic purposes. These should be carefully avoided by the electrogilder. They frequently contain only 20 to 30 per cent. of metallic gold, and are therefore very misleading.

(*C*) *Potassium Cyanide.*—It is of the greatest importance that the cyanide used in making up gilding solutions should be the purest obtainable. Before using, therefore, it should always be tested according to the methods described in Chapter IX.

Methods of preparing Depositing Solutions.—Gold solutions may, like silver, be prepared by either electrolytic methods or chemical methods. With due care both methods will give equally satisfactory results. Directions will, therefore, be given for both.

(*A*) *Electrolytic Methods.*—To prepare one imperial gallon of solution containing 1 oz. (Troy) of gold. Dissolve 4 oz. (Troy) potassium cyanide in one imperial gallon of distilled water (or 137 gr. in 5 litres to contain 34·2 gr. of gold). Pour the solution into a sufficiently large glass or earthenware vessel either round or oblong. Place inside this vessel a porous cell containing a strong solution of potassium cyanide. The level of the solution inside this cell should be about the same as that outside, or a little higher.

The following diagram (Fig. 59) illustrates the arrangement.

The anode should be of fine gold, weighing about 1½ oz. Troy (= 46·6 gr.), and rolled to as large an area as the size of the vessel will allow. The cathode which is placed inside the porous cell is preferably a strip of fine silver of the same length as the depth of the cell, and as wide as the latter will allow. If current from a dynamo or accumulators is not available, the most convenient form of supply is two large bichromate or Bunsen cells connected in series. The

E.M.F. required is from 3 to 4 volts. The time occupied will of course depend upon the capacity of the cells, and the current must be continued until the weight of the anode is reduced to about 10 dwts. The progress of the operation may be readily ascertained from time to time by weighing the anode.

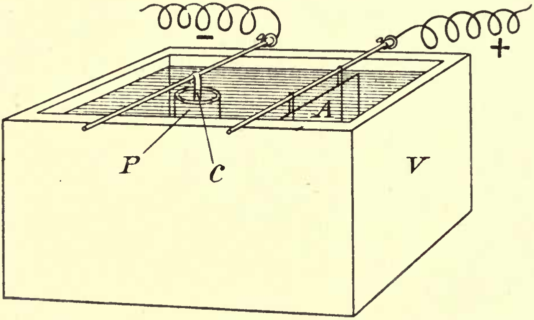


FIG. 59.—Electrolytic method of preparing gilding solution.

V, outer vessel.
P, porous cell.
A, anode of fine gold.
C, cathode of silver.

In plating establishments where the deposition of gold is only a comparatively small branch, as is often the case, this will be found a very convenient method of preparing solutions: especially if the operators have little chemical knowledge. The apparatus may be arranged just before leaving for the night, and with cells of a fair capacity the solution will be complete next morning; no intermediate attention is required, particularly if bichromate cells or accumulators are used.

Before actually using the solution for gilding it will be found advantageous to boil it for an hour or so.

(*B*) *Chemical Methods.*—In making solutions by these methods either metallic gold or gold chloride may be used. If the former is employed, however, the first stage of the operation is its conversion into the chloride. This, as will have been gathered, is done by dissolving it in a mixture of three parts hydrochloric acid and one part nitric acid.

For this purpose, the gold should be cut up into small pieces and placed in a thin conical-shaped glass flask or beaker. The acid mixture is then poured on to the gold and gentle heat applied by placing the vessel in hot water or on a sandbath. A vigorous chemical action ensues, the gold being attacked by chlorine which is liberated in the interaction of the two acids. It will be found better to add a relatively small proportion of acid at first (say 50 to 100 c.c. for 1 oz. of gold), and when this is saturated, as will be observed by the cessation of the chemical action, it may be poured off into an evaporating dish, and a further quantity of acid added according to the amount of gold left. In this way an excess of acid is avoided. When the whole of the gold is dissolved the solution must be slowly and carefully evaporated by heating in a porcelain evaporating dish until the liquid shows signs of thickening, when it is set aside to cool. When cold the whole mass will consist of fine needlelike crystals of gold chloride. Special care must be taken, however, not to dry up the liquid in evaporating, as in that case some of the $AuCl_3$ product may at 185° C. be reduced to $AuCl$, above 185° C. to metallic gold. If by any accident this occurs an addition of *aqua regia* must be made as found necessary. If the gold salt is not required for immediate use in making up solutions, it may be stored in the crystallized form or dissolved in distilled water kept in a stoppered glass bottle, and used as needed.

For the remaining stages of the preparation of electro-gilding solution by chemical methods, a number of different formulæ have been recommended, the chief feature of many of them being their complexity. Only three will, however, be described here, each of these being thoroughly reliable. The second is the most generally used, with varying proportions of gold content according to the class of work done.

FORMULA I.—

Gold (converted into gold chloride)	1 oz. (Troy)	34·2 gr.
Or gold chloride	2 oz. ,,	68·4 ,,
Potassium cyanide	Q.S.	
Water (distilled)	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres

The gold chloride is dissolved in about a pint of distilled water. A solution of potassium cyanide of a strength of from 8 to 10 oz. per imperial gallon (50 to 62·5 grams per litre) is then prepared, and a portion slowly and carefully added to the gold solution as long as a precipitate is produced. This precipitate (brownish in colour) is gold cyanide, and like silver cyanide it is readily soluble in excess of potassium cyanide; the greatest care therefore must be taken to exactly precipitate the gold as cyanide, and not to redissolve it. The reaction is—

$$AuCl_3 + 3KCN = Au(CN)_3 + 3KCl.$$

The amount of cyanide required in this reaction may be calculated therefore as in the case of the corresponding silver reaction if its percentage purity be known.

After vigorous stirring the precipitate must now be washed thoroughly either by decantation or on a filter. As the amount of solution is not large, the latter method is best. For this purpose fold a circle of filter paper, about 10 ins. diameter, into four folds. Fit the apex into the apex of a 5-in. or 6-in. glass funnel and open in the manner illustrated in Fig. 56.

Pour the solution containing the precipitated gold cyanide on to the funnel, the clear liquor will run through and the precipitate will be retained in the filter. Wash the precipitate several times by pouring on a supply of warm water and allowing it to run through. When the wash waters have been finally drained off, place the funnel in the mouth of a large bottle—a Winchester will do—and continue the addition of the potassium cyanide solution previously made up. The precipitate will thus be slowly dissolved and the solution will run through into the bottle. Care must be taken not to add more of the cyanide solution than is actually required, since many gilding solutions require very little "free" cyanide, and the specific amount of this must be adjusted according to the class of work to be done.

The solution must now be boiled and afterwards made up to a bulk of one gallon by the addition of distilled water.

Formula II.—

Gold (converted into gold chloride)	1 oz. (Troy)	34·2 gr.
Or gold chloride	2 „ „	68·4 „
Ammonia, s.g. 0·880	Q.S.	
Potassium cyanide	Q.S.	
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. „	5 litres

Dissolve the gold salt in about a pint of distilled water, *or less*, not more. When solution is complete, add ammonia slowly until no further precipitate is produced (from $2\frac{1}{2}$ to 3 fl. oz. are usually required), and stir well. A copious yellowish-brown precipitate results, known as *fulminating gold.* The reaction is rather complex, but may be summed up thus:—

$$2AuCl_3 + 8NH_4HO = \underbrace{Au(NH)NH_2 + AuNHCl}_{\text{Fulminating gold.}} + 5NH_4Cl + 8H_2O.$$

This precipitate if allowed to dry is very explosive, so that it must always be kept under water, and for this reason should be well washed by decantation, not on the filter. The first wash-water should be kept for the recovery of any trace of gold which it may contain, and the final wash-water need not be completely poured off. When washing is complete, add to the precipitate a solution of potassium cyanide of a strength of about 8 oz. per imperial gallon (50 gr. per litre), until it is just dissolved, and a clear pale yellow liquid will result. Sometimes a little undissolved matter from the impurities in the cyanide will be noticed, but this may be disregarded. The solution is now boiled for a short time or until there is no smell of ammonia, and then diluted with distilled water to a bulk of one gallon.

Formula III.—

Gold chloride crystals ($AuCl_3.HCl.4H_2O$)	1 oz. (Troy)	31·1 gr.
Powdered potassium cyanide, 95 per cent. . .	14 dwts. ,,	21·8 ,,

Weigh out the above quantities exactly, and place each in a Bohemian glass flask or beaker (say of 8 fl. oz. or 250 c.c. capacity). To the potassium cyanide add 5 c.c. of distilled water. Heat both flasks by placing in a bath of boiling water, so that the temperature does not rise above 100° C. The gold salt will gradually melt into a thick spongy liquid. The cyanide also will dissolve but may require the addition of a little more distilled water—the solution should, however, be kept as concentrated as possible. When the contents of both flasks are perfectly liquid—but not before—add the chloride of gold very cautiously in small quantities at a time to the cyanide solution and shake thoroughly after each addition, still keeping the flasks hot. The chemical reaction is rather violent, but is quite safe if the additions are made slowly. When the last few drops of gold chloride have been added to the cyanide, the liquid will show distinct signs of crystallization, and on putting aside to cool the whole mass will crystallize in large colourless tablets.

Under the above conditions of concentration potassium *auri*-cyanide is formed, the composition of the crystals being $2KAu(CN)_4.3H_2O$ (see p. 218). All that is necessary is to dissolve this salt in distilled water to any dilution required, and a very fine gilding solution results.

This method is unusual and the constitution of the salt in aqueous solution is uncertain, but we have used a solution made in this way on several occasions in commercial practice, and for "bright" gilding (p. 228) an excellent fine yellow colour is produced.

All the above solutions may be worked either cold or hot according to the colour required and the class of work done. It may be stated generally that cold solutions give a lighter tone to the colour of the deposit than hot solutions. It need hardly be mentioned that the latter conduct electricity much more readily than the former.

It will have been noted that in giving details of the composition of gilding solutions no recommendation has been made as to the addition of free cyanide. This is so because, in the opinion of the authors after considerable experience and observation, the proportion of free cyanide in these solutions should be kept as low as possible. All that is required is sufficient to keep the anode surfaces clean in actual working, and it is surprising how little is needed for this purpose. And in the making up of any cyanide solution it invariably happens in redissolving a precipitate in potassium cyanide (whatever the precipitate may be) that a little more than is actually required for dissolving is added, since it would necessitate extreme care and special precautions to gauge exactly the point at which the last particles of the precipitate disappear.

Moreover the operation of gilding as usually practised is the imparting of a mere film of the metal as a protective or ornamental covering, not deposition by weight; consequently the operation is short and the anode is scarcely ever immersed in the solution sufficiently long to become coated with the results of the decomposition taking place at its surface, as would be the case in a corresponding silver solution with a deficiency of cyanide. This, however, is only a comparatively minor reason for the omission of free cyanide. The most important is that in a large majority of cases the electrogilder is called upon to gild articles which have had their surfaces previously carefully prepared by burnishing or polishing; particularly is this the case with standard silver or electro-silver-plated goods. The operation is usually termed "*bright*" gilding. The surface bearing as high a polish as it is capable of, must be given a thin film of gold without in the slightest measure deadening or dulling the surface. Now if the solution used contains a very slight excess of free cyanide, then unless the work is carried out with extreme rapidity, the surface is slightly acted upon and stained before the gold can be deposited, and as a consequence the brilliancy is lost and repolishing and sometimes regilding is necessitated. The same remarks largely apply to other delicate surfaces of silver, such as those finely matted or grained, which are required to show the same appearance when gilt. This point is much more noticeable in hot solutions than in those worked cold, the former naturally being more active chemically. It often happens therefore that a solution for bright gilding which works unsatisfactorily when warmed will give quite good results if allowed to cool and worked only when cold. If accidentally a little too much cyanide has been added to any solution, the ill effects can often be overcome by giving the liquid a prolonged boiling, say for five or six hours. This treatment results in the partial decomposition of the free cyanide present and so assists in restoring correct conditions. The same treatment should be resorted to if the solution has acquired any organic matter.

For the electro-deposition of gold where an appreciable weight of the metal is required the solution conditions are quite different. In this class of work free cyanide is not merely allowable but necessary, and the surfaces upon which the deposit is to be made do not usually require such delicacy of treatment as "bright" work. The proportion of free cyanide generally employed is about one-fourth of the amount used to dissolve the gold precipitate in making up the solution. The quantity of free cyanide in solution can be tested for by the method recommended under silver deposition (p. 211), except in the case of very old solutions where the colour is often so dark as to make it difficult to detect the end of the silver nitrate reaction. In such cases, however, if the solution is unsatisfactory it is better to make a new bath, recovering the gold in the old one as directed later.

In many plating establishments it is customary to keep two separate solutions for the two classes of work described in the foregoing, and this plan will be found very advantageous, since then the best conditions of solution are obtainable for each class.

Anodes.—Anodes in all cases should be of fine gold, and if it is not desired to have a large amount of gold in stock they should be rolled to as thin a degree as is reasonable, so that an anode surface may be obtained at least in some measure commensurate with the surface to be gilt. Some operators and text books recommend platinum as anodes, but there is no advantage obtainable in this way, and so long as this metal is at or about its present market price it is out of the question commercially. If for any reason gold is not available, a piece of $\frac{1}{4}$-in. or $\frac{3}{8}$-in. sheet carbon is the best substitute.

Management of Solutions.—Gold solutions are not particularly difficult to keep in order if proper care is observed to prevent the introduction of foreign matter. As the anode is only very slowly dissolved in the solution, and in the case of solutions for bright gilding scarcely at all owing to the absence of free cyanide, regular additions of dissolved gold must be made to keep up the strength of the bath. This may most conveniently be done by keeping at hand a supply of gold chloride either in the form of crystals or as a concentrated solution. A quantity, corresponding to about $\frac{1}{2}$ oz. Troy of metallic gold to each gallon (3·42 gr. per litre) of the solution requiring the addition, is then converted into a strong solution of the *double cyanide of gold and potassium* by either of the two methods already described. In this way additions may be made without materially adding to the bulk of the liquid in use. It will be found of great advantage after every such addition to boil the solution for a short time and then filter it. These supplies to the solution should be made at regular intervals according to the quantity of work passing through it. The most reliable indication of the need for a fresh addition of gold to a solution is found in the colour of the deposit. The characteristic rich yellow tint of fine gilding is lost and the deposit is either of a pale brass colour or of a reddish copper colour according to the current conditions.

Special treatment of Articles preparatory to Gilding.—Gold can be deposited on most metals directly without any intermediate coating of another metal; the general preparatory treatment discussed in Chap. VIII. is therefore usually adopted for preparation for electrogilding. A few special points, however, deserve mention. In the preparation of surfaces for the classes of gilding variously known as "dead," "frosted," "satin," "matte," and "grain," sand-blasting is now very largely employed and a great diversity of effects may be thus produced. In all cases of the electro-deposition of metals the surface of the deposit to a large extent partakes of the same characteristics as the surface of the metal being plated. Consequently whenever it is desired to have a finished surface on an electro-deposit of a certain character, the surface to be plated should always be given some treatment which will give to it this characteristic at least to some extent. Some very pleasing effects of this nature may be given to gilded articles by using various grades of powdered pumice in the sand-blasting apparatus at pressures varying from 3 lbs. to 5 lbs. per square inch. In many classes of work very lovely *soft* tints may be obtained in the gilding by the ordinary preliminary treatment followed by treatment on the blasting apparatus with a very fine grade of pumice at the *lower* pressure referred to.

Where the sand-blasting apparatus is not available frosted or "satin-finish" surfaces may be produced on silver or copper goods by using strong hard-wire scratch-brushes such as are supplied by makers for this purpose. These brushes should revolve at a speed rather higher than the normal.

Similar effects can also be produced by holding a block of wood firmly on an ordinary "chock" scratch-brush at a point just before it meets the article to be brushed; the bristles thus "spring" forcibly and suddenly on to the article and so impart to it the desired surface.

In gilding copper and alloys rich in copper where a light rich yellow tint is required it is very often advantageous to give the article a slight coating of silver prior to gilding.

At the present time for trade purposes—mainly for the cheaper classes of work—a large amount of gilding is done at a very low rate. The usual method of procedure is to give the article a preliminary film of copper from the alkaline bath, and then rapidly to pass it through the gilding solution to "colour up." A much better method for this class of work is to deposit the preliminary film from a brassing solution (see Chap. XVII.) worked with a very small current, either cold or only lukewarm. Under these conditions the deposit from such a brassing solution as recommended has a colour closely approaching 18-carat gold, and a very brief immersion in the gilding solution will impart quite a rich gold colour.

Reference has previously been made to the gilding of articles, chiefly silver or electro-silver plate, which have been given highly polished surfaces. Such goods must obviously be very carefully handled in preparatory treatment. They should be well washed with a clean sponge in very hot water, then passed through a boiling solution of caustic potash (about 6 oz. per gallon) and rinsed in cold water. The manner in which the clean cold water runs off the surface is an infallible indication to the operator as to whether the surface is free from grease or soapy matter; if not, the treatment must be repeated until water flows off the surface quite evenly.

All the particular types or classes of electrogilding described under the following terms are obtained by preliminary treatment of the surfaces to be gilt; namely, (*a*) Bright gilding, (*b*) Dead gilding, (*c*) Frosted, or "satin-finish" gilding, (*d*) Grained gilding. With reference to these trade terms therefore little need be added to the foregoing details. With regard to bright gilding, however, which was described in discussing the question of free cyanide in gilding solutions, it should be emphasized that the highest possible polish be previously given to the article, or the gilt finish is not satisfactory. It may further be observed that only comparatively thin films of gold can be deposited on these surfaces if the deposit is required to retain all the brilliancy of the original polish. As the gilding increases in thickness it acquires gradually a dull appearance unless special precautions are used, and will in such a case need repolishing.

Grained surfaces are sometimes produced by treating with the finest flour emery. For watch mechanisms and similar classes of work, Roseleur published a method of graining in use largely in Switzerland and France which is of considerable interest. In brief outline this method is, after rendering the surface perfectly smooth and cleansing in the usual manner, to treat the articles with a mixture of finely divided silver powder, potassium bitartrate and common salt in about the following proportions:

Finely divided silver	5 parts by weight
Potassium bitartrate	40 ,, ,, ,,
Common salt	100 ,, ,, ,,

The silver powder may be obtained by hanging strips of copper in a dilute solution of silver nitrate, so throwing down the silver as a metallic precipitate, which must be carefully washed and dried. The three ingredients are thoroughly mixed together and made into a thin paste with water. This paste is carefully and equally brushed over the entire surface to be gilt with a strong bristle brush, imparting the while a brisk and firm circular motion either to the article or to the brush or to both. The coarseness of the grain may be influenced by varying the proportions of tartar and salt in the mixture—an excess of the salt producing a larger grain.

Electric Current Conditions in Gilding.—Requirements in electrogilding vary so greatly that it is difficult to lay down definite rules as to either voltage or current density to be employed. The former, however, should never be allowed to fall below 3 volts, and for irregular surfaces and large articles of hollow ware 4 volts will give more satisfactory results.

In ordinary gilding operations by far the most reliable guide in the determination of correct current conditions is the colour of the deposited gold. This should be closely observed and the current regulated so as to produce continuously throughout deposition a deposit of a deep yellow or light yellowish-brown colour, having of course the fine grain or pearly texture of electro-deposited metal. Any deeper shade of colour, such as a distinct brown (which is very liable to be produced), will prove unsatisfactory after final scratch-brushing.

Gilding Insides of Hollow Vessels.—This is a very usual requirement in electrogilding, particularly "bright" gilding. The article to be gilt inside is filled with the solution and connected in some convenient fashion to the negative pole of the dynamo or battery, and a small sheet gold anode is hung in the centre of the liquid connected to the positive pole. For this class of work it will be found most convenient, however, to use a long and narrow piece of thin sheet gold as anode and to bind it firmly round a piece of hard wood about $\frac{5}{8}$ or $\frac{3}{4}$ inch in diameter and from 8 to 12 inches long, according to the usual depth of the work to be gilt. The gold sheet need not be as long as the wooden rod, but it is advisable that it extend so far along the rod that when immersed in the gilding solution the copper connecting wire is not also immersed. The anode and rod should now, for at least three or four inches of their length, be covered tightly with two or three thicknesses of fine chamois leather or swansdown of good quality. This arrangement serves a double purpose. In the first place it prevents a possible short-circuiting of the current owing to the anode touching the bottom or sides of the article during gilding, and secondly it enables the operator by the thorough saturation of this leather covering to draw the solution round the edges of the article, particularly irregular edges, lips of cream jugs, etc. This idea is of course adaptable (and often convenient) to other branches of electro-deposition as well as gilding, and is known in the trade as a " doctor."

Colour-Gilding.—No electro-deposited metal hitherto known is, at any rate so far as colour is concerned, so extremely sensitive to the slightest change in either current or temperature conditions or composition of electrolyte as gold. A few simple experiments in gilding with only the conditions of temperature varied will exemplify this and incidentally reveal and suggest to artistic workers some considerable possibilities in metal colouring.

This colour sensitiveness of electro-deposited gold has given rise to a branch of the industry (perhaps more largely practised in the United States than in England) known as *colour-gilding.*

The principal colours aimed at in this class of work are known as *red*, *green*, *yellow*, and *rose-colour*, but a number of different shades under each of these descriptions are obtainable.

As has just been observed, varying conditions of temperature and current will readily produce varying tints of colour in the deposited metal. In actual practice, however, the colours enumerated above are usually obtained by very slight variation in the composition of the solution employed; though the beginner in the art will find it a very great advantage to thoroughly familiarize himself with the changes obtainable by the regulation of *external* conditions before going on to the actual use of the solutions shortly to be described.

The basis of all solutions for colour-gilding is the *double cyanide of gold and potassium* made up according to either of the formulæ of pp. 223 to 226. It will, however, be usually found advantageous to dilute the solutions thus made by adding an equal bulk of water or more in order to reduce the gold content per gallon to about one-half or one-third of that recommended for ordinary gilding, the different tints of colour being as a rule more readily obtained from weaker solutions, *i.e.* those containing not more than 10 to 14 dwts. per imp. gallon (= 8·33 to 11·66 dwts. per U.S. gallon, or say $3\frac{1}{2}$ to $4\frac{3}{4}$ gr. per litre). Indeed some operators prefer baths containing as low a proportion of metallic gold as 4 dwts. per gallon. The deciding factor in the matter is, however, the *depth* of colour aimed at; if dark or deep tones are required, the metallic gold content should never be less than 10 or 12 dwts. per imperial gallon to obtain the best possible results.

The modifications of the ordinary gilding solution just referred to, usually employed for the various classes of colour-gilding, are obtained by the addition of very small proportions of other metals, mainly silver, copper, arsenic, and occasionally lead. A large number of different formulæ will be found scattered through the literature of electro-deposition, but the following will be found to yield excellent results with a little practice and proper attention to detail.

1. *Red-gilding.*

One imperial or $1\frac{1}{5}$ U.S. gallon of ordinary gilding solution containing 10 dwts. metallic gold.

200 grains of pure copper acetate (crystallized).

The copper acetate should be finely powdered and made into a thin smooth paste by the addition of distilled water. A weak solution of potassium cyanide must now be added very carefully and slowly until the copper salt is just dissolved. Add the resulting liquid (after filtering to remove impurities) to the gilding solution and boil the whole for 15 to 20 minutes.

In working this solution, which should be done at a temperature of about 70° C., it is most essential for the operator to realize that it is rarely necessary to make any greater addition of copper salt to the solution than is recommended above; and in all further additions to the bath the above proportions of copper and gold must be adhered to. It must be remembered that gold is the more electro-negative element present, and as such has a decided tendency to deposit first. After the first addition therefore more copper should never be added without a proportionate amount of gold in order to correct this tendency.

This latter point will further suggest the necessity of using a current slightly stronger than for ordinary electro-gilding. This indeed is necessary in all colour-gilding operations where the effects are sought to be obtained by adding to the bath solutions of more electro-positive metals.

2. *Green-gilding.*

One imperial or $1\frac{1}{5}$ U.S. gallon of ordinary gilding solution containing 10 dwts. metallic gold.

150 grains pure recrystallized silver nitrate.

50 grains caustic soda (quality not less than 85 per cent. NaOH).

The silver nitrate is dissolved in a sufficiency of distilled water and a weak solution of potassium cyanide added until the cyanide of silver precipitate which at first forms is completely dissolved. The resulting solution is then added to the gilding solution and the whole thoroughly stirred. Finally, add the caustic soda (first dissolved in a little water) and boil the resulting solution for twenty minutes or so.

This solution, worked at a temperature of about 70° C., yields a rich green-coloured gold of a rather dark shade. If a lighter shade is required, a rather larger proportion of silver must be added. It is better, however, to try the bath first with the above proportions and not to add any greater amount of silver until found necessary.

For green gilding some authorities recommend the addition of *arsenic*, usually in the form of arsenious oxide, As_2O_3 (more correctly arsenious anhydride). This should be dissolved in a strong solution of caustic soda and only added to the bath in very small proportions, with or without the simultaneous addition of silver. Some very pleasing shades of green gold are obtainable by these means, but arsenic alone as the added ingredient is not so reliable as silver, and in any case as small a proportion as possible to obtain the desired effect should be employed. It is very liable to spoil the gilding solution completely if by any means the bath acquires an excess.

Arsenical gold baths give the best results if a slightly *weaker* current is employed than would be the case in normal gilding operations.

3. *Yellow-gilding.*

This colour is obviously the effect obtained from the ordinary gilding solution. As the term is applied in schemes of colour-gilding, however, a very light tone of yellow, sometimes called Roman gold, is usually meant. This, where required to contrast with green or red gold in the schemes of gilding presently to be described, is not always easy to obtain. The normal colour of electrogilding is, or should be, a rich, rather dark shade of yellow, and it is consequently a little too dark to contrast properly with the red or even green tones obtained as above.

In this class of colour-gilding, however, no additions which can be made to the bath itself, with the exception perhaps of a very small amount of caustic soda, will prove so satisfactory as a proper manipulation of *external* conditions, *i.e.* temperature, voltage, and current density.

The best results are obtained from solutions containing not more than 8 to 10 dwts. metallic gold per imp. gallon ($2\frac{3}{4}$ to $3\frac{1}{2}$ gr. per litre). If the solution is newly made by either of the chemical methods before described, an addition of from 25 to 50 grains of caustic soda per gallon (0·36 to 0·72 gr. per litre) should be made. The best working temperature will be found to be not more than 60° C. with an E.M.F. of 2·5 volts, though both this factor and that of current density is largely dependent upon the class of work done. If the articles have deep recesses, a greater E.M.F.

is necessary. Exact conditions can only be determined by actual experiment.

Newly-made solutions give as a rule the best results in light yellow tones, since baths usually yield darker deposits as organic matter and other impurities are acquired in process of working.

Rose-coloured gold.—The varied tones of colour which may be described under this general heading are usually obtained by the addition of both silver *and* copper to the gilding solution.

The proportions already detailed under the respective descriptions of *red* and *green* gilding are suitable for developing this colour, but it is obvious that many varieties of tone may be obtained by varying these proportions.

An exceedingly rich effect which might be classed under the title rose-coloured gold is obtainable by first giving the article a very thin, almost infinitesimal, deposit of copper in a copper solution composed of copper sulphate and alum (see Chap. XI., p. 250). It is then thinly gilded in the yellow gilding solution and again treated in the copper vat, and finally shaded off in a normal gilding solution, using a fairly strong current.

In finishing coloured gilding pleasing effects are often obtained, particularly on ornamented surfaces having high reliefs, by very gently rubbing the raised portions with finely powdered borax or pure anhydrous sodium carbonate. This should be done by hand or a very soft swansdown dolly, and great care must be taken not to scratch the surfaces.

A sand-blasting apparatus such as is described in Chap. VII. is an invaluable adjunct to colour-gilding. Indeed for many effects needed to meet the requirements of modern art it is absolutely essential, and very careful note should be made of the recommendations in the section treating on that subject as to the use and applications of sand-blasting.

"**Parcel**" **and** "**Partial**" **Gilding.**—The use of these two terms in trade circles, often as if they were synonymous, has given rise to some confusion as to their exact meaning and application. According to the best usage and the highest authorities, however, the former term—*parcel gilding*—should be confined strictly to the art of gilding one article in a variety of colours, *i.e.* relieving the various characteristics of the surface of a chased or embossed article in red, green, or yellow gold according to any colour scheme devised by an artist or by the operator himself.

The term *partial gilding* on the other hand should be applied only to the part-gilding of an article—where for example one part of a surface is required to be finished in copper or silver and the remaining part (often chased, embossed, or engraved portions) gilt.

These two branches of the art of gilding afford considerable scope for the exercise of mechanical ingenuity and artistic skill.

Both classes of work are done by means of "*stopping-off*" varnishes—prepared according to one or other of the directions given below.

Asphaltum stopping-off varnish.—Dissolve a sufficiency of asphalt together with a little mastic (resin from the mastic tree) in oil of turpentine until the liquid is of the consistency of thin cream. Apply with a camel's-hair brush.

Copal varnish.—Take sufficient good quick-drying copal varnish and add to it ultramarine, or chrome yellow, with thorough incorporation until a thin paste is obtained. This also is applied with a camel's-hair brush, and care must be taken that it is thoroughly hard and dry before immersion in the plating solution.

Common Brunswick black mixed with a little fine asphaltum powder is also favoured by some operators.

Suppose an ornamented silver shield is required to be gilt, and finished to show a groundwork of fine yellow or green gold and all raised or embossed parts, say leaves, flowers, etc., coloured with red gold. The operator will first gild the shield over its *entire* surface in a solution giving the required yellow or green colour of the groundwork (in any colour scheme the lightest shade is given first). It is then taken from the solution, carefully washed and dried out, and with a fine camel's-hair brush every part of the shield which, when finished, is to show the yellow (or green) colour is carefully covered with the particular stopping-off varnish chosen. This is the part of the operation needing the greatest skill, and some considerable practice is necessary to become efficient. The article is then exposed to a moderate dry heat for as long a time as may be necessary thoroughly to dry and harden the varnish. When this is accomplished it is washed with warm water or sprayed and rinsed through a moderately hot solution of caustic potash. Any stains which may happen to appear on the surface should be removed by rubbing gently with a clean rag or piece of linen dipped in potassium cyanide solution. It is then finally rinsed and immersed in the red-gilding solution and the deposit continued from this solution until a sufficient depth of colour is obtained.

After the gilding is completed the varnish is removed by means of a soft brush thoroughly saturated with benzene or best turpentine. If the varnish is very refractory, as sometimes happens in cases where the baking or drying operation has been carried to extremes, it may be quickly and thoroughly removed by pouring over the surface pure concentrated sulphuric acid. Obviously great care is required in doing this, but the method is very effective.

The Assay of Gold in Gilding Solutions.—As already observed earlier in the present chapter, the exact assay of gold is a matter of skilled practice, and where absolute accuracy is required it is not advisable for the electrogilder to attempt this himself unless he has considerable knowledge of analytical chemistry. For all ordinary workshop purposes, however, the following method may with a little practice be carried out by an intelligent worker and will be found to give results quite sufficiently accurate. The principle of the method is based on the precipitation of the gold in a finely divided *metallic* condition by means of ferrous sulphate solution. It is absolutely necessary, however, for obtaining this precipitate that the whole of the cyanide contents of the solution should be decomposed, and this is done by boiling with hydrochloric acid. The details of the method are as follows.

Take a measured portion of the solution to be tested, say 2 British fluid ounces (one-tenth of an imperial pint) in a 12-oz. beaker and add not less than twice its bulk of strong hydrochloric acid. Boil the resulting liquid until there is no smell of cyanogen gas (the familiar odour of potassium cyanide itself). In the case of strong solutions a greater amount of acid is sometimes required. This part of the operation should be performed in a fume cupboard or well-ventilated place. Now add an excess of a clear solution of ferrous sulphate and allow the beaker to stand about twelve hours in a warm place. Under such conditions the gold is completely precipitated as a fine powder. The solution is then filtered and the gold powder washed on the filter with hot water, the filter and its contents are carefully dried and transferred to a weighed crucible. The crucible is then placed over a small bunsen flame and heated until the filter paper is burnt to a white ash. After cooling in a desiccator it is reweighed, and the difference in weight indicates the amount of metallic gold in the sample tested.

Recovery of Gold from old Solutions.—A similar procedure to the foregoing will be found the best method for recovering gold from old or spoilt solutions, as the metal is obtained in a form suitable for redissolving in *aqua regia* to make a new solution.

An alternative method is to evaporate the solution to dryness and thoroughly mix the residue with litharge (lead oxide) in rather more than an equal bulk. The mixture is then fused, and the whole of the gold will be absorbed by the lead which will collect in button form at the bottom of the crucible. The lead button is then dissolved in warm dilute nitric acid and thus separated from the gold which remains undissolved in the solution in a finely divided metallic condition.

Stripping Gold Deposits from old Work, etc.—This is a problem presenting some little difficulty owing to the fact that any mixture which will dissolve gold will also keenly attack the basis metal of the article. Many different methods have been suggested, but by far the best is the electrolytic method.

This is carried out by making the article the *anode* in a solution of potassium cyanide containing about half a pound of cyanide per gallon. A strip of thick gas carbon forms a good cathode, and a voltage of not less than 4 or 4½ volts should be employed.

Even by this method there is considerable risk of the basis metal being attacked as soon as any part of the gold coating is dissolved, but if the article is given a gentle motion in the solution the gold is acted upon almost uniformly and consequently the operation can be stopped immediately the gold is dissolved and any further action prevented.

Simple Immersion Processes for Gilding.—Owing to the greatly superior advantages of electrogilding by separate current, simple immersion processes have now a very limited application, and only a brief reference need be made to the subject. A difficulty inherent to nearly all published processes for immersion gilding is that the deposits obtained are so often patchy and irregular and readily show stains, particularly if the articles treated have any considerable surface. As would naturally be expected, the best results are obtained if the articles have been first given a thin coating of silver. A surface of fine silver only is thus presented to the action of the gilding bath, and the chemical exchange of metals is equal at all points.

One of the best simple immersion solutions is a modification of that recommended by Langbein, viz.

Chloride of gold	1	part	by	weight
Pure caustic potash	3	parts	,,	,,
Crystallized sodium phosphate	5	,,	,,	,,
Potassium cyanide	16	,,	,,	,,
Water	100	,,	,,	,,

The chloride of gold is dissolved in a little distilled water and the potassium cyanide, previously made into a strong solution in water, is added. The caustic potash and sodium phosphate are then dissolved in the remainder of the water required to complete the bulk of solution, and added to the cyanide solution.

The resulting bath is boiled for a short time and is used at practically a boiling point temperature.

The same precautions with regard to the preparation of surfaces must be observed in simple immersion gilding as for the separate-current process.

CHAPTER XI

THE DEPOSITION OF COPPER

UNDOUBTEDLY the most extensive commercial application of the art of the electro-deposition of copper lies in electrolytic refining operations, a constantly increasing proportion of the world's output of refined copper being produced by electro-deposition. As the electrolytic refining of metals does not, however, come within the scope of this work no attempt will be made here to discuss this section of the subject, which certainly demands at least a complete volume for adequate treatment.

Of other applications of the electro-deposition of copper the more important are electrotypy; the production of tubes, wire and sheet copper; and the coating of other metals, mainly iron, zinc, and alloys of the baser metals, with copper, for either protective or ornamental purposes. Of these again only the last-named can be regarded, strictly speaking, as electroplating; but as the main lines of research and progress in the history of the deposition of copper have arisen chiefly in connection with the development of the former industrial applications, they deserve at least a brief account in the following pages.

Properties of Copper.—Copper is a lustrous metal of a peculiar reddish-brown colour. It is extremely tough and can be readily drawn into wire or hammered out into thin leaf. In its pure state it is an exceptionally ductile and malleable metal, but a very small percentage of some impurities considerably impairs these qualities.

Electro-deposited copper, newly liberated from an electrolyte under correct current conditions, has a most pleasing and characteristic salmon-pink colour.

Copper is not very susceptible to the action of dry air at ordinary temperatures, but in a moist atmosphere it is readily attacked, and if much carbon dioxide (CO_2) is present the surface becomes coated with a greenish coloured stain which is a basic carbonate of copper somewhat troublesome to remove. Heated in air or oxygen, black copper oxide is formed.

Next to silver, copper is the best conductor of electricity and is undoubtedly the most efficient metal to use for current distribution in electroplating outfits.

Nitric acid, either dilute or concentrated, dissolves copper very readily, but hydrochloric acid and dilute sulphuric acid attack the metal but slowly. Concentrated sulphuric acid is without action on copper if cold, but on heating, copper sulphate is formed with liberation of sulphur dioxide (SO_2), thus:—

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

Compounds of Copper.—Copper forms two series of compounds, originating from two oxides, cupric oxide CuO, and cuprous oxide Cu_2O, respectively. The latter are colourless, but the former in their usual condition, which is hydrated, are either blue or green.

The most common salts of copper are the sulphate, chloride, and nitrate. Of these the first named is by far the most important in electro-deposition, since it is rarely that either metallic copper or any of its salts other than the sulphate is used, in the first instance at any rate, for making up electrolytic solutions of copper.

Copper sulphate, often known as blue vitriol or bluestone, is produced in large quantities as a bye product in smelting operations and other chemical industries. In its usual form, crystallized out from aqueous solutions, it occurs in characteristic blue triclinic crystals having the formula $CuSO_4.5H_2O$. Its solubility in water is as follows:—

	Temperature. Degrees centigrade.						
	10°	20°	30°	50°	70°	90°	100°
Parts of $CuSO_4.5H_2O$ soluble in 100 parts of water	36·95	42·31	48·81	65·83	94·60	156·44	203·32

It is practically insoluble in alcohol.

If crystallized copper sulphate is heated to 100° C., water is expelled and a bluish-white powder is obtained containing only one molecule of water, $CuSO_4.H_2O$. On continuing the application of heat up to 200°–260° more water is driven off, but it is very difficult to obtain the salt wholly anhydrous.

Commercial copper sulphate, particularly the recrystallized salt, is generally of a high degree of purity—98 to 99 per cent. Its usual impurity is iron, of which small traces are often found in the trade varieties. The following is one of the best methods of testing for this impurity:—

Dissolve 4 grams of the salt, powdered in 100 c.c. of distilled water. Add 5 c.c. of pure nitric acid warm for five minutes, and then add ammonium hydrate in excess until a clear deep-blue liquid is obtained. Keep warm on a hot plate for about twenty minutes, then filter through a white filter paper, and wash the filter with dilute ammonia until the blue solution is entirely removed. If iron is present, the paper will show a reddish stain of ferric hydroxide.

Copper nitrate is formed by dissolving copper in dilute nitric acid and allowing to crystallize out. This salt is extremely deliquescent and very readily soluble in water. Its formula is $Cu(NO_3)_2.3H_2O$.

Cupric chloride, $CuCl_2.2H_2O$, is formed when copper is dissolved in *aqua regia* or by dissolving cupric oxide in hydrochloric acid. It is a deliquescent salt, easily soluble in water. The trade varieties usually contain traces of copper sulphate and iron salts.

Cuprous chloride, Cu_2Cl_2, may be prepared by boiling a solution of cupric chloride in hydrochloric acid along with copper turnings or foil; the nascent hydrogen thus liberated reduces the cupric salt to the cuprous. Cuprous chloride is insoluble in water so that when the liquid is poured into water, the salt is precipitated as a white crystalline powder. It dissolves readily in ammonia and in alkaline chlorides.

This salt is at present little used in electroplating operations, but proposals have often been made for its use, for reasons of greater current efficiency. According to the electrolytic theory of valency it will be clear that, theoretically, double the amount of copper should be deposited from electrolytes of the cupr*ous* salts than from those of the cupr*ic* compounds; consequently if it is found possible to use the former salts, a very great saving of current should be effected.

The great obstacle has been their very unstable character and the consequent difficulty of obtaining a suitable electrolyte. It has recently * been found, however, that a saturated solution of cuprous chloride in solutions containing about 25 per cent. of sodium chloride together with about 5 per cent. of free hydrochloric acid yields results showing a current efficiency of 90 per cent., the conductivity of the solution being stated to be equal to that of the ordinary copper sulphate solution generally used.

Solutions for Deposition.—Solutions for the electrodeposition of copper are divided into two classes, "acid baths" and "alkaline baths."

The former class presents by far the greater number of advantages in respect of simplicity, ease of working and high conductivity, but is unfortunately entirely unsuitable for use in plating the more electro-positive metals, zinc, iron, tin, etc., owing to the ease with which these latter displace copper from most of its compounds. Whenever, therefore, these metals or their alloys have to be coppered, the alkaline solutions must be chosen. For electrotypy and the solid deposition of copper in the production of tubes, sheet, wire, etc., as also for coating brass and similar metals, the acid baths are invariably used.

Acid copper solutions.—In their simplest form these

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* Thompson and Hamilton, *Trans. Amer. Electro-Chemical Soc.*, May, 1910.

solutions are copper sulphate dissolved in water together with a slight excess of sulphuric acid; and such solutions of a strength of from 1½ lbs. to 1¾ lbs. of copper salt per imperial gallon (1¼ to 1½ lbs. per U.S. gallon) yield excellent deposits of copper.

The usual formula is as follows:—

Copper sulphate	1¾ lbs.	875 gr.
Sulphuric acid	4 to 8 oz.	125 to 250 gr.
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

In modern practice, however, some modifications of these baths have been introduced which deserve attention in detail, the object being to obtain increased conductivity of solution and a finer quality of deposit.

Many years ago Sir J. W. Swan drew attention to the fact that exceedingly minute additions of glue or gelatine to some copper depositing solutions exercised an important modifying influence on both the conductivity of the solutions and the character of the deposit. In the case of solutions of copper nitrate, for example, which under ordinary circumstances do not give at all a satisfactory deposit of copper, the addition of a very small proportion of glue made it possible to obtain a beautifully smooth, reguline, and coherent deposit of copper at a fairly high rate of deposition.

Since that time many operators have made use, to a greater or lesser extent, of what are now generally known as "addition agents" not merely to copper solutions but to those of other metals, as has already been indicated. In this connection, however, electrolytes of copper have been more extensively experimented with than have other metals, as indeed is natural in view of the extensive applications of copper depositing.

Before dealing with the various re-agents suggested or actually used, it should be explained that in the present state of our scientific knowledge of the exact nature of the chemical and electro-chemical actions occurring during electrolysis it is impossible to explain satisfactorily the reason of many effects observable in practice. But there seems good reason to believe that many substances in electrolytic solutions play a part very analogous to that familiar in chemistry as catalysis due to catalytic agents, *i.e.* substances which take part in or modify a chemical action without themselves entering into combination or being changed in composition.

In some recent researches it has been suggested that these addition substances act as colloids, which, given favourable conditions, move to the cathode, and materially affect the character of the metallic deposit by cutting down the size of the crystals of the precipitated metal, and in this way allow of the use of greater current densities without as a result giving rise to rough or nodular deposits.

It is of the greatest importance, however, to realize that these actions depend not only on the particular addition agent used but on the chemical constitution of the electrolyte. For example, Müller and Bahntje* found that "in acidified copper sulphate solutions, starch, and gum arabic, did not move to the cathode and did not cut down the size of the copper crystals when the solution was *slightly* acid, but did both these things when the solution was made *more* acid."

It has indeed been observed in regard to electrolytes of other metals that addition substances were much more effective in solutions which contained an excess of free acid.

These addition agents are by no means confined to organic compounds like glue, gelatine, or starch, but include a number of inorganic compounds, particularly salts of the more extremely electro-positive metals, such as the alkaline earths and aluminium and tin. Salts of the last two named have often been used in acid coppering baths.

Since this subject is at present in a very incomplete state of development, much investigation remaining to be made, it is obviously impossible to lay down here any specific formulæ as the best for all purposes; the choice of an addition

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* *Zeit. Elektrochemie*, **12.** 320 (1906).

re-agent must be dependent upon local conditions and particular requirements. Of a very large number of substances recommended for addition to acid copper baths the following should be named as the most generally used.

Organic compounds.—Benzoic acid, tannic acid, gelatine, glucose or dextrine and hydroxylamine.

Inorganic compounds.—Alum (the double sulphate of aluminium and potassium), sodium chloride, ammonium chloride, and aluminium sulphate.

According to our experience the latter class—the inorganic salts—are to be preferred to the former. There seems little doubt that gelatine alone, though under favourable conditions allowing the use of higher current densities in electrolytes, has a tendency to render the deposit brittle.

Both alum and aluminium sulphate give very good results. The following formula, which has recently been strongly recommended by an American writer, is an example of several of this class—

Copper sulphate crystals $CuSO_4.5H_2O$	$1\frac{3}{4}$ lbs.	1 kg.
Sulphuric acid	3 oz.	107 gr.
Alum	2 to 3 ,,	72 to 107 gr.
Water	$\frac{5}{6}$ imp. gall. or 1 U.S. ,,	5 litres

A report of a fairly exhaustive research into this question of addition agents to copper sulphate solutions, by a Chinese graduate (Ching Yu Wan) of Columbia University, U.S.A., has recently been published,* and the results are extremely interesting as bearing on the question of obtaining pure deposits from impure solutions. According to this investigator, the most successful addition agent of a large number tried particularly in solutions containing up to 8 per cent. of arsenic was a combination of an organic and inorganic compound in the shape of gelatine and common salt. The

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* (Abstract) *Metallurgical and Chemical Engineering*, June, 1911, vol. ix. No. 6, pp. 318–19.

results showed that a deposit of the highest purity and greatest ductility was obtained by the addition of from 0·01 to 0·02 per cent. gelatine and 0·02 to 0·03 per cent. of sodium chloride. It must be noted, however, that these experiments were conducted in electrolytes containing arsenic, which substance itself may act as an addition agent, and influence the deposit though not itself liberated.

Of very great importance also is the amount of free sulphuric acid allowable in acid copper solutions. The effect of free acid is to increase appreciably the conductivity of the solution and at the same time to facilitate the dissolving of the copper anode, thus maintaining the strength of the bath.

Considerable diversity of opinion and of practice exists in regard to the question of the most suitable proportion of free acid to use, but the determining factor is really the particular purpose of the electrolyte, whether to be used for protective coatings, for solid deposition, or for refining operations.

Cowper-Coles * for solid deposition of copper has obtained excellent results from the following solution :—

	Oz. per imp. gall.	*Percentage by weight.*
Copper sulphate $CuSO_4.5H_2O$	32	14·87
Sulphuric acid H_2SO_4	12·6	10·77
Water		74·36

But such a proportion of free acid is rather too high for electrotypy, or for ordinary plating operations.

For the latter it may be taken as a fairly safe generalization that the proportion of free sulphuric acid should not exceed 8 oz. per gallon (50 gr. per litre), and many experienced operators prefer slightly less than this proportion, particularly if an inorganic addition agent be used, but to a large extent this point depends also on the current density employed and will be discussed again later.

Alkaline Copper Solutions.—The basis of practically all

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* *Journ. Inst. of Elec. Engineers*, vol. xxix., January, 1900, p. 276.

alkaline copper baths in commercial use now is the double cyanide of copper and potassium—a solution very analogous to that used for the deposition of silver. Some few writers recommend in preference the less poisonous tartrate bath made usually by dissolving a copper salt in a strong solution of potassium sodium tartrate together with an excess of caustic soda. But such a bath is inferior in many respects to the cyanide solution.

The simplest method of making the latter is to dissolve copper carbonate or copper acetate in a strong solution of potassium cyanide in such a proportion as to obtain a metallic content of not less than 2 oz. per imperial gallon ($1\frac{2}{3}$ oz. per U.S. gallon, or $12\frac{1}{2}$ gr. per litre).

These salts of copper (the carbonate and acetate) are, however, relatively rather expensive, so that in general workshop practice the solution is made, starting from metallic copper, or copper sulphate, which latter is much the cheapest copper compound available.

To prepare the cyanide solution from metallic copper, dissolve 3 to 4 oz. of grain copper in warm nitric acid (1 part acid, 1 part water). Dilute the solution to about 1 imperial pint or more by adding water. Make up now a strong solution of sodium carbonate and add this to the copper solution, stirring meanwhile, until no further precipitation occurs. The precipitate is copper carbonate; wash this with warm water two or three times; and finally add to it a strong solution of potassium cyanide (4 oz. per pint or 20 gr. per 100 c.c.) until the precipitate is completely dissolved. Note the quantity of cyanide solution used and add 10 per cent. more as free cyanide. Boil the resulting solution for a few minutes and make up the bulk to one gallon by adding water. This method is a very old one and is largely used in the older plating establishments, with the addition usually of ammonia or ammonium carbonate.

A more convenient method, however, is to prepare the solution from copper sulphate. The following formula will yield excellent results—

Copper sulphate ($CuSO_4.5H_2O$) . . .	16 oz.	500 gr.
Ammonia, 0·880	Q.S.	
Potassium cyanide 95 per cent. . .	18 oz.	560 gr.
Potassium bisulphite	2 to 3 „	62·5 to 93·75 gr.
Water	1 imp. gall. or 1⅕ U.S. „	5 litres

Dissolve the copper sulphate (powdered) in about one quart of water, and when completely dissolved add ammonia until the bluish-white precipitate, which at first is observed, completely redissolves, and an intense deep-blue solution results. The effect of the addition of ammonia to copper sulphate is first of all to throw down a basic sulphate of copper; then as further ammonia is added this dissolves, and the deep-blue solution obtained is known as an aqueous solution of cuprammonium sulphate ($CuSO_4.4NH_3.H_2O$). The potassium cyanide which meanwhile should have been dissolved in about 1½ pints of water is now slowly added to the copper solution obtained as above, and towards the end of the addition it will be noted that the deep-blue colour changes to a purple, and then the liquid quickly becomes clear and colourless. If the potassium cyanide is of a weaker strength than above specified, more will be required, but in any event the best guide as to the quantity of cyanide to use is to note the point of the complete discharge of the blue coloration which marks the formation of the double cyanide of copper and potassium. Further additions beyond this point are for free cyanide, and should not much exceed 20 per cent. of the quantity used to obtain the double salt. The potassium bisulphite dissolved in a small quantity of water is then added, the solution boiled for a few minutes, and the liquid made up to one gallon with water.

The addition of the potassium salt is made to improve the conductivity of the bath, the double cyanide solution alone being relatively rather a poor conductor. Several other salts have been recommended in this connection, notably potassium carbonate, but inasmuch as the bath while in use gradually acquires a considerable proportion of this salt through decomposition and contact with the atmosphere, it is inadvisable to make any such addition when preparing the solution.

Another formula which yields a solution giving a very fine deposit of copper, and which we have often used for ornamental copper coatings on zinc and similar metals or alloys, is one of several originally introduced by Roseleur. As given below, however, it is slightly modified :—

Copper acetate	6 oz.	187 gr.
Anhydrous sodium carbonate . .	4 „	125 „
Sodium bisulphite	4 „	125 „
Potassium cyanide, 95 per cent. .	8 „	250 „
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. „	5 litres

To prepare the bath, make up the copper acetate into a paste by adding a little water as required. Dissolve the sodium carbonate in about one pint or a little more of water and add to the copper compound. Stir the resulting mixture vigorously. The acetate is thus converted into the carbonate of copper. Now add the sodium bisulphite dissolved in a further pint of water, and finally the potassium cyanide also dissolved in a sufficiency of water. The resulting liquid should, and if pure materials have been used will, be practically clear and colourless. It must now be boiled for half an hour or so, made up to correct bulk by the addition of water, and is then ready for use.

This bath may be used either hot or cold, but is preferably worked at a temperature of from 60° to 70° C.

Of other alkaline solutions for coppering which have been suggested the only ones which need be mentioned here are the tartrates to which reference has already been made.

The two following are representative solutions of this class.

Formula (1) (Weil)—

Copper sulphate	$7\frac{1}{4}$ oz.	225 gr.
Potassium-sodium tartrate . . .	36 ,,	1125 ,,
Caustic soda	17 ,,	530 ,,
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres

The copper salt is dissolved in a sufficiency of water, say one pint, and added slowly to the remainder of the water in which the tartrate and caustic soda are jointly dissolved. If any undissolved substance remains in solution after vigorous stirring it should be filtered off.

Formula (2) (Elsner)—

Potassium bitartrate	8 oz.	250 gr.
Potassium carbonate	1 ,,	31·25 gr.
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres
Copper carbonate	Q.S.	

The potassium bitartrate is dissolved in the whole of the water by boiling, and freshly precipitated wet copper carbonate stirred into the solution to as great an extent as the liquid will dissolve. The addition of the small proportion of potassium carbonate ensures the alkalinity of the bath.

Neither of the foregoing baths are, however, so reliable as the cyanide ones previously given.

It may be of interest also to mention that Dr. F. W. Kern, whose nickel fluosilicate bath is referred to in the following chapter, has more recently patented (Amer. pat. 946.903, Jan. 1910) an exactly similar solution for the deposition of copper, the approximate formula being:—

Copper fluosilicate, 10 parts	by weight
Ammonium fluoride and aluminium fluosilicate, 5 parts each	
Water, 100 parts	

In the case of copper, however, the patentee prefers to add a small proportion of gelatine.

An important point with regard to cyanide coppering solutions is the proportion of free cyanide necessary or advisable. The action occurring in these baths, according to Hittörf, is, at the cathode the liberation of potassium (K) and the deposition of copper as a secondary action, and at the anode the separation of the complex radicle $Cu(CN)_2$; dissociation of the double cyanides occurring thus:—

$$KCu(CN)_2 = K + Cu(CN)_2 \text{ (compare silver).}$$

The potassium ion attacks the surrounding molecule of double salt and liberates copper, thus—

$$K + KCu(CN)_2 = 2KCN + Cu \text{ (deposited).}$$

The anion $Cu(CN)_2$ is of course liberated at the surface of the anode, which is of sheet copper, and the cyanogen radicle (CN) seeks to combine with the metal to form copper cyanide (CuCN). Consequently as each molecule of copper is deposited at the cathode an equivalent of copper cyanide forms at the anode.

Copper cyanide, however, like the corresponding silver salt, is insoluble in water, and even in potassium cyanide is soluble with greater difficulty than silver cyanide. Hence the necessity, even to a greater extent than in silver baths, for the presence of free cyanide. On the other hand, it must be borne in mind that cyanide copper baths are usually worked warm, 70° to 80° C., and under these circumstances the single cyanide is more soluble than in cold solutions.

In workshop practice, therefore, a proportion of 20 to 25 per cent. of free cyanide is generally sufficient, and it will be found advisable in the case of a new solution to commence with 10 to 15 per cent. as instructed, and add a little more from time to time as the bath is worked and as found necessary.

A large excess of free cyanide is very harmful, particularly in coating zinc and iron and steel goods. Furthermore, in the case of coppering from the cyanide bath it is not so essential as in silver plating that the proportion of free cyanide be high enough to keep the anode surface absolutely free from the film of single cyanide which forms, inasmuch as the time of immersion is comparatively very brief, the purpose being, usually at any rate, to give a preliminary coating only. The bath therefore has plenty of time to effect solution of the anode slime by diffusion.

It will be found necessary from time to time to make further additions of copper to the bath, since under the above circumstances the solution is not sufficiently replenished by solution of the anode. Such additions are best made in the form of copper carbonate—a salt which can be either made in the workshop or obtained commercially of a high degree of purity. Similar additions should also be made in cases where baths contain excess cyanide; a small quantity placed in a muslin bag and suspended in the vat (stirring the latter frequently) will speedily restore such a liquid to correct conditions.

It may here be advisable to remark that in cases where the operator has had little experience in chemical manipulations he will find it of distinct advantage to make up new solutions by means of copper carbonate purchased from reputable manufacturers, the only possible objection being, as has been mentioned, the increased cost.

In such cases the following formula may be adopted:—

Copper carbonate	5 oz.	156 gr.
Cyanide of potassium, 95 per cent. .	8 ,,	250 ,,
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres

Dissolve the cyanide in two pints of water and slowly add the copper compound, stirring until completely dissolved, then add remaining quantity of water.

Anodes.—Whether for acid or alkaline baths anodes should be of pure sheet copper of a thickness of about 0·03 in. and of sizes proportionate to the vat. They should be annealed at a dull red heat before using, and thoroughly cleansed and scoured before immersion in the solution. In acid coppering under correct conditions the anodes will work clear throughout, but in alkaline coppering this is rarely the case, and it is advisable to remove them occasionally for cleansing, the slime formed in cyanide solutions being very refractory and tending to interpose considerable resistance to the current.

Electrical Conditions.—For the alkaline bath the difference of potential between electrodes measured at the terminals of the vat should be about 4 volts. It is difficult to give any figures for current density, as this depends largely on the class of work being dealt with, and as the purpose of alkaline coppering is in most cases to give merely a preliminary film or coating it is also hardly necessary. In acid coppering, on the other hand, the question of current density as well as E.M.F. is of great importance. The latter is usually 1 to 1½ volts, but the former factor varies enormously and depends not only on the nature of the work being done but also on the constitution and temperature of the electrolyte, which likewise affects to some extent the E.M.F.

In the determination of the correct current conditions for the electro-deposition of copper from the acid bath, the following general principle must be foremost in mind, viz. as in all other electrical operations, current density is dependent upon the E.M.F. and the resistance of the circuit. For the same C.D. (current density) a decreased resistance will mean or require a less E.M.F. (see Chapter III.).

Consequently the alteration of any factor in the conditions of electrolysis which will affect the conductivity, or, what is the same thing, the resistance of the electrolyte, will mean a change in the values of both E.M.F. and C.D. required.

Such alterations are caused mainly as follows:—

(1) By increase of temperature of the solution.

(2) By the addition of substances to the electrolyte to increase conductivity.

(3) By the agitation of either cathodes or electrolytes.

(4) By increase of the proportion of free acid.

All these factors, either in combination or separately, have the ultimate effect of allowing a larger current to pass at a lower voltage. In addition, it is most important to bear in mind that solutions having a comparatively small proportion of metal content will only permit of the use of low current densities to obtain satisfactory deposits.

This question has been the subject of research by several experimenters, notably von Hübl, whose investigations have been of great value to subsequent workers. His results, obtained from solutions of copper sulphate alone or with free sulphuric acid only, indicate that for baths of approximately the composition of that on p. 248, the maximum C.D. allowable is from 15 to 20 amperes per square foot of cathode surface, the electrolyte being at normal temperature and in gentle motion.

By means of increase of temperature, addition agents, or agitation of cathodes or electrolyte, however, these values may be very considerably exceeded, as also within certain well-defined limits by increase of free acid. It is not, however, advantageous to go beyond the figure already advised in this direction. Of the other factors tabulated above, the second and third are those most usually taken advantage of.

Solutions containing suitable addition agents yield excellent deposits at current densities of from 25 to 30 amperes per square foot and even slightly higher. Values much above these figures can only, however, be employed in solutions subjected to violent agitation. The most interesting recent experiments in this direction have been those of Mr. Cowper-Coles,* who by means of rapidly rotating cathodes obtained smooth reguline deposits of copper in the production of copper tubes, etc., with current densities as high as 170 amperes per square foot.

General Remarks on Coppering.—The electro-deposition of copper is probably the least difficult of all branches of electroplating, but several important difficulties often arise owing to the nature of the basis metals usually

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* *Journ. Institute of Electrical Engineers*, vol. xxix. p. 265.

dealt with. Iron castings, for example, often give the operator considerable trouble in coppering (as also brassing) owing to their porous nature, by "spotting-out," as it is termed, after plating. No matter how carefully these have been prepared in the first instance before plating, or how thoroughly rinsed and dried out afterwards, small round spots or patches appear at intervals along the surface on standing, and in the case of articles being given a first coating in an alkaline bath, and subsequently transferred to an acid bath for heavier deposit, these spots considerably interfere with the protective value of the deposit. Many suggestions have been made for dealing with this trouble, but one of the simplest and generally a very reliable one is given by Langbein, who recommends after bringing the articles from the cyanide bath their immersion for from three to five minutes in a very dilute solution of acetic acid (1 part acid—50 parts water), afterwards rinsing in clean running water, dipping again for a few minutes in lime water, and finally rinsing and drying off. It is also advisable in dealing with this class of work wherever possible to resort to the sandblast instead of to acid dips and pickles for preliminary cleansing.

Castings of antimony, lead, tin, or zinc, and alloys of these metals are also liable to this trouble and should be given similar treatment. Emphasis must also be laid upon the necessity for a strong and perfect coating of copper to be given to these goods in the alkaline baths before they are transferred to the acid bath, which is usually necessary to obtain a sufficient thickness of deposit for protective or ornamental purposes. If these articles are immersed in acid copper baths, with a coating from the alkaline bath of an imperfect character, they will often be irretrievably injured.

The Assay of Copper Solutions.—A number of methods of estimating the content of metallic copper in plating solutions have at various times been published, and it is not easy to decide which is most suitable for electroplaters' requirements. For obtaining rapid and at the same time accurate results we prefer, however, the volumetric method known as the "iodide"—a method very largely used in works' laboratories in metallurgical practice. This method, while rather more complex than some others, is much more accurate when other metals are likely to be present, and is, therefore, adapted for the estimation of copper in solutions for depositing copper alloys such as brass, bronze, German silver, etc. An experienced works' chemist of the authors' acquaintance writes to us, "From long experience I can recommend the Iodide as an excellent method. The outlay of apparatus is small; the end point with care can be judged to one drop; and with a little experience duplicate assays should not differ by more than 0·1 per cent." The only common metals which interfere are iron and bismuth, and these are not likely to be present in ordinary coppering solutions.

The following is a practical description of this method—theoretical considerations being omitted—for acid copper solutions; cyanide solutions are given a preliminary treatment, as will be explained later.

Measure out by means of a pipette 20 c.c. of the solution to be tested, and deliver into a tall beaker. Add to this a cold saturated solution of sodium carbonate until the copper is *just* completely precipitated—the beaker should be covered as much as possible during this process as the effervescence is rather violent. Stir the solution vigorously and allow to stand until the precipitate settles, so that the liquid may be tested by adding a further few drops of sodium carbonate solution. Now add just sufficient acetic acid to redissolve the copper salt (a small excess does not matter). Weigh out next about ten times as much powdered potassium iodide as copper believed to be present in the sample; in most cases this proportion will be about 4 to 5 grams of potassium iodide. Add this salt slowly and carefully to the solution in the beaker, again keeping the beaker covered to avoid any possible loss. When effervescence has ceased, wash down the sides and rim of the beaker with a spray of distilled water. The solution, which is brown in colour, is now ready for titration, and for this purpose two solutions are required.

(1) *Sodium thiosulphate (hyposulphite) standard solution*, containing 39·5 grams of the pure salt per litre. This solution may be prepared in the workshop, or bought ready standardized. If the former, it must be first standardized by testing it, according to the method now being described against a known weight of pure copper in solution. For platers' requirements it is more convenient to buy the solution prepared—as required. 50 c.c. of this solution are equal to 0·505 gram copper.

(2) *Starch solution.*—This is required as an indicator of the end of the reaction. Prepare by boiling a pint of distilled water and stirring into it 1 or 2 grams of powdered starch previously made into a thin paste with a little cold water.

To carry out the estimation:—Fill a 50 c.c. burette (see p. 177) with the thiosulphate solution, and carefully run the latter into the copper solution in the beaker with agitation of the latter until the brown colour fades to a yellow and the bleaching action of the thiosulphate is only faint by contrast. Now add about 15 c.c. of the starch solution to the beaker content and mix well. Again carefully run in the standard solution from the burette until the violet colour which the starch produces begins to fade; proceed now very cautiously, one drop at a time, shaking vigorously; the colour will slowly fade until one drop bleaches it to a cream shade. This is the end point. Read off the figure on the burette, marking quantity of solution used, then add just one drop more—if this causes a decided lightening of colour where it fell, the titration was not quite complete and the last reading would be correct.

Example of three experiments:—

Burette readings 43, 42·8, 43·1
mean taken as 43.

$$50 \text{ c.c.} = 0{\cdot}505 \text{ Cu}$$

$$\therefore 43 \text{ c.c.} = \frac{0{\cdot}505}{50} \times 43 = 0{\cdot}434 \text{ gram.}$$

This figure 0·434 gram is the weight of copper in 20 c.c. of solution. To obtain the weight in avoirdupois ounces per gallon, multiply by 8. Thus the above solution contained $0{\cdot}434 \times 8 = 3{\cdot}47$ ounces of copper per gallon.

Cyanide solutions of Copper.—These can be assayed by the same method as above described, but the whole of the cyanide must first be decomposed by boiling with excess of sulphuric acid. The addition of sulphuric acid must be made until the precipitate of copper cyanide which first forms is completely dissolved. The boiling of the liquid must be continued until the bulk is reduced to about its original measure, and the assay then carried out according to the directions in the previous paragraph. The decomposition of the cyanide solution must be carried out in a draught cupboard or in the open air, as the poisonous hydrocyanic acid gas is freely evolved.

Estimation of Free Acid in Copper Baths.—The simplest method for workshop purposes is to neutralize the acid by means of a standard alkali solution. This may be carried out by preparing, or purchasing, a standard solution of pure sodium carbonate, containing 10·6 grams of Na_2CO_3 per litre. Take 25 c.c. of the copper solution, dilute with an equal quantity of water and place in a flask or beaker. Now charge a burette with the standard sodium carbonate solution and add this slowly to the copper solution, stirring constantly. Continue the addition until a faint *permanent* precipitate ensues, and read off the figure on burette. Repeat the experiment two or three times until a good agreement between readings is obtained. The principle of the method is very simple. The reaction between the alkali and acid is thus expressed—

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O$$

Molecular weights $106 + 98$

106 parts of sodium carbonate will, therefore, exactly neutralize 98 parts of sulphuric acid, and consequently 1 c.c. of the standard soda solution is equivalent to 0·0098 gram

H_2SO_4. The end of the reaction, showing when the whole of the sulphuric acid is neutralized, is determined by the appearance of a faint green precipitate, which indicates that the copper is now being precipitated as copper carbonate. The first sign of a permanent turbidity, therefore, makes the point at which the burette reading must be taken.

For the approximate estimations, which are often all that is necessary in electroplating practice in the deposition of copper, it will be sufficiently accurate to calculate the proportion of acid present on the basis that

1 c.c. soda solution = 0·01 gram sulphuric acid
or 100 ,, ,, = 1 ,, ,,

Free Cyanide in Copper Solutions.—The estimation of free cyanide in copper solutions is carried out exactly in the manner described at length in the section dealing with a similar estimation in silver solutions (see p. 211).

ELECTROTYPY.

The art of electrotypy is that of the reproduction of exact copies of objects of art, woodcuts, medallions, or even natural objects by means of electro-deposition of a metal, usually copper.

The present chapter, therefore, is a suitable place for a brief description of an art which is closely akin to that of the electroplater, and which indeed the electroplater is often called upon to pursue to a greater or lesser degree. Exigencies of space will, however, preclude anything further than a general outline of the simpler processes in use.

Electrotypy is made possible by reason of the peculiarity possessed by electro-deposited metal of following exactly every line or indentation, no matter how fine, in the object upon which it is deposited. Consequently if this coating, after reaching a sufficient thickness to make it feasible, is removed, its reverse will be a perfect reproduction of the surface from which it has been taken.

The first essential, therefore, is the preparation of the object to receive the deposit. Where this is a metal, the only requirement is to give, by means of moistened blacklead or extremely thin oil or similar material, a slight film which will prevent that perfect adhesion of the deposit which is the aim of the electroplater but obviously not of the electrotyper. Usually, however, moulds must be taken in non-metallic substances of such a nature as to be capable of taking a perfectly fine and accurate impression of the object to be copied. Such an impression is of course a reverse of the actual surface, and the deposit therefore, being taken off this is a true copy of the original.

By far the most generally useful material for this purpose is gutta-percha, alone or mixed with other substances, such as marine glue, lard, or tallow. The main advantages of gutta-percha as a moulding material are that it is, by moderate heating, easily rendered soft and pliable, and yet on cooling becomes sufficiently hard to withstand subsequent treatment, while at the same time it possesses a degree of elasticity which enables it to be used for copying surfaces in high relief.

The methods adopted in moulding depend entirely on the nature of the object to be copied. In the case of simple flat work the original may be placed on a flat board, the gutta-percha softened in hot water, placed on the centre of the object, and pressed carefully into every recess, working from the centre outwards (so preventing accumulation of small air-bubbles) until the surface is perfectly covered.

Usually, however, the work is more intricate and delicate, requiring much more careful and skilful handling, particularly in cases where the object is thin and easily bruised. For such classes of work a preliminary operation technically known as "making the block" is necessary. The "block" consists of two slabs of gutta-percha, one having the article to be copied firmly embedded in it with the surface to be copied uppermost, the other bearing just a faint impression or outline of that surface. These when together are surrounded with a strong iron ring, the depth of which is about

1 inch less than the total thickness of the "block" itself. This procedure enables the operator to apply a much greater pressure exactly where required, so ensuring a clear and well-defined impression.

The whole process of preparation of moulds is, therefore, divided into three stages :—

1. Making the block.
2. Taking the impression.
3. Preparing the mould for the depositing vat.

1. *Making the block.*—First soften sufficiently large slabs of gutta-percha by placing in hot water, or warming in a vessel immersed in hot water. When soft, the operator must be careful not to handle it except with hands thoroughly moistened with soapy water. The same remark indeed applies to anything which the soft gutta-percha is to touch. If the article to be copied has raised portions with corresponding hollows below, the latter must be filled up with the moulding material until the back is quite level with the outer edge. Now take one slab of gutta-percha 1½ to 2 inches in thickness and of an area a little in excess of that of the model. Lay the latter as above prepared on this and press until the lowest edge is just level with the gutta-percha surface. When feasible, loops are sometimes soldered to the back of the model in order to give it a firm "grip" to the block.

The block, after being surrounded by an iron rim deep enough to stand a little above the gutta-percha itself, must now be set aside to cool, and when hard, any portions of the outer edge which stand higher than the model must be pared off.

It will be obvious that the original is now so placed as to stand any pressure which may be applied in making the mould proper.

Next brush the block over with soapy water and take a second slab of softened gutta-percha of similar size and area to the first, and press gently on to the first surface. This block will of course be kept within bounds by the iron rim.

Again set aside to cool. In this way the second or upper slab containing a faint outline of the model is obtained. This must be removed for the second operation. The completed block is now ready.

2. *Taking the impression.*—The next operation is to take the impression. Briefly this is accomplished by pressing a small quantity of prepared gutta-percha into every part of the surface of the model.

Take a sufficiency of softened gutta-percha equal in area to "block" and about 1 inch thick. Knead thoroughly to remove any hard or foreign matter which may be present in the material and until a smooth surface results. Lay this out on a wet flat stone and brush over lightly with fine "electrotype" plumbago. Any air-bubbles or broken surface can now be seen and must be remedied. Again thoroughly brush with plumbago until the surface has a fine polished appearance. Take now the material thus prepared, hold it by the edges with the plumbago surface downwards, allow to "sag" and lower it gradually on to the model. In this way the soft material touches the article in the centre first and is then allowed gently to cover the whole surface. Now replace the top section of "block" and convey the whole to the "press." For large work a toggle press is usually employed, but for smaller articles an ordinary letter-press will be found quite satisfactory.

The block, containing between its upper and lower sections the original model in perfect contact with soft pliable gutta-percha, is now subjected to a moderately firm pressure in such a press. After two or three minutes release the pressure for a short time to allow any imprisoned air to escape. Then screw up to full pressure and leave until the mould is perfectly cold and hard. When this is so take out of the press, and by means of a mallet knock off the iron frame, thus releasing the two sections and allowing the mould proper to be taken away. The latter is now ready for wiring and rendering conductive.

When both sides of an article are to be copied as in statuary, for example, moulding composition must be applied to the bottom section and the object embedded halfway, the dividing line being made very exact. The upper half is then similarly treated and the process continued as above described.

3. *Preparation of mould for depositing vat.*—The methods of preparation of non-conducting surfaces to receive an electrodeposit have already been detailed in Chapter VIII. For electrotype moulds in gutta-percha, fine plumbago or mixture of plumbago with finely divided tin or silver powder is generally employed. The substance used is brushed over the entire surface thoroughly and systematically until every portion is covered. Prior to this treatment, however, the mould must be wired for immersion in the depositing vat. Methods of wiring are innumerable and but few helpful details can be given, the matter depending entirely on the ingenuity of the operator. Copper wire is used, and it is attached by warming it slightly and pressing superficially into the surface of the mould, holding until cold. Or in cases where the mould is fairly heavy, attachments are made by piercing the block with a hot wire and passing copper wire to and fro through the block, the wire showing at the back being covered with a thin strip of gutta-percha to prevent deposits taking place. It is obviously advisable to make as many such attachments as possible, particularly at remote portions of the surface, in order to assist in the rapid coating of the mould with copper on first immersion in the bath. When the wiring is complete, the plumbago or conducting material is brushed well round the points of contact and the whole surface polished until it appears perfectly uniform and completely coated.

It is now ready for immersion in the depositing vat, the deposit being allowed to proceed until a sufficient thickness of metal is obtained. The deposit can be readily removed from the mould by gently warming with a blowpipe.

Other moulding methods and compositions.—For the ordinary requirements of the electroplater who may occasionally be called upon to execute small electrotypes, the foregoing details will, it is hoped, be sufficient. For more elaborate work other moulding materials are often necessary. In the case of surfaces much undercut, for example, gutta-percha is not sufficiently elastic, and for these specially elastic materials are used, the most commonly employed being a mixture of glue and treacle. Plaster of Paris, bees-wax, mixtures of ordinary white paraffin wax and bees-wax are also in use as moulding materials, and finally must be mentioned, fusible metal, an alloy of bismuth, lead, tin, and cadmium. This with suitable proportions of its ingredients melts at a lower temperature than boiling water, a very good composition being as follows:—

Bismuth 50 per cent., lead 25 per cent., with 12½ per cent. each of tin and cadmium.

This alloy melts at a temperature of about 60° C.

For fuller details of these compositions and methods of moulding the reader is referred to books dealing entirely with the subject of electrotyping. It is impossible to treat these adequately in the space of the present volume.

CHAPTER XII

THE DEPOSITION OF NICKEL

ALTHOUGH as early as 1843 Prof. Boettger, a German chemist, and one of the pioneers of electro-metallurgy, called attention to the beautiful results obtainable in the electro-deposition of nickel, and indeed suggested for the purpose the very solution now most extensively used, it was not until about 1870 that this branch of electroplating began to take any place of consequence in the industrial arts. Several reasons contributed to this delay, the principal, probably, being the difficulty prior to about 1872 or 1873 in obtaining sufficiently pure metal, and its comparatively high price. Since 1875, however, the progress of nickelplating both in Europe and America has been phenomenal, and to-day from the point of view of extent of application and labour employed, it is the largest single section of the electroplating industry.

This popularity is well deserved. Electro-deposited nickel is not only very pleasing in appearance, whether polished or left dull, but forms an extremely hard and durable protective coating to other metals which are not so impervious to the action of atmospheric and other influences as nickel itself is.

Properties of Nickel.—Nickel is a fine lustrous silver-white metal having a steel-gray tinge. It is very hard, capable of taking a high polish and is fairly malleable and ductile. Its melting point is very near to that of iron, to which metal it is closely related chemically. Nickel is not readily attacked by the atmosphere even at high temperatures. It is slowly soluble in hydrochloric acid or dilute sulphuric acid. Concentrated sulphuric acid dissolves it rather more quickly, but it is most readily soluble in dilute nitric acid. A rather singular feature of nickel is its susceptibility to organic acids. Most of the better known of these acids, such as citric, acetic, tartaric, slowly dissolve the metal, particularly in its electro-deposited condition. One of the present writers has several times successfully used strong solutions of citric acid for stripping nickel deposits, when time has been no object and it was desired to preserve the basis metal as much as possible from attack by the " strip."

Nickel, as electro-deposited, under normal conditions is extremely hard, so much so as to render its subsequent polishing very difficult unless the coating has been made on a perfectly smooth surface. It is, further, very brittle, though in this respect considerably varying degrees are obtainable under different conditions of current and electrolyte. The liberation of hydrogen during the electro-deposition of nickel affects its mechanical properties to a most important extent, and in extreme cases absolutely prevents the formation of either adherent or coherent deposits.

Compounds of Nickel.—The principal salts of nickel of interest to the electroplater are the carbonate, chloride, oxalate, acetate, citrate, and sulphate. Solutions of all these either alone or in combination with other substances have been used or suggested for the electro-deposition of nickel. In addition to these, suggestions have been made for the use of some of the lesser-known organic compounds of nickel, as also recently the double fluorides of nickel and the alkali or alkaline earth metals.

Of these, the sulphate, either single or double (with ammonium), is by far the most extensively used, but it should be observed that excellent results in the electro-deposition of nickel are by no means confined to the sulphate solutions.

Although three oxides of nickel are known having the respective formulæ, NiO, Ni_2O_3, and Ni_3O_4, generally only one series of salts is formed corresponding to the first-named oxide. They nearly all possess in the hydrated condition a characteristic green colour—a peculiarity which enables them to be easily recognized.

Solutions for Deposition.—The solution most widely known, and probably at present most generally used, for nickel-plating is a simple solution of the double sulphate of nickel and ammonium in water, in the following proportions approximately :—

Nickel ammonium sulphate . . .	1 lb.	500 gr.
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres

To prepare this solution it is generally recommended to dissolve the salt in a portion of the water heated nearly to boiling point, and when complete solution is effected, to make up the bulk by adding the necessary quantity of cold water. The great difficulty with this solution, however, of the strength above recommended is its constant tendency to crystallize out, due to the fact that these proportions correspond practically to the point of saturation. We prefer, therefore, to dissolve the salt in *cold* water as follows. Prepare the vat in which plating operations are to be carried out by thoroughly cleansing and rinsing. It is of the utmost importance that the vat itself shall be perfectly clean. Measure into the vat the required quantity of water, preferably distilled or filtered rain-water; the level of the liquid should be at least four inches from the top edge of the vat. Prepare now a number of muslin bags or perforated stoneware vessels and divide the nickel salt into equal portions in these; hang them at intervals in the vat so that the salts are just immersed and stir the solution occasionally. In this way the water will absorb the crystals at a normal temperature and the danger of subsequent crystallizing out will be averted. This is also a good plan to adopt when making addition to the vat during working.

When the solution is made, it should be tested for acidity or alkalinity by means of litmus papers. Blue litmus is reddened by acids, and red litmus turns blue when immersed in an alkaline solution. Usually the double sulphate solution will be found neutral. In commencing to work a new solution it is advisable first to pass the current through the vat for a short time by means of nickel sheets acting as both anodes and cathodes, and again test the solution with the litmus paper; if the reaction is still neutral or, as will often be found, slightly alkaline, add a very few drops of sulphuric acid and test again, repeating the operation most carefully until the bath is found to be very slightly acid. In this condition the best results are obtained.

The bath should be worked at a temperature of 20° to 25° C. (Normal temperature = 15° C. = 59° F.)

The reactions which occur during the electrolysis of the double sulphate bath are somewhat complicated and demand careful consideration. It is usually regarded that dissociation occurs thus:—

$$\begin{array}{lll} NiSO_4 & \text{into } Ni & + SO_4 \\ (NH_4)_2SO_4 & \text{,,}\quad 2NH_4 & + SO_4 \end{array}$$

In *dilute* solutions probably this is so, but according to modern research there seems good reason to conclude that in *concentrated* solutions the reaction is rather different, and the ammonium ion only is supposed to be the cation, the rest of the compound forming a complex anion, thus:—

$$NiSO_4(NH_4)_2SO_4 = 2NH_4 + Ni(SO_4)_2$$

The possibility is therefore that in many nickelplating solutions both the above conditions obtain.

Now, when electrolysis takes place, one or both of two actions may occur at the anode either separately or simultaneously.

(1) The anions may be discharged,

or (2) New ions may be formed by combination with the anode metal.

If the first occurs, then the anion SO_4 or the complex anion $Ni(SO_4)_2$ combines with the water of the solution, thus—

$$(a)\ 2SO_4 + 2H_2O = 2H_2SO_4 + O_2$$
$$(b)\ 2Ni(SO_4)_2 + 2H_2O = 2NiSO_4 + 2H_2SO_4 + O_2$$

i.e. sulphuric acid is formed with the liberation of oxygen.

If the second occurs, then direct union takes place between the nickel of the anode and SO_4 or $Ni(SO_4)_2$, thus—

$$(a)\ SO_4 + Ni = NiSO_4$$
$$(b)\ Ni(SO_4)_2 + Ni = 2NiSO_4$$

At the cathode, on the other hand, the reactions which may occur are—

Either (1) The discharge of the cations Ni and $2NH_4$ respectively,

or (2) The discharge of the cations $2NH_4$ with the consequent liberation of metallic nickel as a secondary reaction with the undissociated molecules of nickel ammonium sulphate, thus—

$$2NH_4 + NiSO_4(NH_4)_2SO_4 = 2(NH_4)_2SO_4 + Ni$$

The first of these results in a deposit of metallic nickel with simultaneous liberation of $2NH_4$ which breaks up into $2NH_3$ and H_2 (ammonia and hydrogen gas). The alternative reaction also gives a deposit of metallic nickel with, however, the formation of ammonium sulphate.

A study of these reactions, which necessarily are but briefly outlined above, then reveals the fact that the constitution of the nickel solution during or after electrolysis will depend—other conditions of temperature and current being normal—upon the solubility of the anode, in other words on the extent to which it neutralizes the anions.

Suppose for the sake of argument and taking the older view of the dissociation reactions that the whole of the latter combines with the metal of the anode, then the net results of electrolysis would be :—

$$\begin{array}{cc} \textit{At cathode.} & \textit{At anode.} \\ \left.\begin{array}{l} Ni \\ 2(NH_4)HO + H_2 \end{array}\right\} & \left\{\begin{array}{l} SO_4 + Ni = NiSO_4 \\ SO_4 + Ni = NiSO_4. \end{array}\right. \end{array}$$

The bath would gradually become alkaline owing to the liberated ammonia, and at the same time would acquire an increased content of nickel in the form of nickel sulphate. Experience in practical working has shown that this is the case to some extent.

Rarely, if ever, is the anode, however, so completely soluble in the solution by electrolysis as would be required to make the above equations exactly true. Consequently the alternative must also be taken into review, viz. :—

$$\begin{array}{ll} \textit{At cathode.} & \textit{At anode.} \\ \left.\begin{array}{l} \mathrm{Ni} \\ 2(\mathrm{NH_4})\mathrm{HO} + \mathrm{H_2} \end{array}\right\} & \left\{\begin{array}{l} \mathrm{SO_4} + \mathrm{Ni} \quad = \mathrm{NiSO_4} \\ \mathrm{SO_4} + \mathrm{H_2O} = \mathrm{H_2SO_4} + \mathrm{O}. \end{array}\right. \end{array}$$

In the working of these baths, therefore, it is usually found that the increase in alkalinity, if any, is very gradual —a considerable proportion of the liberated ammonia at the cathode being neutralized by a corresponding formation of sulphuric acid at the anode.

To secure the highest possible efficiency in the working of these baths, then, it is essential that periodically the composition of the electrolyte be ascertained in the manner to be explained later, so that any irregularities of constitution may be rectified and the chemical equilibrium of the solution maintained, by the addition either of sulphuric acid, if the bath is found alkaline, of ammonia if too acid, of single nickel sulphate if found deficient in metallic content, or of water if too dense.

It is a significant fact, and one which may be taken to bear out the foregoing theoretical conclusions, that almost invariably an analysis of nickelplating solutions which have been in actual use for any appreciable length of time reveals the existence in the solution of a certain proportion of single nickel sulphate along with the double sulphate of nickel and ammonium, even in cases where the operator in charge has rigorously excluded any addition to the vat other than the double sulphate only.

The following is a typical result, the analysis being made after six years' use of a solution originally made up of the double sulphate of nickel and ammonium, and replenished only by this salt:—

The analysis* showed a metallic content of 2·78 oz. of nickel per gall., and an ammonia content of 0·474 gram per 100 c.c..

This result when calculated out corresponds to the following:—

Content of double nickel salts (nickel ammonium sulphate)	8·80 oz. per gall.
Content of single nickel salts (nickel sulphate)	6·54 ,, ,,

or of double nickel salts, 57 per cent.
,, single ,, ,, 43 ,, ,,

The great drawback, however, to a solution made originally from the double sulphate of nickel and ammonium alone, is its relatively poor conductivity and consequent slowness of working. It is this disadvantage which, in recent years particularly, has turned the attention of investigators to the question of making additions to this bath with a view to decreasing its resistance and even also to the substitution of other possible compounds for use as the basis for nickel baths.

With regard to the former point it may be remarked that several recent writers on electroplating have passed rather severe strictures on some published formulæ for plating solutions on the score of complexity. In many cases this criticism is justifiable, but it must be quite as emphatically asserted that complexity in the composition of plating baths is by no means necessarily an evil. Indeed, experience in practical working has repeatedly demonstrated that the characteristics of many metallic deposits can be profoundly modified, often to their advantage by the addition of various substances to the electrolyte which appear,

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* *Metal Industry*, vol. iv., No. 6 (1912), p. 236.

from a purely theoretical point of view, to be totally unnecessary. A classical illustration of this point is found in the addition of carbon bisulphide and similar compounds to silverplating solutions. Theoretically, so far as present knowledge is concerned, this would appear to be a quite unjustifiable complication, without the slightest probability of obtaining by means of it the effect which is now so familiar to electroplaters.

With reference to nickel, while a simple solution of the double sulphate of nickel and ammonium in water yields very good results, yet there is no doubt that certain additions and modifications of this solution can be made which result in improving both the character of the deposit and the conductivity of the bath.

Before discussing some of the principal substances recommended in this connection, however, it will be advisable to deal with the question of the use of nickel sulphate or single nickel salt—as this substance is sometimes termed. This is a subject which at various times has aroused much controversy amongst nickelplaters, some operators strongly advocating its use as an addition to the bath, others just as strongly opposing it. There is little doubt, however, that for most classes of work and under ordinary conditions of temperature the addition of small proportions of nickel sulphate is of distinct advantage. This appears to be due largely to the fact that the single salt is proportionately much more soluble than the double salt, consequently by its use a greater content of metallic nickel can be given to the vat with the effect of appreciably increasing its conductivity.

The following comparison of the molecular composition and solubilities of the two compounds will be of interest and assistance to the reader.

Nickel Ammonium Sulphate as usually obtained in commerce has a composition corresponding to the formula $NiSO_4(NH_4)_2SO_4.6H_2O$. It is obtained by dissolving pure nickel in dilute sulphuric acid, and adding a molecular proportion of ammonium sulphate to the concentrated acid solution.

According to Link its solubility is as follows:—

	Temperature in degrees Centigrade.							
Parts of $NiSO_4 . (NH_4)_2SO_4$ soluble in 100 parts of water	3½°	16°	20°	30°	40°	50°	68°	85°
	1·8	5·8	5·9	8·3	11·5	14·4	18·8	28·6

Nickel Sulphate is obtained by dissolving metallic nickel, nickel hydroxide, or nickel carbonate, in dilute sulphuric acid. If crystallized out in excess of acid it has the formula $NiSO_4.6H_2O$. The crystals from an aqueous solution have the composition $NiSO_4.7H_2O$. When heated, nickel sulphate crystals lose the greater part of their water of crystallization. At 100° C. only one molecule of water is retained, and above 280° C. this is expelled, leaving the yellowish anhydrous $NiSO_4$.

According to Tobler the solubility of this salt is as follows:—

	Temperature in degrees Centigrade.						
Parts of $NiSO_4$ soluble in 100 parts of water	2°	16°	23°	41°	50°	60°	70°
	30·4	37·4	41·0	49·1	52·0	57·2	61·9

A glance at these figures will reveal the greatly superior solubility of the latter salt over the former. Obviously also the percentage of metallic nickel present in the single salt is much higher than in the double. The single sulphate *alone*, however, is absolutely useless for nickelplating. It can only be employed successfully either in conjunction with the double salt or with other substances, as will be explained later.

A bath containing the single sulphate as an addition, which has been found by the authors to give excellent results, is made up as follows:—

Double sulphate of nickel and ammonium .	12 oz.	375 gr.
Single nickel sulphate	3 to 4 „	93·75 to 125 gr.
Water	1 imp. gall. or 1$\frac{1}{5}$ U.S. „	5 litres

This bath should be prepared in the manner previously directed, and worked at a temperature of about 20° C.

With regard now to the addition of other substances, usually termed "conducting salts," to the double sulphate nickel bath, a truly bewildering variety of compounds have been recommended. These include *inter alia*, ammonium chloride, ammonium sulphate, common salt, potassium or sodium phosphates, magnesium sulphate, potassium carbonate, sodium bi-carbonate, calcium acetate, calcium chloride, and ammonium tartrate.

In addition, many operators have recommended giving a slight degree of acidity to the bath by means of weak organic acids, *e.g.* benzoic acid, boric acid, citric acid, etc.; in several instances claiming thereby not only an increased conductivity of solution but an improved character of deposit.

A typical example of a solution containing one or more of these conducting salts is the following, which is recommended by an American expert, and quoted here as a fair example of a very large number of such formulæ which might be given.

Double sulphate of nickel and ammonium .	8 oz.	300 gr.
Single nickel sulphate	2 ,,	75 gr.
Ammonium chloride	1 ,,	37·5 ,,
Sodium chloride (common salt)	3 ,,	112·5 ,,
Boric acid	2 ,,	75 ,,
Water	$\frac{5}{6}$ imp. gall. or 1 U.S. ,,	5 litres

Such a bath obviously invites criticism on the ground of complexity, and certainly the ammonium chloride may be omitted without making any observable difference to the results. Nevertheless it is indisputable that this, and many similar solutions, yield remarkably good results in practice. They are good conductors, can be worked rapidly without giving off hydrogen to anything like the extent of a normal double sulphate solution, and yield a coherent and adherent deposit of nickel of a good colour.

After considerable observation of the results obtainable from the use of various conducting salts or additions which have been recommended for use in nickel baths, and also after a number of experiments which need not be detailed here, the conclusion we have arrived at is that it is inadvisable at the present stage of investigation in this direction to make any dogmatic statement as to the superiority of any one formula over another, the results from various experiments being almost indistinguishable.

We have, however, obtained uniformly good results from solutions containing potassium chloride, a substance which, so far as we are aware, has not hitherto been noted in this connection. The corresponding sodium compound (common salt) has of course been extensively recommended and used by nickelplaters, but we prefer the potassium salt, not merely because its effect is fully equal, if not superior, to that from common salt, but also because of its distinct advantages, from an electrochemical point of view, of conductivity.

The following is the bath we have used for general work:—

Double sulphate of nickel and ammonium	10 oz.	312 gr.
Single nickel sulphate	4 ,,	125 ,,
Potassium chloride	1 to 1½ ,,	31·2 to 46·6 gr.
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

It cannot be too strongly emphasized, however, that this proportion of potassium *or* sodium chloride must not be exceeded. A great deal of trouble has arisen in recent years from an injudicious and often extravagant use of salt in nickel solutions, and it should be remarked that many operators, while using such additions for nickel-plating copper, brass, etc., prefer to omit them altogether for iron and steel.

The following solutions form a representative selection from a large number of authorities, and are given here in order that the reader may be familiarized with some of the many possible combinations which have been or are used for nickelplating either for general work or particular purposes as noted.

Solution I. (Weston)—

Double sulphate of nickel and ammonium	10 ozs.	375 gr.
Boric acid	3 to 5 ,,	112·5 to 187 gr.
Water	$\frac{5}{6}$ imp. gall. or 1 U.S. ,,	5 litres

With regard to this solution Langbein observes that "it cannot be recommended because the bath works faultlessly for a short time only; all kinds of disturbing phenomena make their appearance, the deposit being no longer white but blackish, and the bath soon failing entirely." He himself recommends the following, which also contains boric acid.

Solution II. (Langbein)—

Double sulphate of nickel and ammonium	6 oz.	225 gr.
Pure nickel carbonate	$\frac{1}{2}$,,	18·7 ,,
,, Boric acid	3 ,,	112·5 gr.
Water	$\frac{5}{6}$ imp. gall. or 1 U.S. ,,	5 litres

Dissolve the nickel ammonium sulphate in water, and when solution is complete add the boric acid. Heat the liquid to boiling point, and then add the nickel carbonate. Allow the whole to boil a few minutes, cool and filter.

Wahl, on the other hand, supports Weston's claim that his bath gives an improved character of deposit, and allows more rapid working.

Solution III. (Desmur)—

Double sulphate of nickel and ammonium	11 oz.	343 gr.
Bicarbonate of soda	$1\frac{1}{4}$,,	39 ,,
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres

Watt, in quoting this solution, recommends it for small work, mounts, etc. The bicarbonate of soda must be added in small portions, waiting after each addition until the effervescence has ceased.

In our experience equally good results can be obtained by substituting potassium sulphate for the sodium salt.

With regard now to solutions other than the double sulphate of nickel and ammonium with or without additions, it has been already observed that single nickel sulphate has a much higher degree of solubility than the double salt. Many attempts, therefore, have been made to utilize this compound as a chief agent in nickel solutions, and of recent years these have been increasingly successful. As has been also stated, however, a solution of nickel sulphate alone is of no use for nickel plating. This salt can only be employed conjointly with "conducting salts." A large number of the special nickel salts sold under registered or trade names are compounds of this order, *i.e.* nickel sulphate crystallized out along with added conducting salts. The latter chiefly consist of the sulphates and chlorides of the alkali and alkaline earth metals.

A type of nickeling solution often recommended which may be considered as coming under the foregoing generalization is that made by dissolving single nickel sulphate in water and adding varying proportions of ammonium sulphate. It is, however, obvious that such a bath is simply another form of the double sulphate bath, and attempts to obtain a solution of high nickel content by dissolving these substances separately and then combining them ends in obtaining a liquid from which the double sulphates quickly crystallize out, or in cases in which a strong solution of ammonium sulphate has been used, in the operator finding green crystals of the double sulphates at the bottom of the vat. This latter action is due to the peculiar property possessed by nickel ammonium sulphate of insolubility in a strong solution of ammonium sulphate—a property often made use of in the recovery of nickel salts from old or spoilt solutions, as will be referred to later.

The more successful solutions of nickel sulphate are those which contain, as conducting salts, potassium or magnesium sulphates, generally in molecular proportions.

The following are examples :—

Nickel sulphate (single nickel salt) . . .	2 lbs.	1 kg.
Magnesium sulphate	1 lb.	0·5 „
Water	1 imp. gall. or 1⅕ U.S. „	5 litres

Langbein quotes the two following formulæ, which are interesting as illustrative of the use of organic compounds with nickel sulphates :—

(1)	Nickel sulphate	7 oz.	218 gr.
	Neutral ammonium tartrate . .	5 „	156 „
	Tannin	15 grains	0·97 „
	Water	1 imp. gall. or 1⅕ U.S. „	5 litres
(2)	Nickel sulphate	7 oz.	218 gr.
	Tartaric acid	4 „	125 „
	Caustic potash	¾ „	23·4 „
	Water	1 imp. gall. or 1⅕ U.S. „	5 litres

Of solutions made from nickel compounds other than the sulphate the most successful are those of organic salts of this metal, notably the oxalate. Good deposits of nickel can be obtained from the double oxalate of nickel and ammonium, $NiC_2O_4 . (NH_4)_2C_2O_4$. This compound, however, has the disadvantage from a commercial point of view that it is a more expensive salt without affording any commensurate advantage. The same remark applies to the double cyanide of nickel and potassium which has been recommended by Gore and other writers. With regard to this latter solution it must also be pointed out that cyanide of nickel is much less soluble in potassium cyanide than the corresponding silver salt, and the solution is a very troublesome one to make.

The following solution by Potts containing nickel acetate yields very good results and is strongly recommended by Wahl:—

Nickel acetate	4½ oz.	140 gr.
Calcium acetate	3½ ,,	109 ,,
Acetic acid	1 British Fl. oz.	28·4 c.c.
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

Dr. F. W. Kern of Columbia University, U.S.A., has recently (Dec. 1909, Amer. Patent 942,729) patented a solution of the fluosilicate of nickel with the addition of either an alkaline fluoride alone, or an alkaline fluoride and a soluble fluosilicate, preferably aluminium fluosilicate. The bath he recommends is as follows:—

Fluosilicate of nickel	10 parts by weight
Ammonium fluoride	5 ,, ,, ,,
Aluminium fluosilicate	5 ,, ,, ,,
Water	100 ,, ,, ,,

Small quantities of ammonium fluoride should be added from time to time to prevent the separation of silica.

According to another writer* the corresponding boric compound (nickel fluo-borate) can also be employed for nickel deposition.

Anodes.—The subject of anodes in nickelplating is an exceedingly important one, and a good deal of attention has been at various times devoted to it. The first factor to be considered is undoubtedly that of the degree of purity. The great improvements which the last two decades have witnessed in the metallurgy of nickel have rendered it quite possible and even common to obtain the metal commercially of a purity of 98 to 99 per cent. The most common impurities consist of iron, cobalt, copper, arsenic, carbon, sulphur, antimony, and bismuth, but none of these, except perhaps the first two and carbon, are present in commercially pure nickel but in mere traces. The metals iron and cobalt

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* *Trans. Amer. Electro-Chem. Soc.*, vol. xviii. (1909), p. 464.

are so closely akin to nickel both in their chemical and electrochemical as well as in their physical properties that they may be disregarded. Great care, however, must be observed to secure anodes free from copper. This latter metal, being very readily dissolved and more electro-negative than nickel, finds its way quickly into the bath and is more easily deposited than the nickel, greatly to the detriment of the colour of the deposit.

With regard to the form in which the metal should be made into anodes, whether *cast* or *rolled* sheets, much discussion has arisen, but the great majority of practical operators prefer the former; and if occasionally the latter are used, they are always considerably in the minority of the total number employed in the vat. The chief advantage possessed by cast over rolled anodes is that the casting, being appreciably more porous in texture than a rolled sheet is much more easily dissolved by the anodic product of electrolytic action.

In neutral solutions, such as nickel baths usually are, it will be readily understood that the anode metal can only be dissolved into the solution by virtue of its combination with the particular product of electrolysis liberated at its surface. When this latter then is close grained and smooth, as is the case in rolled sheets, its physical characteristics do not tend to facilitate combination, but rather to resist attack by the liberated ions. In the case of a porous casting, on the other hand, these *ions* finding their way into the pores of the metal have a relatively far greater surface to act upon, and in the aggregate combine with and so dissolve a much larger proportion of metal.

One disadvantage urged against the use of cast anodes is that they disintegrate rapidly and fall to pieces more quickly than rolled, thus forming a greater proportion of scrap. It must be borne in mind, however, against this, that if, when rolled sheets are used, the solution is not supplied with metal to an equivalent extent as in the case of cast anodes, then the liquid must be periodically renewed by fresh additions of nickel salts to a greater degree than otherwise, and the slight loss in remelting scrap is often more than balanced by the cost of this additional nickel salt.

Anodes are now usually made with projecting lugs perforated as in Fig. 60, so that they can be readily connected by means of hooks to the anode conducting rods. Watt makes the very good suggestion that the connecting hooks when passed through the hole in the lugs be soldered in order to obviate the possibility of an imperfect connection. When working rich solutions it will be observed that their tendency to crystallize out—familiar to all nickelplaters—often leads to the formation of small growths of crystals on the part of the lug of the anode immediately above the surface of the liquid. These crystals once formed easily grow and extend to the hole in which the connecting hook is inserted and consequently materially interfere with the contact of a loosely hung anode. Soldering of course effectually prevents any interference of this kind and ensures a continuous sound electrical connection. The importance of this is obvious.

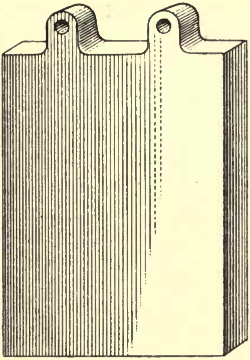

Fig. 60.—Nickel Anode.

Management of Solutions.—Nickelplating solutions are not necessarily difficult to manage or keep in good working order, provided one or two essential points are thoroughly grasped and understood.

The first is the necessity, upon which emphasis has previously been placed, for the solution to be kept neutral or at most only slightly acid. The latter condition is the more advisable inasmuch as a little free acid assists in the effective solution of the anode and consequently in keeping up the metallic content of the bath. Too great acidity, however, is fatal, since in this case hydrogen is most readily liberated at the cathode surface and occluded by the deposited nickel, with the result that the deposit becomes neither adherent nor coherent, and may even be observed to "curl up" or "peel" during the process of deposition. On the other hand, if the bath is allowed to become alkaline, the deposit is usually of a bad colour and often the conductivity becomes impaired. Tests should be made frequently with litmus paper, and in the case of decided acidity one or two muslin bags containing nickel carbonate should be hung at intervals just under the surface of the solution. This salt is insoluble in water but quite soluble in acids, and will quickly neutralize the excess acid. This is best done at night. If the bath is alkaline, sulphuric acid should be added carefully with constant stirring until the point of neutrality or just beyond it is reached.

The second essential in good management is to take steps to ensure that the metallic content of the bath is kept constant. This is accomplished in two ways, first by using a larger anode than cathode surface during deposition, and secondly by periodic additions of nickel salts. It rarely happens even in the best-managed solutions that as much metal passes into the bath from the anode as is deposited upon the cathode, owing largely to the fact that *free* acid is not allowable; still, much can be done by using cast anodes and arranging them so that their superficial area is always slightly in excess of that of the cathodes. When additions of nickel salts are found to be necessary in the case of a solution of the double sulphate of nickel and ammonia, single nickel sulphate should always be used.

A third point which deserves more attention than usually appears to be given to it is the temperature of the solution. For normal and general working this should be kept as nearly as possible to 20° or 21° C. (68° Fahr.). This temperature is sufficiently high to prevent crystallizing out of the dissolved salts and yet not high enough to tend, as hot solutions usually do, to the too ready liberation of hydrogen. In well-fitted and managed nickelplating shops arrangements consisting of steam or hot-water pipes are made so that the temperature of the vat rooms is kept at or about the point named.

Electrical Conditions.—It is generally known that nickelplating demands a comparatively high voltage, but a mistake often committed by inexperienced operators is to use one much higher than necessary. It is usually advisable at the moment of immersion of articles in a bath to apply a voltage up to about 5 volts until the cathode surface is completely covered with a film of the metal, but after that the voltage between the vat terminals should be reduced to 3 volts, or even slightly less, if the solution used is at all acid.

The current density allowable depends almost entirely on the character of the electrolyte. For solutions of the double sulphate alone, with stationary cathodes, the value must not exceed about 5 amperes per square foot. With agitating arrangements or moving cathode rods a higher value may be adopted. With solutions of the single sulphate and conducting salts, however, double this current—often more—may be used. Exact figures cannot be given owing to the many variations which may be possible owing to local conditions and class of work.

Special Treatment of Articles for Nickelplating.—Owing to the extreme hardness of electro-deposited nickel and the consequent difficulty of polishing it, it is absolutely necessary, in all cases where a *bright* deposit is required, that the surface before plating shall receive as high a polish as it is capable of. For this reason the processes preparatory to immersion in the nickel bath vary somewhat from those adopted for most other classes of electroplating. The principal variation, as will be fairly obvious, is that strong dipping acids and coarse scouring or scratch-brushing must be avoided. As the function of the former is to remove oxides and scale from metallic surfaces, and the latter operation is to clear off stains or tarnish, it will be evident that if the polishing of articles is thoroughly done and they are carried through the plating operation without delay, these two processes are largely rendered unnecessary. It is, however, advisable, after the ordinary routine of cleansing from the films of grease, etc., which usually remain on polished goods, to scour lightly with soda-lime, fine whiting, or precipitated chalk for the reasons that the cleansing operation itself occasionally leaves stains on most surfaces, and that the adhesion of the deposited coating is rendered more reliable by the extremely slight deadness which even the gentlest scouring treatment will leave.

Of the particular metals usually dealt with for nickel-plating those which call for special consideration are Britannia metal, lead or zinc alloys, and iron and steel goods.

Dealing with the former, Watt remarks that "lead, tin, and Britannia metal are not suited for nickelplating, and should never be allowed to enter the nickel bath." The fact remains, however, that a very large amount of Britannia metal has been successfully nickelplated, and though to some extent this class of work has been superseded by silverplated goods, owing to the greatly reduced prices of the last-named which recent years have witnessed, yet it is still carried out for certain requirements, and wonderfully good results obtained.

Several methods have been recommended for the treatment of these alloys, but the most successful results are obtained by giving the surfaces a preliminary coating of brass from the solution recommended on page 350. The articles are first given a high polish by means of dollies with lime and rouge composition, then rinsed through a strong caustic potash boil and immediately transferred to the brassing solution. From this, when the entire surface has received a sound coating of brass, they are taken quickly, rinsed through clean water, then through a second wash-water very slightly acidulated with sulphuric acid, and immersed in the nickel bath.

An alternative method of treatment which results in the articles retaining a high degree of polish is known as "dry cleaning." The bright polished surfaces in this method instead of being subjected to the action of caustic alkalies are thoroughly brushed first with soda-lime, then with the finest whiting or precipitated chalk. A perfectly dry brush is used, and care is taken not to seriously scratch the bright surfaces. The articles are then brassed, and subsequently nickeled in the ordinary way.

Iron and steel goods, particularly in the best classes of work where thick deposits are required, are also very often coppered or brassed in the cyanide baths before nickeling, but this is by no means invariably necessary. A strongly adherent deposit of nickel can be given to iron or steel direct, and it is doubtful if any real advantage accrues in the case of preliminary coppering or brassing, except perhaps in the treatment of cast iron which is often extremely porous, and consequently gives considerable trouble to the nickelplater. It will be found in this case that a thin deposit of *brass* given prior to immersion in the nickel bath will ensure almost perfect adhesion of the nickel deposit. In connexion with iron and steel it must here be pointed out that thin deposits of nickel are almost useless. The deposited metal is always slightly porous, and in a very short time, particularly in an atmosphere at all moist, the basis metal is gradually attacked through the pores of a thin coating and begins to rust. This action once begun speedily ruins the appearance of the article.

Thick deposits resist the atmosphere to a degree far greater than in proportion to their thickness, and as the preparation involved is in either case the same, it is false economy to stint the deposit, seeing that the increased cost of a stronger deposit is so greatly disproportionate to the advantages gained.

It may be advisable to point out with regard to both zinc, tin, and lead alloys and iron or steel goods that owing to the strongly electro-positive nature of all these metals relatively to nickel, a fairly high initial voltage must be used in order to overcome the back E.M.F. which is set up, if nickeled direct without intermediate coatings. If the average distance between anodes and cathodes is not more than 6 to 8 inches, a pressure of not less than 5 volts will be found satisfactory, though in the case of zinc, which of course is the most electro-positive of all, some operators prefer to "strike" with 6 or 7 volts.

In dealing with copper or brass goods these high voltages are not in the least necessary.

In all cases the goods immersed should be completely covered with a film of nickel of a clean white colour in from two to three minutes from immersion, and when once deposition has begun it must not under any circumstances be interrupted until the required weight of metal is deposited.

When goods of very unequal size are being dealt with and passed through the same nickeling bath, it is sometimes an advantage to "strike" in a separate bath, at a high pressure and current density, and then transfer to the bath proper, which in the meantime may be working with other goods. If this plan is adopted, however, the transfer must be effected very quickly or the subsequent deposit will strip.

Stripping of Old Nickel Deposits.—The stripping of old coatings of nickel from articles which are required to be replated is a matter of some little difficulty, as any liquid which can ordinarily be used for this purpose will also attack the basis metal. Reference has already been made to the stripping of nickel coatings by long immersion in organic acids, but this is far too tedious a method for ordinary trade requirements. The formula most generally adopted for stripping nickel is as follows :—

Concentrated sulphuric acid . .	2 parts by weight
,, nitric acid . . .	1 part ,, ,,
Water	1 ,, ,, ,,

The sulphuric acid is added slowly and carefully to the water, and when the mixture has cooled down the nitric acid is poured in. Some operators prefer to omit the water and use a simple mixture of nitric and sulphuric acid in the above proportion, but the action is much slower. In either case the operation must be closely watched and the article taken out of the liquid immediately the coating is completely removed.

The Assay of Nickelplating Solutions.—Although not of such primary importance as in the case of silverplating, it is yet greatly advantageous, and certainly conducive to greater efficiency, that periodically at least approximate estimates should be made of the amount of metallic nickel contained in nickelplating solutions, and for this purpose it cannot be too strongly emphasized that the hydrometer, which is the instrument apparently most commonly relied upon for such tests, is absolutely useless. Worse than useless indeed, for it is misleading. An hydrometer is simply an instrument for determining the specific gravity of a liquid as compared with water—and nothing more—and the specific gravity (or weight compared with water) is of course influenced by the *whole* of the substances contained in the particular liquid. The addition of, say, sulphuric acid or indeed any soluble substance will obviously influence the specific gravity reading just as well as the addition of nickel salts will do so. Consequently a particular reading on a hydrometer scale can convey no reliable idea of the really important factor, viz. the weight of metallic nickel in solution.

Several methods are available * for this purpose, but probably the most accurate as well as the most convenient for electroplaters to adopt is that known as the "cyanometric method," used largely for the estimation of nickel in steel, etc.

To electroplaters, familiar with the chemical reactions of the double cyanides, this method will be readily intelligible,

* See *Metal Industry*, vol. iv., April, 1912; May, 1912; June, 1912.

as it is based on the formation of a double cyanide of nickel and potassium by means of a standard cyanide solution of known strength titrated into the nickel solution to be tested.

The following details of the method have been carefully worked out with a view to the special requirements of nickelplaters.

Prepare first standard solutions of silver nitrate, and of potassium cyanide, exactly as directed in Chapter IX. for the assay of commercial cyanide of potassium.

The silver nitrate solution is that known as decinormal and will contain exactly 17 grams of $AgNO_3$ per litre.

The exact strength of the cyanide solution will of course not be known unless the sample used has been previously assayed. This, however, is not necessary as it can be standardized by means of the silver solution. If the sample used is absolutely pure, the strength of KCN will be 13 grams per litre; as this is extremely improbable, it must be tested against the silver standard and its exact strength determined. It is usual in such a case to determine by experiment the numerical "factor," multiplication by which will bring the figures obtained in subsequent burette readings to that which would have been obtained had the solution been of absolutely accurate strength. An illustration will make this clear. Suppose as the result of the mean of several readings we find that 50 c.c. of potassium cyanide solution are equivalent to 48 c.c. of standard silver (*i.e.* the cyanide is 96 per cent. KCN); then since

50 corresponds to 48,
1 " $\frac{48}{50} = 0{\cdot}96$ = required factor.

The multiplication of the cyanide readings by this figure will therefore bring them up to the equivalent of the silver standard, or which is the same thing, to the readings which would be given by KCN of 100 per cent. purity.

Having now the standard solutions prepared and labelled, the nickel assay should be carried out as follows:—

Take by means of a pipette 10 c.c. of the nickel solution, place in a beaker, add 20 or 30 c.c. distilled water, 10 c.c. of 0·880 ammonia, and 5 c.c. of a 10 per cent. solution of potassium iodide (the reason of this addition will appear later).

Fill two separate burettes with the standard silver and cyanide solutions respectively. See that the burettes are filled exactly to zero, and run into the nickel solution about 2 c.c. of standard silver. This by combination with the potassium iodide, which thus acts as an indicator, causes the solution to become milky by the formation of silver iodide. Now add the standard cyanide solution carefully and slowly, constantly shaking the beaker until the nickel solution changes to a yellow colour and becomes perfectly clear. The nickel has now become converted entirely into the double cyanide of nickel and potassium. As, however, to attain this a little more cyanide than actually necessary has most probably been used, again run in drop by drop standard silver unless and until one drop causes a permanent milkiness after thorough agitation. Now take the readings of both burettes, and correct the volume of cyanide by multiplying by the factor previously determined. Then deduct the volume of silver solution used from the corrected volume of cyanide, thus :—

Say, corrected volume of cyanide . . .	40 c.c.
„ volume of silver	4 „
Nett cyanide equivalent to nickel .	36 c.c.

The equation representing the reaction is—

$$\begin{array}{llllllll} \mathrm{NiSO_4} & + & \mathrm{4KCN} & = & \mathrm{Ni(CN)_2 \, . \, 2KCN} & + & \mathrm{K_2SO_4} \\ 59 & & 4(65) & & & & \end{array}$$

∴ 59 parts nickel require 260 parts of potassium cyanide.
Each c.c. of standard cyanide contains 0·013 gram KCN.
∴ 1 c.c. standard cyanide = 0·00295 gram nickel.

An approximate value sufficiently accurate for practical workshop requirements is, in cases where the amount of sample tested is as above, 10 c.c. Then

Each c.c. standard cyanide solution is equivalent to $4\frac{3}{4}$ oz. metallic nickel per 100 imperial or 120 U.S. gallons.

General Remarks on Nickelplating.—The necessity for absolute cleanliness in nickelplating operations must be very strongly insisted upon. A very short experience in this branch of electroplating will suffice to convince the operator of this, at least in regard to preparation of work for the vat. In silverplating, brassing, or gilding where cyanide solutions are invariably used, if by any chance a slight film of grease should remain on a prepared surface, the action of the strong alkaline cyanide itself is often sufficient to remove it and enable a sound deposit to take place. In nickelplating, however, where neutral solutions are most generally used no such safeguard exists, and the slightest touch with the tip of the finger is often sufficient to prevent perfect adhesion. But this necessity for cleanliness applies not only to the work entering the vat but to the solution itself. Floating particles of dirt or grit are often the cause of serious trouble and are particularly liable to be introduced owing to imperfect rinsing of goods from scouring operations.

Great care should also be taken to avoid the introduction, inadvertently, of caustic potash or cyanide solutions, which are often apt to linger in the crevices and recesses of hollow-ware articles. Cyanide, particularly if used in the preliminary processes, should be thoroughly rinsed away by passing goods through clean running wash-waters and carefully draining.

One of the commonest troubles of nickelplaters is the "pitting," as it is termed, of nickel deposits. Instead of the fine, smooth and even deposit which, under correct current conditions, should be produced, the surface presents in these cases an appearance simulating a number of pinholes. This trouble can be caused by floating particles in the solution, but it is far more often due to the evolution of hydrogen while the deposit is proceeding. The principal conditions tending towards this are, (1) too low a content of metallic nickel in the vat, (2) too high a percentage of free acid, or (3) too strong a current. In either case the remedy is obvious, and the plater should exercise constant observation of the vats while working so as to note any excessive evolution of gas at the electrodes.

Solutions should be thoroughly stirred every evening and water added to make up for loss due to evaporation. Otherwise it is almost impossible to secure that constant condition of the electrolyte which enables the operator to adjust current conditions correctly from day to day.

Recovery of Nickel from Old Solutions.—It is rarely worth the trouble and expense to attempt to recover nickel from old solutions in the metallic form. But as it is a comparatively simple process to precipitate nickel ammonium sulphate from such solutions, it is often worth while, when a bath has become unsuitable from any cause for deposition, to do this and so obtain from the old bath a supply of nickel compound which can be used to make up a new solution. The principle of the method depends on the insolubility of nickel ammonium sulphate in ammonium sulphate. As the latter salt is very cheap the cost of the process is sufficiently low to make it profitable.

It is advisable in the first place to concentrate the solution as much as possible by applying heat to evaporate excess water. When this is done the liquid will begin to show signs of precipitating nickel salts; at this point add a considerable excess of ammonium sulphate and stir vigorously for some time. Allow the liquid now to stand a few hours, then syphon off the clear liquor. Make now a saturated solution of ammonium sulphate, and by means of this wash the precipitate obtained in the vat several times. The precipitate finally remaining will be nickel ammonium sulphate of a high degree of purity.

It can then be utilized for making up a new bath or, if preferred, for strengthening other solutions.

CHAPTER XIII

THE DEPOSITION OF IRON AND COBALT

Iron and cobalt, the latter particularly, are both closely akin in their chemical and electro-chemical properties to nickel. In nature the three metals are usually associated together, and a close study of one will assist considerably in the understanding of all three. The reader who is interested in the electro-deposition of either iron or cobalt should therefore carefully read the chapter on nickel in conjunction with what follows.

The Electro-Deposition of Iron.

Up to the present time the principal commercial application of the electro-deposition of iron has been to give a coating of this metal to the surfaces of engraved copper plates or types used for printing purposes; the effect being to obtain a considerably harder surface and consequently to greatly increase their wearing qualities. The process has often been termed "steeling," but as the deposit usually obtained is almost pure iron this term is a misnomer.

During recent years the deposition of nickel has been strongly recommended and largely used in place of iron for this purpose. But the latter metal has at least one advantage over nickel in that it can be readily removed by a short immersion in dilute sulphuric acid, when necessary to replate after wear. Nickel, on the other hand, is very difficult to remove without risk of injury to the delicate lines of the surface engraving.

A further application of the electro-deposition of iron is now, however, slowly coming into prominence, *i.e.* what has been termed the solid deposition of iron—a process corresponding to copper electrotypy, with the difference usually that the iron reproduction is used as a die for stamping or pressing an ornamental pattern on to other metallic surfaces of a softer nature. An example of this, which may be quoted, consists in taking a copy in reverse of a piece of flat chasing or ornamentation in low relief, executed in a metal like copper or even Britannia metal which is very easy to work. This object, prepared like the metallic mould of an electrotype, is made the cathode in an electrolyte of iron salts until a solid deposit of sufficient thickness is obtained. This deposit is removed from the original surface, and is then practically an iron die possessing in its face a pattern which can be stamped or pressed on any required surface. The process is not difficult, but demands some little care and, as will be seen later, is very tedious.

Properties of Iron.—Pure iron is white and lustrous, capable of taking a brilliant polish. It is unacted upon by dry air, but in moist air a thin film of oxide forms on its surface which rapidly develops into a coating of rust.

Dilute hydrochloric acid and dilute sulphuric acid dissolve iron most readily with rapid evolution of hydrogen. Very dilute nitric acid dissolves the metal with the formation of the ferr*ous* salt, whereas stronger nitric acid gives the ferr*ic* salt. Concentrated nitric acid (sp. gr. 1·45), on the other hand, does not dissolve this metal.

Iron forms three oxides, Ferrous oxide, FeO,
Ferric oxide, Fe_2O_3,
Ferroso-ferric oxide, Fe_3O_4.

Two series of salts are formed, corresponding to the two first-named oxides. Of these the ferrous compounds are the best known and are the only ones of general use to the electroplater, though some operators, including Watt, have claimed that they have obtained good results from some ferric compounds.

Iron Solutions and Conditions of Deposition.—One of the earliest solutions used for iron deposition is that recommended by Varrentrapp,* consisting of a solution of ferrous sulphate in water of a strength of about 1 lb. per gallon, to which is added a nearly equal quantity of ammonium chloride. This latter substance may be omitted, however, without materially affecting the deposit. The principal difficulty with this solution, as with similar ones, is that on exposure to the air the ferrous salt becomes oxidized and an insoluble basic salt is formed which separates out as a green powder and ultimately interferes considerably with the action of the bath. In this respect the double sulphate of iron and ammonium gives better results. It is of the utmost importance that iron solutions be kept neutral, or, like the corresponding nickel solutions, very slightly acid.

In addition, however, to the ammonium compound, other double sulphates of iron can be used with equally good results, notably the double sulphate of iron and magnesium, and of iron and potassium or sodium respectively.

A solution recommended by Klein is made by dissolving as much ferrous sulphate in water as the bulk used will dissolve, and adding an equal quantity of a solution of magnesium sulphate of similar strength. If the solution when complete gives an acid reaction with litmus, it must be neutralized by means of magnesium carbonate, preferably added by suspending the salt in the solution in a perforated tray or muslin bag.

Another solution given by the same experimentalist is formed from freshly precipitated ferrous carbonate dissolved in dilute sulphuric acid.

To prepare the bath, make a strong solution of ferrous sulphate in freshly boiled water. Add to this a solution of ammonium carbonate until no further precipitate is

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* *Dingler's Polytech. Journal*, 187, 152.

produced. Wash this precipitate several times by decantation and then add dilute sulphuric acid (1 part of acid to 2 parts of water) until this precipitate is exactly redissolved. Great care must be exercised not to add an excess of acid. The solution should be made as strong as possible.

Klein recommends that in working the above solution a very large anode surface should be used in order to guard against the bath becoming acid during working. Obviously a large anode surface will tend to supply iron to take up any free acid which may be produced during electrolysis.

Another solution which yields good results and is very simple, is made by dissolving 1 lb. of ferrous ammonium sulphate in one imperial gallon of water (or 100 grams in 1 litre). The close resemblance of this bath chemically to that used for nickel deposition will be noted. It is of the utmost importance that the bath be exactly neutral.

The main difficulty encountered in the working of these and other solutions for the deposition of iron lies in the ease with which ferrous compounds absorb oxygen either from the atmosphere or as the result of electrolytic action, and so form ferric compounds (mainly ferric hydroxide). Such compounds are insoluble in aqueous solutions, though they readily dissolve in excess acids. Solutions containing an excess of acid, however, liberate hydrogen on electrolysis far too readily to yield sound deposits of iron.

A few years ago some exceedingly interesting investigations on the production of pure iron by electrolysis were undertaken by Professors Hicks and O'Shea of the University of Sheffield. By the kindness of Professor O'Shea we are enabled to give the following abstract of the results of their experiments, which should be of considerable assistance to workers in this branch of electro-deposition.

The object of the research thus undertaken was to produce iron free from foreign substances, especially carbon and sulphur. This had not previously been accomplished although Roberts-Austen obtained a sample containing as low as 0·007 per cent. of each of these two substances, whilst Arnold had also obtained electrolytic iron containing 0·15 per cent. sulphur and 0·011 per cent. carbon.

As these previous results had been obtained in both cases from solutions containing ferrous sulphate, and as it was conjectured that the presence of sulphur in the deposit was due to this compound, it was decided to use a salt absolutely free from sulphates or sulphuric acid. Absolutely pure ferrous chloride was first chosen as the electrolyte, but as in various ways this salt alone was found unsuitable for the production of continuous or heavy deposits (as is indeed usual in the case of single salts), the double ferrous ammonium chloride $FeCl_2 . 2NH_4Cl$ was the compound alternatively used. It was prepared by dissolving equivalent proportions of crystallized ferrous chloride ($FeCl_2 . 4H_2O$) and ammonium chloride in water. The latter salt was repeatedly recrystallized from water until it gave no trace of sulphates after standing for 24 hours subsequent to the addition of barium chloride.

It is interesting to note, however, that these investigators found that even when this salt was used a brown precipitate was liable to form and cause great difficulty by settling on the cathode, but of further interest is their statement that "The formation of this precipitate is due to the presence of ferric compounds in the solution, and if care is taken to reduce the ferric compounds before using the solution the formation of the ferric hydroxide practically ceases. Whenever it was necessary then to add fresh material to the electrolytic cell, the solution was shaken with reduced iron powder and quickly filtered before being used so that no ferric compounds were introduced into the cell; under these circumstances the electrolyte remained perfectly clear and even after continuous working for three weeks only a small deposit of ferric hydroxide had collected at the bottom of the cell."

The strength of the solution used was 5 to 6 grams of $FeCl_22NH_4Cl$ per 100 c.c. equivalent to 1·2 to 1·4 grams of Fe (approximately 2 oz. per gallon). To maintain the strength of solution, periodic additions of ferrous chloride and ammonium chloride were made. It is not desirable to allow the iron content to fall too low, for then it would appear that the ammonium chloride is decomposed in such quantities that the iron remaining in solution is precipitated as ferrous hydroxide.

With regard to current density these investigators state that too great a current density causes the deposit to strip from the plate and with the above solution 0·15 to 0·17 amperes per 100 sq. cm. was found to give the best results. It is advisable, however, to strike with a density of 0·2 amp. per 100 sq. cm. until the cathode is completely coated and then reduce it to the above value. The potential difference at the electrodes was kept at about 0·7 volt.

Under the foregoing conditions of electrolyte and current, a pure coherent deposit of iron was obtained. The only remaining difficulty was the formation of microscopic gas bubbles which adhered to the cathode at intervals and protected it from the electrolyte. This difficulty is a very familiar one to all who have attempted to produce thick deposits of either nickel or iron. These workers overcame the trouble to some extent by arranging an automatic glass scraper which periodically moved up and down over the surface of the cathode.

In order to secure the electrolyte from contamination by any impurity of the anode, the latter was enclosed in a porous cell containing a 1 per cent. solution of $FeCl_2 . NH_4Cl$. This anodic solution was charged every 12 hours.

The deposit obtained was of a dense and closely adherent character and silver-grey in colour. It was very brittle but did not possess any great degree of hardness. This latter characteristic is contrary to the experience of Roberts-Austen and others who refer to the great hardness of electrolytically deposited iron. Prof. Arnold, however, who examined a number of specimens produced as above, reported that "it cannot be correctly called hard, as when mounted upon a steel backing it can be pared with sharp scissors and it files easily." The same expert explains the brittleness of the metal as being due "to its deposition in fine needles at right angles to the plane of the cathode."

Successful results in solid iron deposition have recently been obtained by substituting calcium chloride for ammonium chloride as used in the above experiments, and working the bath hot.

Anodes.—Anodes for the electro-deposition of iron should always be of the best Swedish charcoal iron. After working for some little time in any electrolyte they will become covered to a greater or less extent with black slime—most probably carbon. They should, therefore, be periodically cleaned by taking out of the solution and scouring with fine sand, afterwards rinsing in clean water. The area of the anodes should be greater than that of the cathodes.

General Remarks on Iron Deposition.—No great difficulty will be found in the management and working of iron solutions if care is used in making up the bath so long as the operator realizes the necessity of keeping the electrolyte as near the neutral point as possible and will see that it contains a sufficiency of dissolved metal. The most important and at the same time the most usual fault is the liberation of hydrogen. This must not be allowed or the deposit will be speedily rendered useless. It is for this reason that the current density used must be kept low; consequently deposition proceeds very slowly, and when thick deposits are required the progress seems very tedious. A current supply from accumulators is under these circumstances very advantageous and indeed almost essential, for the reasons that deposition may be continued day and night, and both E.M.F. and current density exactly adjusted and kept constant at correct values.

For preparation of work the same directions apply as given for nickel.

Stripping of Old Deposits.—As indicated earlier, deposits of iron are most readily removed by immersion in dilute sulphuric acid (1 of acid to 9 of water). This liquid does not attack basis metals of copper or brass, and is, therefore, usually the most suitable to employ.

The Deposition of Cobalt.

This subject has been hitherto more a matter of laboratory experiment than of workshop practice, probably by reason of the comparatively high price of the metal, together with the fact that to the ordinary observer it is practically indistinguishable from nickel when electro-deposited, and offers only a few advantages over the latter metal. It is, however, in one or two respects, notably in resisting organic acids, superior to nickel, and if the present price could be reduced, there is great probability that it would enter into commercial use in the electroplating industry for special purposes. It is, for instance, much more suitable for a protective coating to cooking utensils than is nickel, and Langbein has suggested its use instead of iron or nickel for facing copper plates. This is quite a feasible suggestion, as a cobalt deposit is extremely hard, and yet more readily removable than nickel when a new coating is required.

The deposit from a good cobalt solution under correct current conditions is harder than that of any other metal ordinarily deposited in the arts with the one exception of platinum, and it is obviously, therefore, suited to imparting a protective coating to the softer metals and alloys, a coating which at the same time is capable of taking a most brilliant polish.

Properties of Cobalt.—Cobalt closely resembles nickel in colour and general properties, but it is slightly harder, and when polished, though brilliantly white, it possesses a bluish cast. It is malleable and ductile, the latter particularly when heated. Its most valuable property, from an electroplating point of view, in addition to its colour and hardness, is that it is practically unaffected by atmospheric action. It is slowly dissolved by both sulphuric and hydrochloric acids, but more readily by nitric acid.

Compounds of Cobalt.—Three oxides of this metal exist, corresponding to the formulæ CoO, Co_2O_3, and Co_3O_4 (note similarity to iron), and give rise to a varied series of compounds. The most soluble, however, are those formed from the first-named, *i.e.* cobalt*ous* salts.

Salts of cobalt can be distinguished, when in the hydrated condition, from nickel by their colour, which is usually pink—of a distinctly characteristic shade. The only salts of interest to the electroplater are the chloride and the sulphate.

Cobaltous chloride, when crystallized out from hydrochloric acid containing the metal or its oxides, deposits itself in dark-red prisms having the composition $CoCl_2 . 6H_2O$. When exposed to the action of sulphuric acid or some similar dehydrating agent, it loses 4 molecules of water and its colour changes to rose-red. Heated to about 100° C., the salt is converted to violet-blue crystals $CoCl_2 . HO_2$, and loses its last molecule of water at 120° C. The salt in this condition is blue, but rapidly turns pink on exposure to the air.

Cobaltous sulphate has the formula $CoSO_4 . 7H_2O$, and crystallizes out from sulphuric acid in dark-red crystals. One of the principal characteristics of this salt is its property of forming double compounds with the alkaline sulphates, ammonium, potassium, and sodium. The most common of these double salts is potassium cobalt sulphate, $CoSO_4K_2SO_4 . 6H_2O$—a salt which in conjunction with a little ammonium sulphate can be used for the electro-deposition of cobalt. Cobalt sulphate is not quite so soluble in water as the corresponding nickel salt.

Solutions for Deposition.—One of the best solutions for the electro-deposition of cobalt up to the present is undoubtedly that invented by Professor Sylvanus Thompson in the year 1887, though very good results can also be obtained from some other formulæ, particulars of which will presently be given.

The main factor in Professor Thompson's patent for cobalt-plating solutions is the use of magnesium salts, and in describing the patent several different methods of making up the bath are quoted. The most usual method is to mix together one volume of a saturated solution of cobalt sulphate, and 20 volumes of a similar solution of magnesium sulphate, but the following alternative suggestions are given by the inventor :—

Take of—

(1) Double sulphate of cobalt and ammonium	1 lb.	500 gr.
Magnesium sulphate	½ ,,	250 ,,
Ammonium sulphate	½ ,,	250 ,,
Citric acid	1 oz.	31·2 ,,
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres
(2) Cobalt sulphate	½ lb.	250 gr.
Magnesium sulphate	¼ ,,	125 ,,
Ammonium sulphate	¼ ,,	125 ,,
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

The similarity of the above solutions in principle to some of those detailed in the chapter on nickel will be noted.

All the above give better results when worked warm than cold; the patentee himself suggests a temperature of about 35° C.

A bath which yields very good results, though scarcely as good a conductor as Thompson's baths, is the following :—

Double sulphate of cobalt and ammonium	6 ozs.	187 gr.
Boric acid	1½ ,,	46·8 gr.
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

This solution is a modified form of one originally suggested by Langbein.

The simplest possible cobalting solution is made up by dissolving 1 lb. of the readily obtainable double sulphate of potassium and cobalt—referred to previously—in one imperial gallon (or 100 grs. per litre) of water. Such a bath is improved by the addition of a small quantity, say 1 oz. per gallon, of sodium hypophosphite. This salt, it may be remarked incidentally, appears to be a very useful addition to cobalt solutions generally.

Anodes.—It is most essential in cobalt-plating that the anodes be the purest obtainable. The colour of cobalt deposits seems to be peculiarly susceptible to changes of conditions of the electrolyte, and is often greatly modified by the presence of impurities from the anode or indeed from any other source. The common impurities are iron, nickel, and arsenic, and occasionally bismuth, but the metallurgy of cobalt has undergone considerable improvements during recent years, and it is possible now to obtain cobalt anodes of a very high degree of purity.

Since cobalt is rather more soluble than nickel in such electrolytes as are outlined above, it is not so essential that *cast* anodes should be used. They may, therefore, be either cast or of rolled sheet as found most convenient to procure. It is important, however, to anneal and thoroughly cleanse them before immersion in the vat.

Current Conditions.—The question of correct conditions in cobalt deposition is very important. The stumbling-block which the beginner will almost invariably find is that of obtaining a dark-coloured faulty deposit, through using too high a current density. In this respect, as in many others, it is very similar to iron, and the same values apply to both metals, *i.e.* about 1½ amperes per square foot. For the first few seconds of immersion, a little higher current may be applied, but it must be quickly reduced.

It appears to us to be probable that by the use of some suitable additive agent in the electrolytes, a higher value might be made allowable—greatly to the advantage of the process—but this point requires further investigation.

The voltage required depends largely on the temperature of the bath as also on the class of work done, but should not much exceed 2 volts, particularly if the solutions are used warm.

Stripping Cobalt Deposits.—Old deposits of cobalt are more conveniently removed than nickel owing to the greater solubility of the former metal in dilute sulphuric acid. For copper and copper alloys which have been cobalt-plated the best treatment, therefore, is to immerse in a solution of dilute sulphuric acid (1 acid, 8 to 10 water). This solution has little or no effect on the basis metal.

In the case of basis metals like iron or zinc, the process must, however, be carefully watched and the article taken out of the stripping liquid immediately the deposit is removed, since such metals are very readily attacked by the acid.

CHAPTER XIV

DEPOSITION OF ZINC AND CADMIUM

THESE metals closely resemble each other both in physical and chemical properties, and are usually found associated in nature. Of the two, zinc is at present much the more important and the cheaper. Cadmium, however, possesses certain very useful qualities which are gradually bringing it into greater prominence in the arts, and the subject of its electro-deposition will consequently assume some degree of importance. Greater prominence, however, must necessarily be given in the present chapter to zinc.

The Deposition of Zinc.

Zinc has for a long period been largely used for imparting a protective coating to iron and steel, but most generally this has been carried out by means of the process technically termed "hot-galvanizing."

This process consists essentially of a simple immersion in molten zinc—a thin coating of the metal in consequence adhering to the immersed article if properly cleansed and prepared. The term "galvanizing" applied to such a method is, however, obviously a misnomer, since this term implies electrical agency or the use of an electric current, which is not the case.

Up to recent years this process for zinc deposition has practically held the field and even now is largely employed, but electro-deposition methods are now prominently to the fore and their use is increasing since, as compared with the former and older method, they possess several important advantages, which may here be enumerated.

These are—1. That from suitable electrolytes a perfectly adherent and coherent coating of a fair degree of thickness can be built up; whereas in hot galvanizing only a comparatively thin coating can be acquired.

2. The physical quality of the deposited metal is much more completely under the control of the operator, and Philip * has found that the same weight of zinc per unit of surface of iron has a greater protective action against certain tests when deposited electrolytically than when deposited by the ordinary hot galvanizing process.

3. The physical and mechanical properties of the *basis* metal are much less liable to be detrimentally influenced when the zinc deposit is given in an aqueous electrolyte than when in a hot bath of molten zinc. An illustration of the vital importance of this point is found in the case of hardened and tempered steel articles which by careful manipulation have been given certain qualities required for special trade purposes. These properties may conceivably be entirely destroyed by the alterations in temperature which immersion in molten zinc would necessitate.

Other advantages, such as greater smoothness of deposit, and less liability to loss of metal in dross and waste, have also been claimed for the electrolytic process.

It should also be remembered that, as in most cases of metal obtained by electrolysis, electro-zinc deposits have a high degree of purity, certainly much higher than many grades of commercial zinc possess, and consequently are not so liable to the disintegrating action which impure zinc undergoes in the presence of weak acids, alkalies, or even water itself (see below).

Properties of Zinc.—Zinc is a bluish-white metal closely resembling tin. It is moderately hard and fairly

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* Watt and Philip, *Electroplating and Electro-refining*, pp. 633, 634.

malleable and ductile. It exhibits the latter properties to its greatest extent when heated to from 100° to 150° C. At a little over 200° C., however, it becomes extremely brittle and may be powdered. Zinc is slowly attacked by the atmosphere, and according to Davies * it is attacked and slowly dissolved by water. The susceptibility of zinc to the action of acids largely depends on its degree of purity. Pure zinc is only very slowly dissolved by dilute sulphuric acid, while if only a small percentage of impurity is present it is rapidly dissolved with copious evolution of hydrogen gas. The reason for this lies in the fact that the usual impurities present, such as lead, tin, iron, and carbon, are more electronegative than zinc itself, and form galvanic couples, over the entire surface acted upon by the acid, in which the zinc is electropositive to each of the other metals present. A miniature primary battery is, therefore, set up, and by electrochemical action, zinc dissolves and hydrogen is evolved from the negative elements. The surface of the zinc is thus continually being exposed to this action, which continues until the metal is completely dissolved. With pure zinc, on the other hand, the film of hydrogen formed by the combination of the metal with the SO_4 radicle remains on the surface of the zinc, and prevents further action by the acid.†

Zinc is also very soluble, under similar conditions, in hydrochloric acid, and also in strong solutions of the alkalies, *e.g.* potassium or sodium hydroxide. In this case also hydrogen is evolved and an hydroxide of the metal formed which is soluble in excess of the alkali solution.

The common impurities of commercial zinc are iron, lead, cadmium, carbon, and traces of antimony and arsenic.

Compounds of Zinc.—Two oxides of zinc are known, the monoxide ZnO, and the peroxide ZnO_2. The former is the most stable and gives rise to all the commoner zinc salts. Of the latter the most important in electro-deposition are the chloride and sulphate.

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* *Journ. Soc. Chem. Ind.*, vol. 18 (1899), page 102.

† Roscoe and Schorlemmer, *Treatise on Chemistry*, vol. ii. p. 641.

Zinc chloride ($ZnCl_2$) is a white soft waxlike substance usually obtainable in the form of cakes or sticks. It is very deliquescent, and soluble both in water and alcohol. When dissolved in its own weight of water a clear solution results. Dilute solutions of zinc chloride are often opalescent, but may be rendered clear by the addition of HCl. The usual impurities of trade varieties of this salt are iron, zinc sulphate, and traces of the heavy metals as well as arsenic.

Zinc chloride forms double compounds with the corresponding ammonium salt, $ZnCl_2.2(NH_4)Cl$ and $ZnCl_2.3(NH_4)Cl$. Those double salts have been suggested and often used for zinc deposition.

Zinc sulphate, $ZnSO_4.7H_2O$, commonly known as white vitriol or zinc vitriol, is usually obtained as colourless needle-like crystals, similar to Epsom salts (magnesium sulphate). It is readily soluble in rather less than its own weight of water, but insoluble in alcohol (compare the chloride). It is obtained on a very large scale commercially by roasting ores containing zinc sulphide (ZnS) in air, thus oxidizing the sulphide to sulphate, afterwards dissolving the latter salt out in water, evaporating, and allowing to crystallize. As usually placed on the market it has a high degree of purity; the usual impurities are arsenic and iron.

Zinc sulphate forms a series of double salts with the alkali sulphates having the same general formulæ, *e.g.* $ZnSO_4.K_2SO_4.6H_2O$, the double sulphate of zinc and potassium. Both this salt and the corresponding magnesium compound have been largely used for the electro-deposition of zinc.

Solutions for Deposition.—A very large number of solutions have at various times been tried and used for electro-zincing, but though different workers have obtained rather variable results, the general consensus of opinion amongst practical operators is that those of the sulphate, alone or with other salts, give for general purposes the most reliable results obtained up to the present, with the minimum of trouble in working.

Philip * summarizes the result of a series of investigations which he has made into the question of suitable electrolytes for the deposition of sound and adhesive coatings of zinc upon iron as follows :—

" Aqueous solutions of zinc sulphate, and of this salt mixed with about molecular proportions of sodium sulphate, potassium sulphate, ammonium sulphate, aluminium sulphate, and magnesium sulphate, all gave electrolytes from which good and adherent deposits of metallic zinc could be obtained by electrolysis, but on the whole a solution of zinc sulphate and magnesium sulphate in molecular proportions, and containing about 30 ounces (avoir.) of zinc sulphate per gallon was the solution which yielded the most satisfactory results. Zinc deposited from this solution did not contain more than a very small trace of magnesium, and it is quite possible that the amount detected (0·028 part per cent.) may have been due to the small traces of magnesium salt dissolved in the electrolyte adhering to the deposited metal."

More recently attempts have been made to improve zinc baths by the use of substances as addition-agents, and very promising results are being obtained in this direction. Notable instances which may be cited are the addition of ferrous sulphate (patented by Cowper-Coles) and aluminium sulphate, which appears to be largely used in American and Continental practice; also organic additions such as glucose or grape sugar, and a class of substances known as glucosides, which as additions to zinc baths are patented by Classen (U. S. Pat. 809,492, 1906), an example being licorice root.

A point upon which great emphasis must be laid is that good results in zinc deposition cannot be obtained from solutions which are weak in metallic content. It may be taken as a fairly safe generalization that whatever bath be used the proportion of metal should not be less than from 4

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* Watt and Philip, *Electroplating and Electro-refining of Metals*, p. 631.

to 5 oz. per gallon (25 to 31 gr. per litre). With such or a greater strength, current densities of a fairly high value (25 to 30 amps. per sq. foot) can be used, and a greatly superior quality of deposit obtained than with the lower current densities necessitated by poorer solutions. The reason for this rather peculiar feature of zinc deposition is generally supposed to be due to the extremely electro-positive nature of the metal; hydrogen being more easily liberated, the proportion of gas to metal is abnormally high with low currents.

In giving details of the composition of specific baths for zinc deposition it will be convenient to adopt the following classification, (*a*) neutral or slightly acid baths, (*b*) alkaline baths.

(*a*) Of the former class the sulphate solutions are by far the most important, and these will first be described.

Solution I. (Richter)—

Zinc sulphate ($ZnSO_4 . 7H_2O$) .	50 oz.	1·56 kg.
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. „	5 litres

This solution, as will be noted, is exceptionally rich in metal, and should be worked with a current density of not less than 25 to 30 amperes per sq. foot. With low currents there is a tendency to liberate hydrogen, and render the deposit loose and powdery. It is a particularly suitable bath for large wrought- or cast-iron work, also for iron or steel wire. It is, however, of great importance that the anode surface immersed shall be fully equal to if not greater in area than the cathode. The temperature of the solution also is an important feature in obtaining successful results. In any case this should not be below 30° C., and it is advisable to work at 50° C., or even more.

Solution II. (Philip)—

Zinc sulphate ($ZnSO_4 . 7H_2O$)	30 oz.	937 gr.
Magnesium sulphate ($MgSO_4 . 7H_2O$) . .	25 „	780 „
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. „	5 litres

This bath, which is typical of a number of other similar zinc solutions used in modern commercial practice is really a simple aqueous solution of the double sulphate of zinc and magnesium, and similar results are obtainable from the corresponding potassium compound. It is best worked warm at a temperature of from 50° to 70° C.

Solution III.—

Zinc sulphate	2 lbs.	1 kg.
Aluminium sulphate . . .	1½ oz.	46·9 gr.
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

4 ozs. (or 125 gr.) of alum may be substituted for aluminium sulphate in this solution with practically the same effect, and periodical additions of either of these substances should be made to the bath as experience indicates, the purpose of these salts being to allow currents of a higher density to be used in working.

The influence of aluminium sulphate on zinc baths has been already referred to, and it may be of interest to remark here that an explanation of the phenomenon offered by a recent writer * is that the aluminium salt ($Al_2(SO_4)_3$) dissociates in solution into aluminium hydroxide and sulphuric acid. Under these circumstances the former acts as a colloid, which moves to the cathode, and influences the size of the deposited crystals in the same manner as starch or gum arabic in an acid copper bath (see page 249).

Solution IV. (Cowper-Coles patent)—

Zinc sulphate	40 ounces	1·25 kg.
Ferrous sulphate . . .	5 ,,	156 gr.
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

The inventor states that the ferrous sulphate gradually becoming oxidized to ferric sulphate by the action of the atmosphere takes up acid from the bath, and so tends to

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* Schlötter, *Galvanostegie*, vol. i. 38–51 (1910).

keep it neutral. This solution is used with lead anodes, which are insoluble, and the strength of the electrolyte is kept up by continually pumping the liquid through scrubbers of coke charged with zinc dust or zinc oxide. By this method also the ferric salt is once more reduced to ferrous sulphate by contact with the zinc dust, and the solution consequently maintained at the correct constitution.

Mr. Cowper-Coles considers that the presence of ferrous sulphate tends to prevent the formation of powdery deposits which Mr. Arnold Philip * thinks are probably caused by the formation of an oxide or hydrate of zinc. It appears to us, however, that the action of this salt is very analogous to that of aluminium sulphate (see p. 315), and its influence on the deposit may, in all likelihood, be similar.

Other solutions for the deposition of zinc of the same type as the above, which have been suggested are, the double chloride of zinc and ammonia, the double chloride of zinc and sodium or potassium, and one of equal molecular proportions of zinc chloride and aluminium chloride, but none of these present advantages over the sulphate baths.

(*b*) Of distinctly alkaline baths for zinc deposition only one calls for detailed description, viz. the cyanide bath.

This bath appears to have been originally introduced by Watt, who obtained a patent for it in 1855. It can be made either chemically or electrolytically, but the inventor preferred the latter method, and carried it out as follows.

Two hundred ounces of potassium cyanide were dissolved in 20 gallons of water, and to this solution were added 80 ounces by means of liquid ammonia. The solution was thoroughly stirred and filtrated and then electrolysed by means of large zinc anodes and small copper cathodes—the latter enclosed in ferrous cells. Electrolysis was continued until the bath had gained a metallic content of about 60 ounces.

Watt also recommended the addition of 80 ounces of

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* Watt and Philip, *Electroplating and Electro-refining of Metals*, p. 636.

potassium carbonate, but the solution works quite well without such addition.

A solution very similar in composition and working qualities to the above is made up chemically as follows :—

Zinc sulphate	15 ounces	468 gr.
Potassium cyanide	Q.S.	
Ammonium carbonate . . .	5 ounces	156 gr.
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

A strong solution of potassium cyanide is made up containing 1 lb. per imp. gallon (100 gr. per litre), and added to the zinc salt, which has been previously dissolved in half a gallon (2½ litres) of water, until the white precipitate which at first forms is redissolved. The solution must be constantly stirred during the process to ensure complete conversion of the zinc salt to the double cyanide, and about 10 per cent. more cyanide added to form free cyanide. Add then the ammonium carbonate dissolved in a little water and, if necessary, make up the bulk of the liquid to 1 gallon or 5 litres, by adding water.

The cyanide solutions work very well and give good results, particularly for small work and thin deposits, but they are not suitable for thick deposits, and for larger work they are very costly.

One other alkaline bath may be given brief mention, viz. zinc hydroxide ($Zn(HO)_2$), dissolved in excess of caustic potash. It is formed very simply by dissolving in water sufficient zinc sulphate or chloride, to give a strength of 3 ounces of zinc per gallon of resulting solution, and adding a strong solution of caustic potash until the precipitate which first forms is redissolved.

During the last few years, a number of patents for solutions for zinc deposition have been taken out both in Europe and America. Very few of these, however, possess any features of interest or novelty; most are based on additions to the sulphate bath, such as sodium sulphate, sodium chloride, and salts of ammonium, aluminium, etc. The one possessing greatest novelty is that of Dr. Kern, who has patented a fluosilicate bath analogous in composition to those already described for copper and nickel. The formula recommended is—

Zinc fluosilicate	12 parts by weight
Aluminium fluosilicate . . .	10 ,, ,, ,,
Ammonium fluoride	5 ,, ,, ,,
Water	100 ,, ,, ,,

with the addition of small proportions of grape sugar.

Anodes.—Except in cases where the supply of metal into the electrolyte is regulated by special methods, as in the Cowper-Coles process to be described later, anodes for zinc-plating should be of the purest zinc obtainable, and it will usually be found advantageous to procure them in the form of cast plates, $\frac{3}{8}$-inch thick or more, so that their current-carrying capacity is high. Lead is the commonest impurity of zinc, and it is very difficult to procure the latter "lead-free." Fortunately, however, this impurity is not important, and there is now no difficulty in getting metal of 98 to 99 per cent. purity, so that other metals present are only in very low proportion.

Current Conditions.—The voltage required in zinc deposition varies somewhat according to the composition and temperature of the electrolyte, zinc sulphate baths requiring rather a higher value than some others. In most cases, however, from 4 to 6 volts will be found satisfactory.

The current densities in general use range from 25 to as high as 45 amperes per square foot. The sulphate baths, as a rule, give excellent results with C.D.'s of approximately 30 amperes per square foot.

Management of Zinc Solutions.—The most important point in the control of the electrolytic deposition of zinc is to keep up the strength of the bath in metallic content. In stagnant solutions this is a matter of some little difficulty, as any appreciable degree of free acid is not allowable. Cowper-Coles, in connection with the solution No. IV. described on p. 315, has devised and patented the method there detailed of overcoming this difficulty, viz. by continually pumping the electrolyte from the vat during electrolysis and forcing it through coke scrubbers containing a plentiful supply of zinc oxide or zinc dust. The solution is thus not only kept fully charged with metallic zinc, but, for the same reason, prevented from becoming acid. The pumping arrangement is so devised that the level of the solution inside the vat is kept practically constant, but as the electrolyte is denuded of its metal at the cathode it is taken off, pumped through the zinc dust, and enters at the other end of the bath. Philip, whose investigations on the subject of zinc deposition have already been referred to, points out in a discussion of the Cowper-Coles process, that the zinc solution could under similar conditions be kept saturated by pumping it through scrubbers containing zinc and copper or zinc and carbon in intimate contact—the electric couple thus formed setting up local action and neutralizing the acid present with solution of zinc. Methods of this description are not patented.

The main advantage claimed for the Cowper-Coles process is that the use of zinc dust is considerably cheaper than an equivalent of zinc in the form of any of its salts. It is a matter of some doubt, however, whether on the basis of present-day prices this claim could be substantiated to any great extent.

It may be pointed out that the zinc bath can also be kept neutral by suspending zinc carbonate at various points in contact with the liquid, particularly if agitating arrangements are employed. The salt can readily be prepared in the workshop by first dissolving zinc in sulphuric or hydrochloric acids, and precipitating as carbonate by adding a strong solution of washing-soda crystals.

In attempting to obtain *thick* deposits of zinc considerable difficulty is often experienced through the tendency which seems to be inherent in all these solutions to deposit the metal in a spongy tree-like condition, particularly on the edges or extruding points of the cathode. The best method apparently available at present to overcome this trouble is to use an organic addition agent such as grape sugar. A fruitful field of investigation, however, lies open in this direction.

Special Treatment of Articles for Electro-zincing.—For zinc deposition the electroplater is often, indeed usually, called upon to deal with one of the most difficult and troublesome basis metals known to platers, *i.e.* cast iron. The porous nature of such surfaces combined with the difficulty often encountered of removing scales and oxide render the problem of preparation no easy one to solve. Electrolytic cleansing and pickling are now usually resorted to as described on p. 155, the sodium sulphate bath being very useful, with arrangements for reversing currents.

Probably, however, the best results are obtained by combining these methods with sand-blasting; the sand blast should be used immediately prior to immersion in the depositing vat.

Philip in the treatment of high-carbon steel wire adopted the expedient of cleansing by running it as anode through a preliminary vat of zinc sulphate solution immediately before it entered the depositing vat proper. Cowper-Coles describes * a method, based on the same principle, in which the articles are immersed in the zincing vat in the ordinary manner, but for the first 2½ minutes they are made *anodes* instead of cathodes, the current being reversed; after that period the direction of the current is again changed, and the deposit takes place in normal fashion; the adhesion of the zinc coating was found to be considerably better than in the case of plates treated in the ordinary manner.

Testing Zinc Deposits.—Several methods have been designed for testing the quality and thickness of zinc

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* *Electrician*, vol. xliv., 1900, p. 434.

deposits, but as a general rule these tests are only relative, and are thus of value mainly as a means of roughly comparing the thickness of a number of different specimens of zinc-plated iron articles. The best known of these "tests," and probably the most generally convenient for workshop practice, is that suggested by Sir W. H. Preece. This test has been slightly modified by Mr. Arnold Philip, and the following description is that given by this authority. "The zinc-coated iron is immersed in a saturated solution of copper sulphate at a temperature of 15° C. for one minute, then immediately removed, and placed under a rapidly running stream of water from a tap in which it is well shaken. In this way is removed any of the loose flocculent deposit of copper which has been formed on the surface of the zinc by zinc displacing the copper from the copper sulphate solution, but if the zinc has been so far removed as to expose the surface of the underlying iron to the action of the copper solution a much more coherent deposit of bright copper is formed on the iron *which is not removed by shaking under the water stream.* The number of successive times, therefore, that a zinc-coated piece of iron will withstand this treatment is a measure of the thickness and regularity of the zinc coating."

The copper sulphate solution must only be used for one immersion and then thrown away, as of course it becomes contaminated with zinc. In the case of steel goods it should be noted that the copper deposited on such surfaces when revealed to the action of the solution can sometimes easily be removed by rubbing with the finger—no steps should, therefore, be taken to remove the deposit of copper other than shaking under running water. If the whole of the zinc is not removed, the copper is easily washed away by this treatment.

Mr. Philip has found that the protective effect of the zinc depends upon how it has been applied, and states that the same *weight* of zinc per unit of surface has a greater protective action against the Preece test when deposited electrolytically than when deposited by the ordinary "hot-galvanizing" process.*

The Deposition of Cadmium.

This subject is at present of academic rather than of practical interest, very few commercial applications having been found for the metal from an electroplating point of view. Cadmium possesses, however, some very useful properties, and there is at any rate the probability that in the future its electro-deposition will find some useful application.

It may be of interest to observe that a few years ago one of the present authors in a series of experiments dealing with the deposition of the principal *white* metals of commerce electroplated a number of small trays with a coating of each of the following metals, silver, nickel, cobalt, zinc, tin, lead, and cadmium, and exposed these for some months to ordinary atmospheric influence in various rooms. Several interesting results were obtained bearing on the action of the atmosphere on electro-deposited metals, but a point of great interest relating to cadmium was that, when polished, the deposit of this metal had a colour more nearly approaching that of silver than any of the others, and *retained* its polish much longer than silver without tarnishing or discolouring.

The metal is rather high in price, but as it occurs fairly abundantly in nature this should be reduced if a steady demand arose.

Properties of Cadmium.—Cadmium resembles zinc very closely both in physical, mechanical, and chemical properties. It is a shade whiter in colour than zinc, but has a slightly bluish cast. It is very malleable and ductile at a normal temperature, but when heated becomes brittle. When polished it resembles tin, but takes a more brilliant polish than this metal and is somewhat denser. Cadmium is not

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* Watt and Philip, *Electroplating and Electro-refining of Metals*, p. 634.

attacked by air at ordinary temperatures and is only slowly dissolved by strong acids. For the purpose of preparing electrolytic solutions, it is most conveniently dissolved in dilute nitric acid (1 acid, 1 water).

Compounds of Cadmium.—The salts of cadmium are closely analogous to those of zinc. The principal ones are the nitrate, sulphate, chloride, and carbonate. The distinguishing feature of cadmium is its formation in chemical reaction of a yellow sulphide insoluble in alkalies. It can thus be tested for in alkaline solution by the addition of ammonium sulphide or sulphuretted hydrogen gas, and distinguished from all other metals by this yellow precipitate. For making electrolytic solutions the nitrate is most commonly employed as a starting-point; formula—

$$Cd(NO_3)_2 . 4H_2O.$$

Solutions for Deposition.—The most successful solutions for the electro-deposition of cadmium are those of the cyanides. Solutions of the sulphate, alone or in combination with other salts, have often been tried, and some operators have claimed good results therefrom, but for most classes of work the double cyanide of cadmium and potassium will be found most reliable.

As far back as 1849, Russell and Woolrich obtained a patent for a cyanide solution for the deposition of cadmium, and the method they adopted for making the solution is as convenient a one as could be devised, viz. to prepare a solution of cadmium nitrate either by dissolving the metal in dilute nitric acid or by dissolving the salt directly. Add to this a solution of sodium carbonate until no further precipitate is produced. Stir vigorously and wash the precipitate with warm water, allow to settle, and decant the clear liquid. The compound thus obtained is a normal carbonate of cadmium. Prepare now a strong solution of potassium cyanide (1 lb. per imperial gallon, or 100 gr. per litre) and add this slowly with constant stirring until the whole of the cadmium salt is dissolved and a clear liquid results.

A further addition of about 10 per cent. must be made for free cyanide, and after boiling the solution is ready for use.

The strength of the bath may be varied considerably, but it is not wise to attempt to work a cadmium solution weak in metallic content. The following proportions will be found satisfactory:—

Cadmium nitrate	1 lb.	500 gr.
Sodium carbonate	Q.S.	
Potassium cyanide	Q.S.	
Water	1 imp. gall. or 1⅕ U.S. „	5 litres

If metallic cadmium is used 5½ ounces (170 gr.) will be required to yield the above proportion of the nitrate.

The bath may also very conveniently be formed electrolytically in the manner described for silver (page 184). The electrolyte should be made up by dissolving 1¼ lbs. of 95 per cent. potassium cyanide per imperial gallon of water (or 125 gr. per litre). The anodes should be of a fair thickness, say ¼ or ⅜ of an inch, and it will be found convenient to use strong strips of lead as cathodes enclosed in porous jars also containing cyanide solution.

The only objection to this method as in the case of silver is the difficulty of adjusting exactly the proportion of free cyanide—a large excess must be avoided, since in this case there is a decided tendency to roughness of deposit.

Current Conditions.—The voltage usually advised for cadmium deposition is 3 to 4 volts, but good deposits can be obtained with lower values than these figures, particularly if the solution is used warm. It is, in fact, advisable to employ as low a voltage as possible, otherwise the deposit is liable to be rough and crystalline.

CHAPTER XV

THE DEPOSITION OF LEAD, TIN, AND ANTIMONY

At the present moment, and writing from an electroplating point of view only, the three metals dealt with in this chapter here, with the exception possibly of tin, are of comparatively little interest for the practical worker.

It is quite possible and even probable, however, that the immediate future will witness an increase of the commercial possibilities of electroplating with these metals, and some little space should therefore be devoted to an outline of the principal methods of their deposition.

Deposition of Lead.

The electro-deposition of this metal has received considerable attention in modern times from the refining point of view, several processes for the electrolytic refining of lead having been worked with more or less success. The greatest difficulty has been found in the choice of a suitable electrolyte, owing to the peculiar and characteristic tendency of this metal to deposit in tree or fern-like crystals from simple solutions of its salts, a familiar illustration of which is found in the old experiment of growing a "tree" by the simple immersion of a strip of zinc in a strong solution of lead acetate. On *electrolysis* of lead solutions similar effects are obtained.

Properties of Lead.—Lead is a very soft metal of a bluish-white colour, and when freshly exposed to the atmosphere presents a bright metallic lustre. It speedily oxidizes, however, to a slight extent, and is covered with a dull film after a short exposure in air. It can easily be rolled to extreme thinness, but it cannot be drawn into wire. If repeatedly melted, lead becomes hard and brittle, due, according to some authorities, to the formation of oxide. Lead containing also small percentages of impurities, notably antimony, zinc, bismuth, and arsenic, is decidedly brittle. The most important property of lead from the point of view of use as a deposited coating, is its power of withstanding water and most acids to an appreciably greater degree than most of the common metals. It is this latter property which is likely to lead to its adoption as a protective coating to some of the harder metals and alloys for particular purposes.

Compounds of Lead.—The most important of lead compounds is the monoxide (PbO) commonly known as "litharge," though as many as five different oxides are known. Of the salts of lead the best known are the chloride ($PbCl_2$), the nitrate ($Pb(NO_3)_2$), the carbonate ($PbCO_3$), and the sulphate ($PbSO_4$). Other salts which have been brought into prominence in electrolytic practice recently are the fluosilicide ($PbSiF_6$) and the perchlorate ($Pb(ClO_4)_2.3H_2O$).

Solutions for Deposition.—One of the oldest published formulæ for lead deposition is the following:—

Litharge (PbO) . . .	5 parts by weight
Caustic potash	50 ,, ,, ,,
Water	1000 ,, ,, ,,

The caustic potash is dissolved in the water, the solution raised to boiling point, and the powdered litharge added; boiling is continued until a clear solution results. It is very difficult, if not impossible, however, to obtain a deposit of any appreciable thickness from this bath, though it is quite suitable for thin coatings.

In our experience the best solution at present available where thick deposits are required is that used in the Betts process of lead refining by electrolysis. This solution consists of an aqueous solution of lead fluosilicide with about 10 per cent. of free hydrofluoric acid. Generally, however, a small percentage of glue or gelatine is added to prevent or reduce the tendency, which, even in this electrolyte, is evident, to the formation of "trees" on the cathode edges.

For hydrofluoric acid, pyrogallic acid is occasionally substituted with beneficial results.

The following formula has been found by one of our colleagues to yield an excellent deposit in continuous electrolysis for upwards of 60 hours :—

Lead fluosilicide	8 oz.	250 gr.
Pyrogallic acid	1 ,,	31·2 ,,
Glue	1 ,,	31·2 ,,
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres

The anode readily dissolves in the electrolyte and, when pure lead is employed, no slime is formed.

Some very good results have recently also been obtained* from solutions of lead perchlorate in water. Such an electrolyte is an extremely good conductor and yields a beautifully smooth coherent deposit. Mathers has carried out experiments with the bath, but finds that the best results are only obtained when a small proportion of peptone is added. These experiments, it may be remarked, simply bear out the experience of most investigators in this direction, that the use of some addition agent is absolutely necessary in lead baths to prevent treeing.

The proportions of the bath recommended by Mathers are as follows :—

Lead perchlorate [$Pb(ClO_4)_2 3H_2O$]	1 lb.	500 gr.
Perchloric acid ($HClO_4$)	$\frac{1}{2}$,,	250 ,,
Peptone	0·05 per cent.	
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres

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* *Transactions of Amer. Electro-chemical Society*, vol. xvii. (1910), p. 261.

The effect of the peptone gradually wears off as the bath is worked, and further similar additions must be made about every four days.

The constituents of the bath should be freshly prepared as required, and the following directions are taken from the paper to which reference was made above.

Perchloric acid is formed from sodium perchlorate by treating with excess of concentrated hydrochloric acid. The mixture is filtered through asbestos, and the residue, which is sodium chloride ($NaCl$), is washed with a further small quantity of concentrated HCl. The filtrate consists of an aqueous solution of perchloric acid, hydrochloric acid, and a small proportion of sodium perchlorate. By heating to 135° C. the hydrochloric acid is volatilized, leaving an almost pure solution of perchloric acid.

Lead perchlorate is formed by neutralizing this acid with litharge (lead monoxide).

With the bath as above formed and with careful periodic additions of peptone, current densities up to 27 amperes per square foot can safely be used.

Anodes.—Anodes for lead-plating should be as pure as possible. Electro-negative impurities, which may easily be present, readily find their way into the electrolyte and are accordingly deposited, with material effects, on the quality of the deposit. In either of the two baths last described pure lead anodes are readily soluble, so that the metallic content of the solution is continually replenished; and obviously the degree of purity of the latter is dependent entirely upon that of the metal of the anode itself.

Nobili's Rings, or Electrochromy.—A peculiar phenomenon of some lead electrolytes is their tendency to deposit peroxides of lead on the *anodes*. These peroxide films, if produced under correct conditions and in an extreme degree of thinness, give most beautiful colour effects. Nobili was the first to observe this peculiarity, and the production of these effects is now known under his name.

A good solution for the purpose is that proposed by Becquerel and made by dissolving litharge in a solution of caustic potash.

Becquerel's formula is as follows:—

Litharge	10½ oz.	328 gr.
Caustic potash	14 ,,	436 ,,
Water	1 imp. gall.	5 litres

The required weight of caustic potash is dissolved in water, the solution raised to boiling point, and the litharge added slowly with constant stirring.

The articles to be treated are prepared exactly as if for plating and suspended in the solution from the anode rod, the cathode being a piece of platinum or copper wire. The films of colour are produced very quickly, being successively yellow, green, red, violet, and blue. The current must be low and adjusted according to the distance between the electrodes. Too high a current or too long immersion completely spoils the colour effects.

Variations of the patterns formed by the colours, can be made by introducing cardboard discs with perforated designs, between the anode and cathode.

Some little practice and experience is, however, necessary to obtain good results in this field. Each difference of shape or size in the article treated demands a variation in current conditions or time of immersion, and the correct values can only be determined by experiment.

Deposition of Tin.

Tin is largely used as a protective coating to iron and steel goods, but in the case of a large majority of such articles it is applied by the simple method of dipping the work, after previous cleansing, into a bath of molten metallic tin. This is both a simpler and cheaper method of depositing tin than processes involving the electro-deposition of the metal from aqueous solutions. In spite of this, however, a good deal of electro-tinning is carried on in the Midlands;

its application being mainly to small goods and to some extent to providing an intermediate coating to articles of iron and steel which are to be subsequently silvered or nickelled.

Properties of Tin.—Tin is a very lustrous white metal which is not acted upon by air, hence its suitability as a protective coating to more readily oxidizable or tarnishable metals. It is malleable and ductile, can be beaten out into leaf (tin-foil) or drawn into wire. If, however, it is heated to just over 200° C. it becomes curiously brittle and may be powdered. With regard to hardness it comes between zinc and lead, being harder than the latter metal but not quite so hard as the former.

Tin is readily attacked by nitric acid of a specific gravity of 1·24, but the strongest *pure* nitric acid (sp. gr. 1·5) is without action upon it. It is slowly soluble in dilute nitric acid. For the requirement of the electroplater tin is usually best dissolved in strong hydrochloric acid; stannous chloride being formed with the liberation of hydrogen. From this salt as a starting-point most electro-tinning solutions are made.

Solutions for Deposition.—A large number of solutions have at various times been suggested for the electrodeposition of tin, and the choice of a solution depends largely upon the particular kind of work to be done and the conditions with regard to temperature of working and current available. Any of the baths given below will yield good results if made and used according to the directions outlined.

Formula I.—

Metallic tin	2 oz.	62·5 gr.
(converted into stannous chloride by dissolving in hydrochloric acid)		
Pure potassium hydroxide (caustic potash)	4 oz.	125 gr.
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres

Just sufficient acid should be used to dissolve the tin;

and the potassium hydroxide, previously dissolved in 2 quarts of water, is then added. A precipitate of stannous hydrate is first formed and then redissolved. If required, a further quantity of potash may be added to effect complete solution. The bulk is then made up to 1 gallon by a further addition of water as necessary, and boiled for a short time before use.

Formula II. (Roseleur)—

Stannous chloride	1 oz.	31·2 gr.
Pyrophosphate of soda . .	10 ,,	312 ,,
Water	5 imp. gall. or 6 U.S. ,,	25 litres

The pyrophosphate of soda is dissolved in the water and when solution is complete the tin salt is added. The best method of adding the latter is to enclose it in several muslin bags and hang these just under the surface of the liquid. Stannous chloride is soluble with difficulty in the pyrophosphate solvent, and this is practically the only way to ensure its complete solution.

This bath is decidedly one of the best, particularly for thin coatings of tin. The objection principally made with regard to it is its comparatively small content of metallic tin. It is this which renders it unsuitable for thick deposits; but it is very largely used for electro-tinning where only thin films are needed.

It is best worked warm and requires a voltage of about 3 volts.

Formula III.—

Stannous chloride	½ oz.	15·6 gr.
Potassium cyanide	3½ ,,	109 ,,
Potassium carbonate . . .	30 ,,	937·5 gr.
Water	2½ imp. galls. or 3 U.S. ,,	12 litres

The bath is made up by dissolving the tin salt in sufficient water, then adding the potassium cyanide and finally the potassium carbonate, each previously dissolved in water.

Further additions of water are made to bring up the required bulk.

The above solution is representative of several others in which potassium cyanide is used. They are not as a rule very good conductors, but with a fairly high voltage good deposits can be obtained. Their most suitable application lies in the treatment of articles which are to be tinned simply as a preliminary coating to some further deposit of another metal.

Other solutions which deserve mention are those composed of the double chloride of tin and ammonium and the double oxalate of tin and ammonium. The latter of these compounds gives the best results.

The following formula is based upon that given by Classen for the electrolytic separation of tin in electrochemical analysis:—

Tin chloride (Crystallized salt)	4 oz.	125 gr.
Ammonium oxalate	9 ,,	280 ,,
Oxalic acid	$\frac{1}{2}$,,	15·6 ,,
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres

Dissolve the tin salt in sufficient water and the ammonium oxalate and oxalic acid together in half a gallon (or $2\frac{1}{2}$ litres) of water. Add the latter to the tin solution with vigorous stirring. The white precipitate which first forms will redissolve, but the solution is rarely quite clear though sufficiently so for practical purposes. Add the remaining water required and boil the liquid for a short time.

This solution yields good deposits and possesses the distinct advantage that a tin anode dissolves comparatively freely in the electrolyte.

Most tinning baths recommended, for example formulæ I. and II., require periodic additions of tin salt to keep up the strength of the bath.

The Management of Tinning Baths.—When, as is largely the case in practice, electro-tinning simply means a thin coating sufficient to present a good appearance, there will be found little difficulty in working any of the foregoing solutions. If, however, deposits of any appreciable thickness are required, several difficulties arise. The deposit from ordinary baths has a very great tendency to become crystalline and brittle, and this is more decided, the longer the immersion. In this connection the influence of addition-agents has been largely studied during recent years, and, as is the case with lead, it appears almost essential to make some such addition to the bath to obtain good results.

Glue (or gelatine) is a very successful agent for this purpose, an addition of 0·1 per cent. having a remarkable effect on the character of the deposit, and at the same time allowing the use of a higher current density.

Other addition substances which have been recommended include glucose, saccharine, acetone, and the organic salts of aluminium or iron, but it must be noted that the effects of such agents are not permanent, and further additions must be made from time to time as found advisable.

Tinning by Simple Immersion.—The use of simple immersion processes of tinning is fairly widespread. Tin is a very useful metal as an ornamental coating to small iron or copper or brass articles such as hooks, eyes, pins, buttons, etc., and consequently a demand exists for a simple method of producing tin deposits on such articles. One of the most common solutions for this purpose, and a very good one, is prepared by dissolving cream of tartar in water, using as much of this salt as the quantity of water taken will dissolve; add about $\frac{1}{2}$ an ounce of stannous chloride to each gallon of the liquid and raise to boiling point. The articles to be treated should be contained in a tin sieve or the solution may be placed in a strong solid tin vessel and the articles agitated, as Langbein suggests, with a tin rod.

Another very simple bath is that proposed by Elsner, which, with copper or brass goods, yields reliable results. It consists of $\frac{1}{4}$ of an ounce each of sodium chloride and tin chloride dissolved in 1 gallon of water (or 7·8 gr. of each per litre). This solution also is used hot.

For iron articles a solution of tin chloride in alum is often employed. About 5 ounces of alum (ammonium alum is best) are dissolved in 1 gallon of water, and about $\frac{1}{4}$ an ounce of tin salt added.

In cases where a rather better class of deposit is required, articles for simple immersion tinning in the above or similar baths should be placed in contact with pieces of zinc. In this way a quicker action ensues owing to electro-chemical action, and a stronger and more durable deposit results.

Articles for simple immersion tinning must of course be as thoroughly and systematically cleaned as for the separate current process. After treatment in the tinning bath they are generally dried and polished by shaking with sawdust in a tumbling barrel revolved either by hand or by power, as shown in Fig. 52.

Deposition of Antimony.

The deposition of antimony is rarely practised, but as this metal possesses a few properties which render it useful for certain purposes, and which might ultimately prove of value in the arts, a brief outline of the commonly known processes for its electrolytic deposition may be useful to the student.

Properties.—Antimony is a fine lustrous silver-white metal. It is hard and extremely brittle, and can readily be powdered. It is practically unaffected by exposure to air at ordinary temperatures. Under similar conditions also it is unaffected by dilute sulphuric acid. Nitric acid converts it into a white powder—namely, oxide—the exact composition of which varies according to the strength of the acid. Perfectly pure antimony is somewhat difficult to dissolve, but the commercial variety is readily dissolved by hot hydrochloric acid, also in the cold by *aqua regia*. The common impurities of the metal are arsenic, iron, lead, copper, traces of silver and gold, also sulphur.

The most common compound of antimony is the trichloride ($SbCl_3$), but other salts which have been used in its electro-deposition are the double tartrate of antimony and potassium (*tartar emetic*), the double chlorides of antimony and the alkalies, and the corresponding double fluorides.

Solutions for Deposition.—The best known solution for the deposition of antimony is the tartrate. It is made up very simply according to the following formula:—

Double tartrate of antimony and potassium	4 lbs.
Hydrocloric acid	2 „
Water	1 „

Water and hydrochloric acid are mixed in the above proportions and the antimony salt slowly added.

This solution gives good results, but like most antimony baths only a comparatively low current density is allowable—about 5 amperes per sq. foot.

The following solution, due to Roseleur, also yields a good deposit, but must be worked hot—practically boiling.

Antimony tersulphide	½ lb.	250 gr.
Sodium carbonate	1 „	500 „
Water	1 imp. gall. or 1⅕ U.S. „	5 litres

The sodium carbonate is dissolved in the water, the antimony salt added, and the whole boiled together for an hour or so. Below boiling point the solution tends to throw down a precipitate; hence the requirement that it should be used hot.

Deposited antimony obtained from the foregoing solutions is rather gray in colour, not so white as the ordinarily occurring metal. It will, however, take a high polish and retain its colour for a considerable time.

A very peculiar phenomenon in the electro-deposition of antimony is the occurrence of *explosive* antimony. This was first noted and has been extensively studied by Gore. He obtained from a solution of 1 part of antimony chloride and 5 parts hydrochloric acid (and other similar solutions) a deposit of amorphous antimony which under some conditions changes to the crystalline variety, and develops an intense heat, sometimes to an explosive degree. The cause of this is said to be due to the presence of antimony chloride in the deposit itself. The phenomenon is referred to here as showing how unsuitable the chloride is for ordinary requirements in the deposition of antimony.

It is interesting to note that while the bromide and iodide compounds of antimony have the same tendency as the chloride to give explosive deposits (though in less degree), the fluorides do not give such results. This point suggests the possibility of the employment of the fluorides in antimony deposition, particularly if an addition-agent was also employed. This, however, demands further investigation.

Anodes.—The anodes employed in antimony deposition should be of the pure metal, preferably cast. Some writers recommend platinum, but the use of this metal is inefficient and at the present time out of the question by reason of its cost.

General Remarks.—Antimony deposits require careful treatment after withdrawal from the vat. The deposited metal readily stains, and if scratch-brushed a fine wire brush should be used. It is better, however, to brush lightly over with fine whiting and water and then transfer to the polishing lathe for any further treatment.

One application of this metal in electro-deposition which might well be further extended lies in the treatment of articles for metal colouring. The films of deposited antimony impart very pleasing tones to silver goods in cases where artistic decorative finishes are required. The first solution outlined is a very reliable one for this purpose and is not difficult to manage. Delicate differences of "tone" may be readily obtained by varying the time of immersion.

CHAPTER XVI

THE DEPOSITION OF PLATINUM AND PALLADIUM

The constant and great increase in the price of these metals during the last decade or so has strongly militated against the application of their electro-deposition in many directions in which but for their cost they could be very usefully employed. Particularly is this the case in giving ornamental and at the same time protective coatings to silver and silver alloys. Still the subject of the deposition of these metals is one of some importance owing to their peculiar properties of withstanding so completely many of the most powerful chemical reagents known. It is these properties, indeed, which have given rise to one of their most useful applications in industry, *i.e.* the manufacture of chemical apparatus. In this field also is found their greatest use from the point of view of their electro-deposition, particularly with platinum.

The two metals are very closely akin in physical and in many chemical properties, and generally occur together in nature, pure palladium being often found in platinum ore. Platinum, however, is much the more important of the two.

Deposition of Platinum.

Properties of Platinum.—The pure metal is tin-white in colour with a greyish cast. It is fairly soft, being similar in this respect to copper, though when electro-deposited from the phosphate solution described below, it appears hard, like nickel. Next to gold and silver it is the most malleable of metals. Its great power of resisting chemical reagents has already been referred to. In this respect it is superior to gold. No single acid will dissolve it, but like gold it is soluble in *aqua regia*, giving rise when the solution is crystallized to the formation of platinichloric acid (H_2PtCl_6).

Platinum as obtained in commerce is rarely if ever pure; it contains up to 2 per cent. of iridium (a metal belonging to the same chemical group), and thus alloyed it is even more useful in the arts, being more impervious still to the action of acids. This peculiarity has led recently to the suggestion of the feasibility of depositing alloys of platinum and iridium.

Compounds of Platinum.—The principal compounds of platinum from the point of view of the electroplater are platinichloric acid, previously referred to, which is very soluble in water, platinic chloride ($PtCl_4$), potassium chloroplatinate, $K_2(PtCl_6)$, and the corresponding ammonium compound $(NH_4)_2(PtCl_6)$, usually known as ammonium platinichloride.

Solutions for Deposition.—The solution in our experience most generally reliable for the deposition of platinum for decorative purposes, where a comparatively thin coating is sufficient, is that introduced by Roseleur and made up as follows:—

Metallic platinum	1 oz.	31·2 gr.
Ammonium phosphate	12 ozs.	375 ,,
Sodium phosphate (Na_2HPO_4) .	4 lbs.	2 kg.
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres

The platinum must be dissolved in a sufficiency of *aqua regia* and evaporated until the solution can be crystallized out (see Chap. X. p. 223). The crystals must then be dissolved in distilled water, say one quart, meantime the ammonium and sodium salts should be dissolved, the former in one quart and the latter in two quarts of water. The ammonium phosphate is now added to the platinum solution, a dense lemon-yellow precipitate being produced. This should be disregarded and the sodium salt added with constant stirring. A practically clear solution will result. This solution must now be boiled to expel any free ammonia and to improve its working qualities. It is then ready for use. A further addition of water will be necessary, however, to make up for loss by evaporation. This bath, as most others for platinum deposition, is worked hot with a voltage of about 4 volts.

It will be found necessary from time to time to make up a new solution in the same way, as the bath becomes exhausted owing to the insolubility of platinum anodes. The authors have found this a better plan than making additions of platinum salt, the exhausted solution being boiled down to a small bulk and added to the new one.

It may be of interest to observe that (about 15 years ago when the metal was considerably lower in price) one of the authors worked a similar solution to the above for some time for applying decorative coatings to silver articles. The deposited metal has an exceedingly fine artistic appearance —a steel-gray colour—the tone of which can be slightly varied by altering the distance between anode and cathode. On chased or embossed surfaces, particularly those in fairly high relief, some very pleasing effects were also obtained by partially gilding the raised portions after coating with platinum. The procedure adopted was, first, to coat the entire surface with a thin deposit of platinum, and then to "stop-off" the groundwork of the ornament and the plain surface with a varnish, such as is described on p. 239, so revealing only the portions to be gilt. The article was next rinsed in weak caustic potash, and rapidly passed through an alkaline copper solution (see p. 253), thus imparting an extremely thin film of copper. It was finally immersed in the ordinary gilding bath for a short time, dried out through hot water, the varnish removed by benzene, and scratch-brushed by means of a very fine *German silver* wire brush. This method was found preferable to the converse process which is possible, *i.e.* first coating the article entirely with gold, stopping off the raised portions and depositing the platinum over the gold on the revealed surface. The colour of the deposited platinum was not so good.

Another solution which can be recommended to give good results is Böttger's formula, as quoted by Langbein. The platinum salt used in this instance is ammonium platinic chloride. The following directions are those given by Langbein (slightly modified).

Dissolve 15 oz. of citric acid in ½ imp. gallon (or 0·6 U.S. gallon) of water. Add caustic soda to this until the acid is quite neutralized; raise the resulting liquid to boiling point, and add with constant stirring 2 oz. of ammonium platinic chloride. Continue heating until solution is complete, dilute to 1 imp. (or 1·2 U.S.) gallon, and add ½ oz. of ammonium chloride. This bath also is worked hot and yields a deposit similar in character to Roseleur's bath.

Some interesting experiments have recently* been carried out by McCaughey and Patten with solutions of potassium chlorplatinate for platinum deposition. A simple solution of this salt in water yields its metal to more electropositive elements by simple immersion. Copper, for example, readily becomes coated with a loosely adhering film of metal by immersion in such a solution. This constitutes a difficulty in using this bath for electro-deposition, a difficulty which, however, where thick deposits are required, may be overcome by giving the article a thin preliminary coating of gold.

The investigators above referred to obtained some encouraging results in the electro-deposition of platinum from an electrolyte made up by dissolving potassium chlorplatinate in water and adding a considerable proportion of citric acid. The solution which they found most successful was made up in the following proportions:—

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* *Trans. Amer. Electr. Chem. Socy.*, vol. xv. (1909), p. 523; also vol. xvii. (1910), p. 275.

Potassium chlorplatinate . .	2 parts by weight
Citric acid	10 ,, ,, ,,
Water	100 ,, ,, ,,

The corresponding ammonium salt may be substituted for the potassium compound with, in some respects, even better results.

This bath is rather difficult to manage inasmuch as it appears to be necessary to keep up the strength of the solution to the above standard. Additions of the platinum compound must therefore be regularly made as the bath is worked, as also of citric acid from time to time.

A very simple platinum solution, described by Langbein, is made by dissolving 1 oz. of platinic hydroxide in a solution of 4 oz. of oxalic acid and diluting to one imperial gallon by the addition of water. This bath also must be replenished by additions of the oxalate, and it is recommended to use a little free oxalic acid.

Langbein states that a deposit of any required thickness can be obtained from the foregoing solution, and that the metal obtained is sensibly harder than that from the alkaline baths. The working temperature should not exceed 70° C.

Treatment of Articles for Deposition.—Gold, silver, copper, German silver, or brass articles can be given a deposit of platinum direct from the phosphate bath, but iron should be previously coppered or gilt. The other baths mentioned have rather a tendency to deposit their metal, by simple immersion, on copper, and it is advisable, therefore, in using these solutions to give a preliminary coating of silver or gold. Gold is more suitable as being more electro-negative than silver, but if only thin films of platinum are deposited the colour is somewhat affected.

Deposits of platinum of any appreciable thickness require scratch-brushing or scouring in order to bring up the colour. Fine German silver wire brushes should be used in the former case, and flour pumice powder or whiting in the latter.

Simple Immersion Deposits of Platinum.—Very thin films for ornamental purposes are sometimes given to silver or silver-plated goods by simple immersion in a solution of platinum, but such deposits have a decided tendency to be dark coloured, and not very adherent, though very useful for ornamental purposes such as the antique colouring of silver surfaces. A good solution of this kind is obtained by dissolving 5 dwts. ($\frac{1}{4}$ Troy oz.) of platinum in sufficient *aqua regia*, evaporating the solution down to a syrupy consistency, then adding distilled water to make up one gallon of solution. This liquid gives the best results when used warm, and the length of immersion regulated as found necessary. A brief treatment is generally sufficient.

Deposition of Palladium.

Properties of Palladium.—The colour of palladium is of a shade somewhat between silver and platinum. It is very ductile and malleable. It does not oxidize in the air at ordinary temperatures and, while possessing some of the properties of silver, it is distinctly superior to that metal in contact with the atmosphere as it is quite unattacked by sulphur compounds. Palladium dissolves readily in hot nitric acid, particularly if the metal is not quite pure. In the spongy form palladium is also soluble in hydrochloric acid, but in its compact form it is scarcely attacked either by hydrochloric or sulphuric acids.

Compounds of Palladium.—The principal salts of palladium are the chloride ($PdCl_2$), the nitrate [$Pd(NO_3)_2$], and the cyanide $PdCN_2$. The chloride forms also a large number of double compounds of which the chief are those of the alkalies and ammonia, *e.g.* potassium palladiochloride K_2PdCl_4, ammonium palladiochloride $(NH_4)_2PdCl_4$. The cyanide also forms a double salt with the alkalicyanides, the potassium salt having the formula $K_2Pd(CN)_43H_2O$.

Solutions for Deposition.—The best known solution for the electro-deposition of palladium is that proposed originally by Bertrand, being a simple solution of the double chloride of palladium and ammonia in water together with an excess of ammonium chloride. The proportions usually taken are as follows :—

Ammonium palladiochloride . . .	1 oz.	31·2 gr.
Ammonium chloride	1½ ,,	46·8 ,,
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

The solution should be used very slightly warm with a voltage of from 4 to 5 volts.

Of other solutions which have been suggested only the cyanide needs mention here. Gore and several other writers recommend this bath, though Langbein considers it inferior to the chloride solution above. It may be made by precipitating palladium cyanide from a solution of the chloride and after well washing the precipitate redissolving in potassium cyanide. The solution should contain not less than 2 oz. of the metal per gallon and very little free cyanide.

Under these conditions we have found this solution to work fairly well in giving thin protective films to silver or silver plated goods.

Anodes for general work should be of the metal itself, but Cowper-Coles, in using the chloride solution for coating reflectors, employs carbon anodes.

CHAPTER XVII

THE DEPOSITION OF BRASS AND OTHER ALLOYS

The subject of the deposition of alloys from electrolytic solutions is at once exceedingly interesting and complex. While the theoretical considerations involved are extremely complicated, the practical difficulties to be overcome are equally formidable.

Most probably this accounts for the fact that of an enormous number of commercial alloys in everyday use in the arts, brass (a copper-zinc alloy) is the only one used to any considerable extent in the electroplating industry.

Before proceeding to the discussion of the practical electro-deposition of brass, as well as of one or two other alloys which deserve mention, it will be advisable to consider to some extent at least the chief theoretical principles which govern the deposition of metals from mixed electrolytes.

It is a fact familiar to observant electroplaters that an electrolytic solution may contain a number of different metals and yet yield only one at the cathode as the result of the passage of a normal electric current. Several different explanations have been put forward to account for this very well-known phenomena. The simplest, most feasible, and the one now most generally adopted is that of Le Blanc. In his classical text-book on Electro-chemistry this authority lays down the following conception of electrolysis by a moderate current in complex solutions: "*All of the ions in the solution take part in the conduction of the electric current, but only those ions the separation of which requires the least expenditure of work or energy are deposited or separated at the electrodes.* Thus it may happen that ions which conduct scarcely a measurable part of the current play the most important part in the chemical decompositions at the electrodes, in so far as they are formed with sufficient rapidity." *

Le Blanc uses the following illustration, which will assist in making the matter clear. "Suppose a fairly concentrated solution of a mixture of potassium, cadmium, copper, and silver salts be electrolyzed with a moderate current between platinum electrodes. In conducting the current, potassium, cadmium, hydrogen, copper and silver ions migrate to the cathode. At the cathode from actual experiment it is known that the silver is first deposited. This deposition goes on until the number of silver ions remaining is no longer sufficient for the current density maintained, when the copper begins to separate in the same manner. Following copper, cadmium, and finally hydrogen is deposited. These results are obtainable by actual experiments and are simply explained by the following statement.

"Those ions separate first which give up their electric charges most easily. The other ions must wait their turn in the order of their ease of deposition." The ions most easily giving up their charges are, of course, the electro-negative ones.

A careful consideration and study of the foregoing will convince the student of the supreme importance of the "electro-motive force" factor in all cases of mixed electrolytes. A specific E.M.F. between electrodes will maintain a definite current density, and on the latter will depend the weight of metal deposited, or in other words, the number of ions liberated. An increase in E.M.F. therefore implies an increased C.D. and *vice versâ*. Reverting to the illustration quoted above, the deposition of silver will go on so long as there are sufficient silver ions for the particular current density maintained. When this ceases to be the case, then the copper ions are called into play to carry the current and later the cadmium and so on.

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* Le Blanc, *Text-book of Electro-chemistry*, English translation, p. 303.

Now in an earlier chapter it has been explained that different metals require different values of E.M.F. to effect their liberation from electrolytes in the metallic form. Suppose, therefore, that the E.M.F. used in the above example was only sufficient for the liberation of silver, then directly the whole of the silver ions had been deposited the passage of the current would be stopped and electrolysis would cease.

This principle is of great importance and plays a preeminent part in the applications of electrolysis to the separation of metals either for refining or for electro-chemical analysis; and it must be regarded as of equal importance in the question of the deposition of alloys or mixed metals from electrolytes. A study of it will reveal the conditions necessary for the deposition of alloys. These are mainly as follows :—

Either (1), the particular solution used must be such that the compounds of the metals contained are as nearly as possible equal in the values of their heats of formation —this, it will be remembered, denotes the specific E.M.F. required for decomposition. In such a case the metals concerned require practically the *same* E.M.F., and so long as the ions of each are present in the correct proportion the tendency will be for them to be deposited simultaneously so long as this value of E.M.F. is maintained.

Or (2), the current used, being of a sufficient E.M.F. to liberate the more electro-positive metal, is also of a density so high that the number of more electro-negative ions in the vicinity of the cathode is not sufficient to convey all the current from the solution to the cathode, and therefore the more electro-positive ions are called upon to take part in the process as well as the electro-negative.

Both the above conditions obtain to a greater or lesser extent in the practical electro-deposition of alloys.

This naturally leads us to lay down the dictum, which cannot be too strongly emphasized, that in all experiments in the electro-deposition of alloys and indeed in workshop practice a voltmeter is almost essential to secure continuously the best results. Obviously also when the current has once been regulated to secure the desired E.M.F., the conditions of supply must be such as to ensure that it shall be kept constant.

In this connection it may be well to point out again the advantages of supply from accumulators rather than from the dynamo, particularly if the latter is at all liable to vary in voltage owing to variations of speed, a circumstance which is not unusual in factory driving.

The point of first importance in the deposition of alloys is to obtain uniformity of composition in the deposit, and here is the greatest difficulty. In a large number of cases of binary alloys particularly it is comparatively easy to obtain a deposit of the two metals concerned, but to obtain a definitely ascertained proportion of the metals together over an appreciable period of time from one electrolyte is a very different matter.

In discussing the question of brass, however, it may be urged that the *colour* is the main desirability, and the exact proportion of the two metals concerned, copper and zinc, is immaterial. For any deposits, however, beyond the merest film, uniformity of *composition* is essential to uniformity of *colour*, and the latter is therefore just as important in the case of brass as in that of other alloys where colour is not so material. Hence the necessity for a thorough grasp of the foregoing principles and their application.

Properties of Brass.—Brass, as is well known, is an alloy of copper and zinc. These two metals alloy in practically all proportions, but for industrial purposes the proportions most commonly used are from 60 to 70 per cent. copper and 30 to 40 per cent. zinc. Those alloys containing less zinc are usually the most malleable and ductile. Dutch metal, which is simply brass containing rather more copper than ordinarily, is exceedingly malleable and can be rolled to an extreme thinness in imitation of leaf gold. Brass of average composition is not so susceptible to the action of the atmosphere as is pure copper; hence its suitability for protective films, and also for intermediate coatings preliminary to deposits of silver, gold, or nickel. A brassing solution in thorough working order is always useful in general plating shops from this point of view, and it might with advantage be more extensively used than appears to be the case at present.

With regard to colour, which is possibly the most important property of brass from the electroplater's standpoint, the characteristic pure yellow colour of the alloy is shown most uniformly in alloys of from 60 to 70 per cent. copper and 30 to 40 per cent. zinc., and it is the object of brass-plating usually to obtain a deposit of as near this composition as possible. In the manufacture of copper-zinc alloys, considerable modifications of texture and of colour are obtainable by the addition of very small percentages of some other metals, and there is good reason to believe that similar modifications can be obtained in electrolytic deposits of brass. This aspect of the subject, however, requires and deserves careful investigation and research, since little can be said on the point at present.

Solutions for Deposition.—The only practical solutions in use at present for the deposition of brass are the cyanides. Many attempts have been made to devise an acid bath for use in this direction, but without avail. The chemical and electro-chemical properties of the two metals concerned are so widely different as to render it unlikely that a simple mixture of solutions of their simple salts only can be made to yield a satisfactory joint deposit. This will be fairly evident on reference to the relative position of the elements in the electro-chemical series. The double cyanides of these metals are, however, so stable in composition, so much less easily decomposed chemically than the simple salts, and possess heats of formation so nearly equal, that they are obviously the most likely compounds to use for joint deposition of the metals.

The preparation of the solution is carried out in a way very similar to the cyanide coppering solution, but before detailing the composition of the plating bath, one or two theoretical points should be noticed.

(1) Copper in cyanide solutions acts as a univalent element, zinc on the other hand is bivalent; consequently the proportion of the two metals deposited by the same current are as 63·5 (the chemical equivalent of univalent Cu) and 32·5 (the chemical equivalent of Zn). If, therefore, equal proportions of the two metals in double cyanide solutions were mixed together and electrolyzed, we should expect, under correct conditions of E.M.F., a mixed deposit of the composition, 63·5 Cu : 32·5 Zn, which, it will be noted, is an ordinary commercial brass. Moreover, in view of the above, it is obvious that in order to get such a result it would seem to be necessary that equal proportions of the two metals should be present. This is borne out by practical experience, and while admittedly it is possible by manipulation of current conditions and temperature to obtain a good brass deposit from solutions containing less zinc, it is very much more difficult. This point must be borne in mind, since some text-books and writers recommend the preparation of a brassing solution from the commercial metal itself with approximately the composition 2 of Cu, 1 of Zn. Such a plan, it will be clear, is not favourable to the best results.

(2) The chemical constitution of the alkaline double cyanides formed by the two metals zinc and copper respectively, is not quite analogous. The double cyanide of zinc and potassium has a composition corresponding to the formula $K_2Zn(CN)_4$, while that of copper and potassium, on the other hand, in aqueous solution is practically $KCu(CN)_2$. In preparing a solution, therefore, of the mixed cyanides it will be obvious that the zinc salt will require a much larger proportion of potassium cyanide (approximately double) than a corresponding weight of copper. This point should be borne well in mind, not only in making up a new solution for electro-brassing, but also in replenishing an old one—the fact being, as will be deduced, that the electrolyte has a constant

tendency to dissolve a greater proportion of copper than zinc from the anode.

In view of the foregoing, therefore, it is strongly recommended to make up brassing solutions from zinc and copper or their compounds separately, and not from metallic brass.

One of the best and most widely used electro-brassing baths is the following:—

Copper sulphate	$\frac{1}{2}$ lb.	250 gr.
Zinc ,, ...	$\frac{1}{2}$,,	250 ,,
Ammonia (0·880)	Q.S.	
Potassium cyanide	Q.S.	
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres

Powder the copper salt in a mortar and dissolve together with the zinc salt in about a quart of warm water. To this solution add liquid ammonia until the precipitate which first forms is completely redissolved and the solution assumes a deep blue colour (see page 253). Now make up a solution of potassium cyanide by weighing out 2 lbs. and dissolving it in 1 quart of water (or 800 grams per litre); add this to the mixed ammoniacal solution of zinc and copper until the blue colour is completely discharged and a clear, almost colourless, solution results. Note the quantity of cyanide solution required to do this, and add about 10 per cent. additional to form free cyanide. Make up the bulk of the liquid to 1 imp. gallon (or 5 litres) by adding water.

It will be noted that this solution is exactly analogous to that recommended for alkaline coppering on page 253.

The bath should be worked at a temperature of about 20° C., *i.e.* the normal temperature of the workshop. If worked hot, the colour is usually rather too red. Solutions intended to be worked hot should not be so rich in metal content as the above.

Another solution, similar in principle to the above, is that invented by Norris and Johnson (1852), which is composed according to specification as follows:—

Copper cyanide	2 oz.	62·5 gr.
Zinc cyanide	1 „	31·2 „
Ammonium carbonate . . .	1 lb.	0·5 kg.
Potassium cyanide	1 „	0·5 „
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. „	5 litres

Dissolve the cyanide and ammonium carbonate in a sufficiency of water and add the zinc and copper compounds,* stirring until completely dissolved; make up the bulk to 1 gallon (or 5 litres with the above metric amounts) and work at a temperature of about 70° to 80° C.

In modern practice, however, the solution has been considerably modified, the proportion of potassium cyanide given above being too large in comparison with the small amounts of copper and zinc cyanides. Better results are obtained by using 4 ounces of each instead of 2 and 1 respectively.

This bath gives excellent results, but requires careful management.

Some operators prefer to use a bath containing a small proportion of potassium or sodium carbonate, claiming thereby an increased conductivity of solution. Such a bath can be readily prepared as follows:—Take of

Copper sulphate	6 oz.
Zinc „	6 „

Dissolve in water separately and add to each a strong solution of sodium carbonate until no further precipitation occurs. Stir vigorously and allow to settle, then pour off the clear liquid as far as possible and mix the two precipitates, which are copper and zinc carbonates, together. Now add a sufficient quantity of a strong solution of potassium cyanide (2 lbs. per gallon) to completely dissolve these precipitates and a further proportion of about 10 per cent.

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* These can be bought or prepared in the workshop by precipitating a solution of copper and zinc sulphates respectively by means of potassium cyanide.

to form free cyanide. The reaction between the two carbonates and potassium cyanide results in the formation of a sufficient amount of potassium carbonate in solution without making any specific addition of this salt. (See discussion on analogous point in Chap. XI. p. 254.)

A solution deserving of mention, though of rather complex constitution, is that recommended by Roseleur, viz. :—

Copper carbonate	2 oz.	62·5 gr.
Zinc ,,	2 ,,	62·5 ,,
Crystallized sodium carbonate	3 ,,	93·75 ,,
,, ,, bisulphate	3 ,,	93·75 ,,
Potassium cyanide	8 ,,	250 ,,
Arsenious acid	15 grains	1·07 ,,
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres

The weights of ingredients as given above are slightly modified from Roseleur's figures in accordance with what we have found from experience to be advisable.

The solution is best made by mixing the copper and zinc carbonates together with a little water so as to give the consistency of thick cream. Dissolve separately the sodium carbonate and bisulphite in about 1 imperial pint of water each, and add them slowly with constant stirring in the order named to the copper-zinc compound. Considerable effervescence ensues owing to the liberation of of CO_2, so that the operation should be carried out in a deep vessel. Now add the potassium cyanide which has been dissolved in about a quart of water, and stir until the solution becomes practically clear and colourless. If the cyanide used is of a low percentage, more than the above amount may be necessary. Finally add the arsenious acid (white arsenic) dissolved in a sufficiency of *hot* water in which a little KCN has been dissolved, and make up the bulk of solution to 1 gallon by adding water.

It is advisable to boil the solution for a short time before using. In actual working it may be used either hot or cold, but the colour is rather too coppery at a high temperature.

The addition of arsenious acid to this bath is of interest, since this substance has been rather extensively used in brassing solutions for the purpose of obtaining brighter deposits. Like carbon bisulphide in silver solutions, however, arsenic should be used in very small quantities and with judgment. There is no doubt that the character and colour of the deposits are appreciably influenced thereby, but any accumulation of it will ruin the working qualities of the bath, and render the deposit useless for all ordinary requirements.

General Remarks on Brassing Solutions.—Experience has shown that deposits of metal obtained from brassing solutions—in colour particularly—are very readily influenced by very small and apparently insignificant additions to the bath. It has furthermore been observed that the addition of certain substances has the effect of materially increasing the conductivity of the electrolyte. The attention both of experimentalists and of practical workers has accordingly been given to these points to a considerable degree, and many modifications of the ordinary cyanide bath have been proposed. Some of these, such as the addition of sodium carbonate to improve conductivity and arsenious acid for colour, have received mention already. Other recommendations include the addition of sodium bisulphite, and small proportions of the organic salts of iron, *e.g.* ferrous acetate or oxalate. These latter are useful addition agents to brassing solutions, but care must be taken to have plenty of free cyanide present, or there is a possibility of complex chemical reactions occurring which may precipitate some of the zinc.

Some very experienced operators regard the presence of a large excess of ammonia as advantageous in these solutions, particularly when thick deposits are required, and there is little doubt that this is the case, since by its means solution of the anode is facilitated, giving consequently a more uniform composition of the bath.

Anodes.—Though the use of copper and zinc anodes alternately in brassing baths is sometimes adopted, it will be found most generally advisable to use rolled brass only, and the anode surface immersed should *always* be in excess of the superficial area of the articles being plated.

Current Conditions.—The voltage required for brassing solutions is usually from 4 to 6 volts. Exact figures for either this or current density cannot be given, since these depend on local conditions of composition of solution, temperature, and class of work. The operator should determine by experiment what readings give the best results for the particular work upon which he is engaged, and endeavour to keep these values constant.

Management of Solutions.—To obtain consistently good results from an electro-brassing bath is not a very easy matter, particularly in giving thick deposits. It is always advisable to note the appearance of the anode and prevent the formation of any oxide or slime on its surface by the addition of ammonia, or free cyanide, or both, to the solution. Increasing the proportion of free cyanide tends to produce a greater proportion of copper in the deposit, but this can be remedied by the addition of water which tends to facilitate the deposition of zinc. Considerable variations in the composition and therefore colour of a brass deposit may be obtained by varying the temperature, but for most workshop purposes cold solutions are much more convenient; the temperature, however, should, if possible, be kept constant, and any necessary alterations made by varying other conditions of working, viz. composition of solution or conditions of current. If the bath is not working satisfactorily, and the current conditions and free cyanide content appear correct, the operator must determine whether the metallic content of the bath is at fault. This may be done by trying the effect of the addition of either copper or zinc cyanide or, more scientifically, by estimating the amount of each metal present by the method described below. The fault will usually be thus located.

Some interesting researches on the subject of the electrodeposition of brass from cyanide solutions have been undertaken by Field,* whose principal conclusions may be briefly summarized thus:—

(1) Conditions which tend to raise the E.M.F. increase the percentage of zinc in the deposit. Such conditions are: (*a*) Dilution of solution; (*b*) increase of temperature.

(2) Anodes are freely soluble with warm agitated solutions even in the presence of only small amounts of free cyanide.

(3) The effect of free cyanide is to (*a*) increase the percentage of copper in deposits; (*b*) increase the evolution of hydrogen; and (*c*) induce abnormal anode efficiencies.

It is further concluded that free cyanide does not impart conductance to a solution in the same way that acid affects a copper sulphate solution, but simply makes the anode products dissolve more readily.

Deposits of brass may be made directly upon all metals and alloys without intermediary coatings. Indeed, brass is almost equally, if not quite, as useful as copper as an intermediate coating itself prior to deposition of other metals. Watt recommends the use of a warm solution for brassing lead and pewter, the former particularly—a strong current should also be used at the moment of immersion in order to coat rapidly every part of the surface being plated. As in the case of coppering, the greatest trouble to the operator is usually given by cast-iron, and a similar treatment should be adopted as recommended for coppering (see page 260).

Estimation of Metallic Content of Brassing Solutions.—The estimation of the copper content of a brassing bath is best carried out by means of the method already fully described in Chap. IX., page 261. The presence of zinc does not interfere. The estimation may be made on a separate sample of solution or on the copper precipitated from the sample taken for the zinc estimation as described below.

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* *Trans. of the Faraday Society*, vol. v., Sept., 1909, pp. 172–196.

For the following excellent method of estimating zinc we are indebted to our friend Mr. F. Ibbotson, B.Sc.

Measure by means of a pipette an exact amount, from 25 to 50 c.c. of the solution, and transfer to a large beaker. Add to this hydrochloric acid, stirring until the whole of the cyanide is decomposed, and the solution is distinctly acid (test with litmus paper). Now add first 4 or 5 c.c. of sulphurous acid, then ammonium thiocyanate solution until no further precipitate is produced. (This precipitate contains the whole of the copper and may, by redissolving in nitric acid, be used for copper estimation, as mentioned above.) Transfer the whole solution containing the precipitate to a graduated flask holding 300 c.c. Carefully add distilled water until the 300 c.c. mark is reached.

Now filter off through a dry filter paper, and measure out 250 c.c. exactly of the filtrate. This will contain $\frac{5}{6}$ths of the zinc. This solution must now be rendered exactly neutral or very slightly acid. The best method is to add ammonia until the liquid is just alkaline (test by litmus), then add hydrochloric acid drop by drop until the neutral point is reached or the character made slightly acid. Weigh out now an amount of ammonium phosphate of between ten and twenty times that of the weight of zinc supposed to be present—it is usually possible to form an idea of the zinc present between such limits—and add this to the zinc solution with continuous stirring preferably on a warm plate. The resulting precipitate which contains all the zinc as zinc ammonium phosphate is at first very flocculent, but soon becomes dense and crystalline, and easily settles. Filter, and transfer the precipitate to a weighed crucible. Strongly heat now over a Bunsen burner until the salt is white throughout (test by pricking with a pointed glass rod). Allow to cool in a desiccator and weigh. Deduct, of course, weight of crucible, and the result is the amount of zinc as pyrophosphate ($Zn_2P_2O_7$). This salt contains 42·55 per cent. of zinc, so that by multiplying the result by 0·4255, the exact weight of metallic zinc in $\frac{5}{6}$ths of the sample is ascertained. If, say 30 c.c. of solution was originally taken, we have obtained the weight of zinc in 25 c.c. To ascertain the weight per gallon this figure must be multiplied by 181·5 (4540 c.c. = 1 gallon).

The technology of the electro-deposition of alloys other than brass is at present in a very imperfect condition, and this part of the subject is consequently of laboratory rather than of workshop interest. The following are a few of the principal alloys which have been suggested for electro-deposition, but none have yet assumed any commercial importance.

Copper Alloys.—(1) *Bronze* (copper-tin). The solution generally considered best for this alloy is the oxalate, made up by dissolving separately 4 oz. of copper sulphate, and 2 oz. tin bichloride ($SnCl_2$). To each solution add an excess of ammonium oxalate solution until the precipitates which at first form are redissolved. Add a little free oxalic acid to both and mix together, making up the bulk to one imperial gallon by the addition of water. The solution should be boiled before use.

(2) *German silver* (copper-nickel-zinc). The usual proportions of this alloy are from 15 to 20 per cent. nickel 55 to 60 per cent. copper, and 25 to 30 per cent. zinc. A mixture of the double cyanides of each of these metals with potassium in about these proportions forms probably the best solution for deposition.

The alloy is, however, rarely if ever used, though Watt recommends it for coating revolvers, dental instruments, scabbards, etc.

Nickel Alloys.—In addition to German silver referred to above, several alloys of nickel have been suggested for electro-deposition of which the following are the principal.

(1) *Nickel and Iron.* Solution recommended is a mixture in any proportion desired of the double sulphates of these

metals and ammonium. The bath must be exactly neutral, or *very slightly* acid.

(2) *Nickel and Cobalt.* This alloy has been suggested by Weiss, who recommends the following as a suitable solution—

Nickel ammonium sulphate . .	8 oz.	250 gr.
Cobalt ammonium sulphate . .	2 „	62·5 „
Ammonium sulphate	3½ „	93·7 „
Water	1 imp. gall. or 1⅕ U.S. „	5 litres

(3) *Nickel and Zinc.* Alloys of these two metals have also been proposed, the electrolyte being a mixture of the two sulphates, with nickel sulphate in greater proportion, and a little ammonium sulphate.

Silver Alloys.—A number of silver alloys have been proposed at various times for electro-deposition, many of which have been patented. The principal are silver and platinum, silver and zinc, silver and cadmium, silver and tin. In each case the cyanide solution is suggested.

Tin Alloys.—A recent proposal of some interest is to deposit an alloy of tin and lead from a solution based on the Betts formula, to which reference has been made on page 326.

CHAPTER XVIII

FINISHING PROCESSES

The finishing of electroplated surfaces is a subject of considerable importance to electroplaters, though in many branches of the industry it is considered and carried on as a separate trade. It is, however, not possible within the limits of the space here available to give a detailed description of all the methods in vogue, and only a general, though it is hoped useful, outline will be attempted.

The subject may be divided into two distinct types, (1) hand-finishing, (2) machine-finishing. The former is mainly confined to the silver and gold-plating industries; the latter is used in all branches of the art of electroplating.

1. **Hand-finishing.**—This term, though formerly possessing a wider significance, is now practically confined to the operations of "burnishing" and "handing."

Burnishing essentially consists in imparting a fine smoothness and brilliant lustre to a surface by means of a perfectly smooth tool of a very hard nature usually either steel or bloodstone held firmly in the hand and pressed over every portion with an even pressure. Some illustrations of the various shapes of these tools are given in Fig. 61, and in Fig. 62 is illustrated the correct method of holding them.

A large number of different patterns and sizes of these burnishing tools are required owing to the variety of the surfaces to which they are applied. Some considerable experience is necessary in the operation in order to obtain the absolute evenness of surface necessary for brilliance and perfection of finish. The effect of burnishing is really to lay down or make quite flat and smooth the surface of metal operated upon, and as a result light is reflected from every point of such a surface quite evenly and regularly, so conveying to the eye a fine lustre or mirror-like appearance. All electro-deposits of metal are more or less uneven on their upper surface owing to the fact that the deposit does not cover the article like a sheet of rolled metal, but is liberated from the solution in infinitesimally small grains. Viewed through a powerful microscope such a deposit, particularly if of appreciable thickness, has an appearance which may not inaptly be described as that of a number of tiny hills congregated close together with a number of equally tiny valleys lying between.

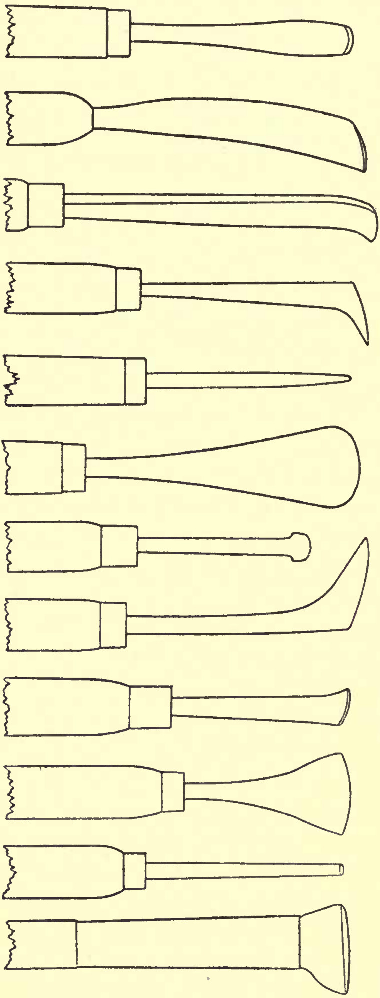

Fig. 61.—Burnishers of various shapes.

Burnishing, therefore—to follow out the illustration—is a process of laying down the hills side by side until they exactly fill up the valleys and the character of the surface is changed into that of a plain.

The applications of burnishing lie mainly in the electro-silver-plating and gilding industries, though similar processes are often used in the brass and art metal trades. It is a method of finishing particularly suited to the production of artistic effects, since certain portions of the surface can be burnished and others left dull, the line of demarcation being sharp and well defined, as is necessary in embossed work.

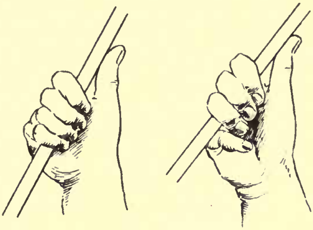

Fig. 62.—Method of holding Burnisher.

Before burnishing, all surfaces should be lightly but thoroughly scoured with very fine sand or whiting moistened with soapy water, then rinsed in warm water and dried with a soft linen cloth. During the process of burnishing the tool is dipped regularly into a solution made by dissolving common yellow soap in hot water, or stale beer, the latter liquid being preferred by many workers for gilt surfaces. For brass, dilute vinegar is usually employed.

"*Handing*" is a process almost peculiar to the finishing of silver and gold surfaces either plated or solid. Even the most efficient burnishing leaves a silver or gold surface with, to some extent, a scratchy appearance; handing consists in carefully polishing such surfaces with rouge and water by means of the palm of the hand or the fingers until all such scratches are eradicated, and in the case of silver the perfect black lustre so characteristic of well-finished silver surfaces is obtained. In the case of gold or gilt work a similar brilliance of polish is obtained but a specially prepared rouge must be employed. When every trace of burnish marks or scratches has been thus removed, the article is thoroughly washed with soap and a sponge in very hot water until entirely cleansed from rouge, then finally dried with a linen cloth and wiped up with chamois leather.

2. **Machine-finishing.**—Machine-finishing is carried out by means of a lathe such as described in Chap. VII., Fig. 44, fitted with buffs, dollies, or mops. The essential difference between this method and that of burnishing may be fairly illustrated from the analogy already made between a surface of electro-deposited metal and a number of hills and valleys. While burnishing levels the surface by laying down the hills, machine-finishing secures the same effect by removing the tops of the hills, or, in other words, rasing them to the level of the valleys. It will be obvious, therefore, that these methods invariably result in some loss of metal. In many cases this is not a matter of much concern, but in others, particularly where the precious metals are concerned, it is. On the other hand, machine methods are much quicker and in very many classes of work much more suitable than burnishing by hand. Nickel, iron, and cobalt deposits, for example, are too hard for the latter process, and must therefore be finished by machine. During recent years also, partly for the sake of economy and partly to obtain a fine finish (showing no traces of burnish marks) with the minimum of handing, machine-finishing has become very popular for silver-plated work, the general methods pursued being very similar to those recommended for nickel-plated goods. The articles *before* plating are given a fine smooth surface and high polish, and after plating are taken direct to the finishing lathes and polished.

The polishing materials employed in machine-finishing are mainly Sheffield or Vienna lime, whiting, Tripoli and crocus compositions, and fine rouge. These are applied by means of felt buffs, fibre brushes, and calico and swansdown mops or dollies attached to the lathe spindles and run at a speed of approximately 2000 revolutions per minute. Nickel deposits are usually finished by Sheffield lime or compositions largely containing this or a similar substance. Calico mops are used for this purpose, and the composition is applied in small quantities at a time to the face of the mop as it revolves; the article is held gently but firmly so that each part is subjected to the action of the polishing agent.

Silver-plated work is generally first treated by means of a soft felt buff with Sheffield lime mixed with a very small quantity of oil. When the operator has gone over the entire surface in this way—very little pressure being needed—the buff is taken off the spindle and a calico mop substituted. To the face of this mop a slight touch of oil is applied together with a little of the prepared lime, and the article held to its surface so that every portion is treated.

A slightly bright but greasy polish results. The calico mop is now changed for one of swansdown, which is treated with a simple mixture of rouge made into a thin cream by the addition of water. This produces the final brilliant black polish, though in the best classes of work it is usual to follow this by the handing treatment previously described.

Copper deposits when required bright are finished by a similar, though rather simpler, process to the above. Generally, however, such deposits are coloured or given artistic light or shade effects by one or other of the processes described in the subsequent chapter.

Deposits of iron, zinc, tin, or lead are not usually given any finishing treatment after deposition further than sand-blasting, scouring, or scratch-brushing.

It should be remarked that a large number of special polishing compositions are now on the market of excellent quality which may be purchased from manufacturers making a speciality of these materials, and should be used according to the directions issued with them.

A particularly important point in the machine-finishing of articles like spoons and forks is the care of the edges.

Unless the operator is both experienced and careful a constant tendency arises, in finishing, to apply too much friction to the edges or to any sharp points such as the ends of spoon-bowls, etc. The fault can easily be avoided by care in applying the felt buffs or mops to the surface of the article, working first from the centres and carefully grading the pressure so that the edges are scarcely touched.

It is necessary also to mention that slight losses occur in polishing by means of handing. It will be observed that after rouge has been applied to a silver surface by the hand the latter is blackened owing most probably to a slight indirect chemical exchange of the rouge (iron oxide) and metallic silver.

The use of the Sand-blast in Finishing.—As well as being often an important factor in preparatory processes, sand-blasting is a very useful occasional adjunct in finishing electroplated goods.

The principal methods of its application are outlined in the following:—

Relief effects on silver or silver-plated goods.—Use the sand-blasting apparatus at a pressure of from 8 to 10 lbs. per square inch with powdered pumice—in the case of silver-plated goods *before* plating. Scratch-brush after plating on a fine brush, then dip rapidly through a hot dilute solution of potassium sulphide (see also p. 367) until the surface assumes a deep bluish-black colour due to the formation of a film of silver sulphide. Then by means of a calico mop or dolly and fine Trent sand gently polish off the colour from all raised or embossed portions of the surface. By careful regulation and variation of conditions very pleasing effects can thus be produced.

Gold or gilt surfaces.—Great care must be taken in treating these surfaces by the sand-blast or they will be completely spoiled. In the case of gilt work the colour of the article when taken from the bath should be rather darker than the final colour required. Scratch-brush gently on a soft brush, then subject the surface to the action of the sand-blasting apparatus at a pressure not exceeding 3 lbs. per square inch with No. 120 pumice powder. The operation should only occupy a few seconds (unless a large surface is treated), and the article is then thoroughly washed in hot water with a sponge to clear away all powder lingering in recesses. It is then finally wiped over with chamois leather.

Nickel-plated work.—In this class of work the use of the sand-blast is mainly to obtain partial effects alternately bright and dull to suit the style of the article. These can be readily obtained in the manner described in Chap. VIII., page 163.

Use of Scratch-brush in Finishing.—Deposits of gold, silver, copper, zinc, and some other metals are sometimes finished by means of the scratch-brush only, without the use of any of the ordinary polishing appliances and compositions. It is obvious that a "finish" imparted in this way will not compare in brilliance of polish with that obtained, say, with felt buffs and mops or by burnishing. Nevertheless the effects obtained are more suitable for certain classes of work, and they can be widely varied by using different types of brushes. It will be found, for example, that scratch-brushes of German-silver wire are particularly suitable for finishing gilt work which is required to have a "dull-bright" effect. In this case a very fine crimped wire is used. For silver and copper deposits also similar brushes are now being used. Indeed, German-silver wire is preferred by many operators recently instead of brass, since thinner wire can be employed to give an equal "resistivity," as it may be termed, to the pressure of the brusher, with the result often of marked improvement in the surface treated.

CHAPTER XIX

METAL-COLOURING AND BRONZING

The terms "metal-colouring" and "bronzing" possess now a wide significance. Broadly speaking they have become almost synonymous and apply to the whole art of the decoration of metallic surfaces, whether by chemical or mechanical methods.

Such a subject cannot be treated adequately within the limits of a brief chapter, but it seemed desirable, as the electroplater is often called upon to do certain classes of work of this kind, to outline a few of the methods in general use, particularly those corresponding to the ordinary requirements of a plating shop.

Preparation of surfaces for colouring.—The general methods of Chap. VIII. for the treatment of metals prior to electroplating are adopted usually for preparation for metal-colouring; little need, therefore, be said on this point. It seems, however, to be necessary to emphasize its importance. Imperfect cleansing, pickling, or dipping can only result in disappointment, for their effects are, inequalities of colouring, failure of the colouring chemicals to act correctly, and general patchiness of the final surface.

The general methods of metal-colouring may be classed under two headings: (1) Chemical (including electro-chemical), and (2) Mechanical.

I. Metal-colouring by Chemical Methods.—The principles involved in these methods are (*a*) to form, on the surface of the particular metal treated, by the agency of heat or some chemical compound, a salt or oxide which possesses some distinctive colour or colours. The formation may be quite a simple one, such as that of silver sulphide on silver surfaces by means of the action of a sulphur compound; or a complicated one, due to the application of a mixture of a number of different compounds, oxides, carbonates, sulphides, or chlorides. Variations of colour are also produced by varying the thickness of the film.

Or (*b*) to give by electro-chemical methods, *i.e.* electro-deposition, a film or coating of some metal or compound, which possesses a desirable colour. The former are the generally adopted methods and will, therefore, be given greater prominence here.

Colouring of Silver.—The production of colour effects on silver is generally known as oxidizing; the term, however, is quite misleading, as silver oxide rarely forms the colouring film or any part of it except to a very slight extent. Sulphur is the chief agent employed in this connection and compounds containing this reagent in some form or other are in very general use, the most popular being potassium sulphide (liver of sulphur). A simple solution of this substance in water is very effective, but other substances are often added to improve either the appearance or adhesive properties of the film of silver sulphide formed. The following is an excellent solution :—

Potassium sulphide	1 oz.	31·2 gr.
Ammonium carbonate	2 ,,	62·5 ,,
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. ,,	5 litres

It is better to dissolve the ammonium carbonate in part of the water separately and add to the sulphide solution when the latter is dissolved. The resulting solution should be worked hot and the time of immersion of the article regulated according to the depth of colour required. A few seconds', or at most half a minute's, immersion is usually sufficient to produce a deep bluish black colour, which is very adhesive and will stand scratch-brushing.

For lighter shades of colouring barium sulphide may be substituted for potassium sulphide, the colour produced varying according to temperature and time of immersion from a light golden shade to brownish-black. The solution should contain about 1 oz. of barium sulphide to each imperial gallon of water.

Another useful agent in the colouring of silver, particularly in the production of antique effects, is platinum chloride. This salt is soluble in both alcohol and water, and solutions of each kind have been used, usually in the proportion of about a quarter of an ounce per imperial gallon. The solution should be used hot, and the article immersed until the surface is uniformly attacked. In the case of alcoholic solutions the liquid is generally applied by means of a camel's-hair brush; the alcohol quickly evaporates and leaves behind a slight filmy grey or greyish black deposit which will stand scratch-brushing lightly, and gives a very pleasing antique effect. The shade of colour may be considerably varied by altering the strength or working temperature of the solution.

A hot solution of antimony chloride in water is also used for a similar effect. Usually from 1 to 2 oz. per imperial gallon is the strength employed, and articles are immersed as long as is found necessary for the desired colour. This solution is often used for the colouring of silver toilet ware, particularly in conjunction with a sand-blast apparatus as explained later.

The artistic effects obtained in the colouring of silver depend to a large extent on the after-treatment of the surface. It is rarely that an article coloured in the sulphide solution, for example, is left exactly as it appears after immersion and scratch-brushing; it is generally treated to obtain light and shade effects according to the type of the ornamentation of the surface.

Such treatment, known as "relieving," consists as a rule in carefully polishing or rubbing off by means of a calico mop or soft brush or the hand with fine whiting or pumice powder the oxidizing colour from the raised or embossed portions of the article, thus producing shades of almost any degree of lightness to contrast with the dark or black coloured groundwork. Surfaces so treated are often given a further treatment by sand-blasting with fine whiting or pumice powder at a very low pressure.

Silver toilet ware and other goods of a similar character are first oxidized either in the potassium sulphide or antimony chloride solution, then relieved according to the taste of the operator, and finally sand-blasted with fine pumice powder at a pressure not exceeding 3 lb. per square inch.

Colouring of Copper.—This metal is probably the most important to be dealt with in a survey of the subject of metal-colouring inasmuch as many artistic effects are given to other metals and alloys by first imparting to them a coating of copper by electro-deposition and afterwards colouring this deposit. Copper also readily responds to the actions of many simple chemical reagents which result in the formation of films of salts of the metal of very pleasing artistic appearance.

The following are the principal solutions and methods in use:—

(1)	Ammonium sulphide	1 to 2 British fluid oz.
	Water	1 imp. gall.

This solution, while very simple, is one of the most useful for obtaining shades varying from light brown to black. The depth of colour varies according to the time of immersion and temperature. Some operators prefer to use the solution warm, but the colour is under more complete control if the bath is cold. The uniformity of colour obtained is entirely dependent on the composition of the surface metal, and consequently more successful results are often obtained on freshly electro-deposited copper surfaces than on solid copper articles, unless of course the latter are given a slight film of metal from a copper depositing bath. When the required depth of colour is obtained the article should be well rinsed in clean water, lightly scratch-brushed, relieved if so desired by means of fine sand, rinsed again and dried and finally thoroughly brushed, with a little beeswax softened by immersion in turpentine over the whole surface, by means of a soft bristle brush—a plate brush of good quality will do very well.

Coppered goods treated in this way possess a very pleasing surface which is improved if the article is periodically brushed over with a very slight film of oil or beeswax as above.

(2) Another solution of very similar character to the above is composed of—

Potassium sulphide	½ oz.	31·2 gr.
Water	1 imp. gall.	5 litres

with the addition of a few drops of strong ammonia.

This bath which is generally used warm gives a varied brown tone on copper, often known as Japanese bronze, the variation of colour depending on the temperature and length of immersion. A few seconds' immersion is usually sufficient. The articles may be finished as directed under (1), or simply scratch-brushed, lightly dried and lacquered (see later).

Solutions of the sulphate or nitrate of copper in water are often used in the colouring of copper or copper plated articles. Such solutions also give varying tones of brown, tending with longer immersion and on heating to black. The following solution is an example:—

(3)	Copper nitrate	4 lbs.	2 kg.
	Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

This liquid should be used warm. If a deep black tone on copper is required the article should be immersed several times, allowed to dry without rinsing, then heated in a lacquering stove or over a Bunsen flame gently, and afterwards well brushed with a soft brush.

A fine antique effect is imparted to copper by the following:—

(4)	Copper nitrate	20 oz.	625 gr.
	Hydrochloric acid	1 lb.	500 „
	Water	1 imp. gall. or 1⅕ U.S. „	5 litres

This solution may be used warm or cold. The effect is more quickly and rather more uniformly obtained if warmed, but the operation must be carefully observed so as to obtain the exact tone desired. The article should be scratch-brushed after immersion, relieved if desired, then thoroughly brushed over with a waxed brush in the manner previously directed or, if preferred, lacquered. Copper, coloured in the above or similar solutions, darkens on exposure to the atmosphere, hence the necessity for treatment with oil, wax, or lacquer.

Green colours on copper are generally obtained by means of solutions of metallic carbonates or chlorides together with acetic acid.

The following are typical solutions:—

(5)	Copper carbonate	½ lb.
	Ammonium chloride	¼ „
	Cream of tartar	2 oz.
	Vinegar or dilute acetic acid	1 imp. pint.

(6)	Ammonium carbonate	½ lb.	200 gr.
	Sodium chloride	2 oz.	50 „
	Copper acetate	3 „	75 „
	Cream of tartar	2 „	50 „
	Water	1 quart	1 litre

The above solutions are used for the darker shades of green (patina). The following yields a lighter shade:—

(7)	Ammonium chloride	4 oz.	125 gr.
	Potassium oxalate	1 „	31·2 „
	Water	1 imp. gall. or 1⅕ U.S. „	5 litres

Langbein recommends a solution of similar constituents dissolved in vinegar.

In using the foregoing or similar solutions for the production of a green patina, the article should be painted with the liquid (or if feasible immersed) as uniformly as possible and *without rinsing* set aside to dry; while drying it should be continually touched with the brush to prevent one part being more deeply affected than another. The operation is then repeated after the lapse of some hours—if possible twenty-four hours should be allowed, so as to enable the action to complete itself as fully as possible—the coating is again allowed to dry with similar treatment, then if necessary treated a third or even fourth time and finally finished off with a soft waxed brush as previously directed.

It is a matter of some importance not to allow the coating of colouring liquid to dry quickly—the slower the better, and some operators therefore add a small amount of glycerine to the bath to retard its action in this respect.

Langbein advises the exposure of articles treated to produce a patina, to an atmosphere of carbonic acid gas (CO_2), by placing them, after brushing over with the solution used, in a hermetically closed box in which are arranged one or two dishes containing a few pieces of marble (calcium carbonate) together with very dilute sulphuric acid, carbon dioxide being thereby evolved in a moist atmosphere, thus facilitating the formation of a patina.

A number of pleasing shades of colour can be imparted to solid copper goods by heating them either clean or coated with some oxidizing substance. A paste prepared by mixing equal parts of finely divided plumbago and the finest jeweller's rouge with alcohol yields good results in this connection Even without such a coating, however, copper heated over a clear spirit flame assumes a number of shades of colour, varying according to conditions, and due to the oxidizing influence of the atmosphere. The colours obtained in this way are often improved by dipping the work for a few minutes in a hot caustic potash boil. It is then dried, and either lacquered or thoroughly brushed with a waxed brush. If an oxidizing paste, such as described, is employed the article should be coated as evenly as possible by brushing the paste over it until each part of the surface is uniformly covered and it should then be placed in an oven or exposed to an even heat. The temperature must be regulated according to the colour required. High temperatures must be employed for the darker shades and the operation continued longer than for light colours. The paste is afterwards removed by vigorous brushing, and the surface finished off by rubbing lightly with a sponge dipped in alcohol and finally with a waxed brush.

Colours produced in this way are usually very pleasing and will resist subsequent atmospheric action.

Colouring by heat as a method of treating copper is, however, obviously confined to solid copper articles and is not available for copper-plated work. For the latter class the methods previously outlined are most suitable.

It may be also remarked here that the commoner metals such as zinc, tin, and lead, and their alloys, are usually coloured by first coating with copper electrically and afterwards treating by one or other of the reagents named in the foregoing paragraphs.

Colouring of Brass.—The direct colouring of brass presents considerably greater difficulty as a rule than that of copper. As will be readily understood, a slight variation in the composition of the alloy gives rise to modifications of the particular chemical actions of the colouring baths used, and consequently to differences in the shades of colour produced. It is, therefore, often found that a process which produces a certain shade of colouring on one class of goods will give a decidedly different shade on another. Wherever special or very exact tones are required it will usually be found the best practice to give the article in question a coating of electro-deposited copper and use this as a basis for the subsequent colouring. This, however, is only necessary in particular cases; for many classes of brass goods the colouring can be imparted directly, small variations of shade not being important.

The following are amongst the most generally useful solutions for brass colouring.

Tones varying from a light straw colour to brown may be imparted by the use of an alkaline solution made up by mixing copper carbonate with caustic soda of a strength corresponding to about 4 oz. of copper salt per imp. gallon. The copper carbonate may be bought ready prepared or made by dissolving metallic copper in dilute nitric acid and precipitating the copper as carbonate by means of sodium carbonate.

The following is a reliable formula :—

Copper carbonate	¼ lb.	125 gr.
Caustic soda	1½ ,,	750 ,,
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

The caustic soda should be first dissolved in the water and the copper salt slowly added with vigorous stirring. The liquid should be used hot and the time of immersion varied according to the depth of colour required; a very light brown colour is first produced passing by longer immersion into a dark greenish shade.

For dark-brown shades on brass, solutions containing arsenic or antimony sulphide (sometimes both) are often used. A solution typical of many recommended by various operators is made up by dissolving antimony sulphide in a hot solution of caustic soda thus :—

Antimony sulphide	½ oz.	15·6 gr.
Caustic soda	4 ,,	125 ,,
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

Immerse the article to be coloured in this solution for a few seconds, then lightly scratch-brush, rinse, and re-immerse, repeating the operation until the colour is sufficiently deep, then finally scratch-brush with a very soft *dry* brush.

Such solutions as the foregoing and other similar containing arsenic often give very pleasing tones of colour, but work best when *freshly prepared.*

Blue colours on brass.—The following solution is very widely used for colouring brass :—

Sodium hyposulphite . . .	8 oz.	250 gr.
Lead acetate	4 ,,	125 ,,
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

The sodium salt is first dissolved in a portion of the water, the lead acetate in the remainder, and the two solutions then mixed. The resulting solution is used either boiling or very nearly so. A light steely-blue colour results on first immersion, the tone slowly deepening as the action continues.

The reactions of this solution on brass are supposed to be due to the slow decomposition of the lead hyposulphite (formed on the mixture of the solutions) into lead sulphide, which reacts upon the brass surface immersed so producing the various colourations.

Some operators prefer to use a solution of double the strength given in the above formula.

Blue-black or black colours on brass are usually obtained by using strong ammoniacal solutions of copper. The following is a good solution :—

Copper carbonate	1 lb.
Strong ammonia	1 imp. gall.

The copper salt is dissolved in the ammonia, the well-known deep blue solution of ammoniuret of copper resulting. To this is added ½ lb. of sodium carbonate dissolved in 1 quart of hot water.

The article is immersed in this solution for a few seconds or until the colour is sufficiently deep, then rinsed in clean water and immersed for a short time in a boiling solution of caustic potash, re-washed, dried, and lacquered.

Hiorns recommends a rather simpler method than the last, viz.: Take 10 oz. copper nitrate, dissolve in 20 oz. of water, and add ammonia until the precipitate which at first forms is *just* redissolved.

The solution should be used hot, and appears to give better results after some little use, but care must be taken not to have any excess of ammonia present, since free ammonia would tend to dissolve the coloured film.

Colouring of Iron and Steel.—Brown colours on iron are obtained by covering with a paste consisting of antimony chloride and olive oil in equal parts and slightly heating. The paste should remain on overnight, then be rubbed off with a soft cloth, and the article again coated with a fresh layer of paste and placed in a warm place for a further 12 hours. The work is then brushed with a stiff brush until the paste is completely removed and afterwards finished off with a soft waxed brush.

Before applying the paste the work must be thoroughly cleaned and given a final dip in a pickle of dilute nitric acid.

Blue-black colours on iron are produced by immersion in a hot solution of sodium thiosulphate of the following strength approximately:—

Sodium thiosulphate . . .	4 oz.
Water	1 imp. gall.

Pleasing shades of gray are given to iron and steel goods by immersion in acid solutions of salts of antimony or arsenic. A typical solution is made by dissolving 2 oz. of arsenious oxide in a sufficiency of strong hydrochloric acid and diluting the liquid to 1 gallon. Such solutions are used hot.

Iron and steel articles are very often coloured by means of heat treatment. A very well-known example of this treatment is the Bower-Barff process, which consists essentially in imparting to the surface of iron a protective film of the black oxide of iron (Fe_3O_4) by means of heating to a red heat in superheated steam. This method, however, obviously demands special apparatus.

In addition to coatings of black oxide produced in this way, steel goods may be readily coloured by heating in air at various temperatures. The following Table * gives details of the colours obtained on steel containing 0·89 per cent. of carbon under different temperature conditions.

TABLE XIV.

Colours obtained at certain temperatures on steel containing 0·89 *per cent. carbon.*

Degrees Centigrade.	*Colours.*
235	Straw
250	Brown
273	Purple
296	Blue
336	Blue-grey
381 to 417	Blue-black

Metal-colouring by Electro-chemical Methods.—Under this heading will be briefly described those processes which depend upon electro-deposition by separate current.

Deposits of *arsenic* either alone or in conjunction with other substances are very often used in this connection.

Arsenic has a grayish-white colour but in its deposition electrolytically various shades may be obtained according to the composition and temperature of the solution and the current conditions employed.

The following will be found a very useful solution :—

Sodium arsenate ($Na_3AsO_4 . 12H_2O$)	$\frac{1}{2}$ lb.	250 gr.
Potassium cyanide	6 oz. (approx.)	187 „
Water	1 imp. gall. or $1\frac{1}{5}$ U.S. „	5 litres

Sodium arsenate is dissolved in half the water, cyanide in the remainder, and the two solutions mixed together and boiled.

The bath is worked hot by means of carbon anodes, and an E.M.F. of from 3 to 4 volts is employed.

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* J. O. Arnold, *Jour. Iron and Steel Institute*, 1910, No. 1.

Another solution of arsenic from which a black pulverulent deposit is obtained, which, however, adheres very well, is made up by dissolving 4 ozs. of arsenious oxide (As_2O_3) in 8 ozs. of hydrochloric acid, and diluting to one imp. gallon by the addition of water. This solution is also used hot with carbon anodes. A current of low voltage is advisable (from ½ to 1 volt).

Antimony is also often employed in the metal-colouring art to produce light grey shades of colour. Methods of depositing this metal by separate current have already been described in Chapter XV.

Black-nickeling.—This is probably the most popular of the processes of metal-colouring which may be classed under separate current methods.

From a suitable solution a very pleasing dead-black colour is produced on almost any basis metal in from twenty minutes to an hour.

The solution used is practically an ordinary nickel-plating solution to which varying proportions of ammonium thiocyanate (NH_4CNS) has been added; together, in many cases, with small proportions of zinc and copper sulphates.

The following formula has been strongly recommended, and has the advantage of being rather simpler than many which appear to be in use:—

Double sulphate of nickel and ammonium	9 oz.	285 gr.
Ammonium thiocyanate	2½ ,,	78 ,,
Zinc sulphate	1 ,,	31·2 ,,
Water	1 imp. gall. or 1⅕ U.S. ,,	5 litres

It is very important that the solution should be *neutral*.

The method of working the bath is much the same as an ordinary nickel-plating. Nickel anodes are used, but the current must have a much lower voltage than in normal nickel-deposition, generally about ½ a volt is sufficiently high. If a higher pressure is used, there is a distinct tendency to whiteness in the colour. Such is the case sometimes even at the voltage recommended; but in this event a little more ammonium thiocyanate should be added, and from time to time also a little zinc sulphate.

In the preliminary treatment of metal for this process the sand-blasting apparatus is a very useful adjunct. By means of Trent sand or a medium grade of powdered pumice a fine matte may be given to the surface of the metal which results in the production, after treatment in the black-nickeling bath, of a beautiful satin-like black finish.

To preserve the appearance of black-nickeled goods they should always be given a coating of clear lacquer, immediately after drying out from the bath.

General Remarks on Metal-colouring.—The operations of sand-blasting and scratch-brushing are both of very great importance in the art of metal-colouring, inasmuch as both the preliminary and final treatment of the surface of the article considerably influence the character of the ultimate finish produced. The art of sand-blasting has already been rather fully discussed in the sections dealing more particularly with electroplating, and the metal-colourer will find a study of those references of advantage. It is also, however, of equal importance to realize the possibilities that lie in scratch-brushing. Indeed some pleasing finishes can be imparted to copper and brass by this means without the use of any chemical reagent whatever. On the latter metal particularly a very popular finish is produced by brushing with applications of fine sand or powdered pumice stone, using as a lubricant either water or a very thin light oil. An appreciable variety can be obtained in such methods by using various grades of brushes, from those of very fine wire (45 or 47 B.W.G.) up to strong frosting brushes.

For the treatment of chemically coloured surfaces the scratch-brush is indispensable in the preliminary operations and after colouring will be found more generally useful than any other process particularly in the case of goods intended for subsequent lacquering as most coloured metals are. When used with judgment very delicate shades of tone are thus produced, but it is obvious that some experience and practice are essential.

A further matter upon which it is necessary to lay considerable stress has reference to the colouring of *electroplated* work. Articles which are intended for subsequent colouring, particularly chemical colouring, should always be given a very substantial coating of the deposited metal. The reason for this is that the chemical action of the colouring bath is usually that of converting the metal upon which it is reacting into some compound, such as chloride, carbonate, sulphide, etc., and if this metal is only a film or very thin coating the action quickly penetrates it and in further operations the metal below is exposed. In the treatment of a zinc article for example, which has been given a coating of electro-deposited copper, and subsequently coloured by means of ammonium sulphide or a similar solution, then relieved on the scratch-brush or calico-mop; it is quite possible for the copper coating if only thin to be entirely converted, on the more exposed parts of the surface, to copper sulphide, with the consequence that in the relieving operation it is readily brushed off, leaving the zinc surface quite unprotected.

Lacquering.—As mentioned earlier in this chapter most metals after colouring are given a coating of lacquer as a final treatment; the purpose being to preserve the colour and finish exactly as it leaves the colouring operations, and to prevent the action of the atmosphere from affecting the appearance when such articles are in use. Lacquers are made in immense variety at the present time, and are prepared by reputable manufacturers with great skill. Many different compositions are used, but essentially lacquers consist of solutions of shellac, seed lac, or celluloid, and similar substances in pure alcohol, acetone or amyl acetate or mixtures of these. Except when required coloured for special purposes, they should be perfectly clear and of a thin consistency.

Lacquers are now made suitable for either hot or cold application. Cold lacquers are generally applied by means of a fine quality camel's-hair brush and then allowed to dry cold, but lacquers for use in this way must be specially prepared and used according to the directions of the manufacturers.

For ordinary lacquering the work should be first warmed to about 60° to 65° C., then dipped into the lacquer, or, if more suitable, brushed over with it quickly and in uniform direction. The article is then suspended in an oven or stove specially fitted for such purposes, heated either by gas, steam, or electricity, but in such a manner that the interior is kept perfectly dry. The temperature of the stove is varied to some extent according to the nature of the lacquer, but is generally from 100° to 120° C., and the process is continued until the coating of lacquer is perfectly dry and hard.

If gas is used for heating, precautions must be taken that no naked flame is brought near to the lacquer since nearly all such liquids are very inflammable.

II. Mechanical Methods of Metal-colouring can be given little description here. They include the use of pigments of various kinds; the application of specially prepared bronze powders, and Dutch-metal or gold leaf; also of varnishes or coloured lacquers, and other kindred processes.

The most common of the operations under this heading are those involving the use of bronze powders and coloured lacquers. The latter particularly are now to be obtained in great variety and of excellent quality; they should be applied according to the instructions issued by manufacturers.

APPENDICES

1. THE ASSAY OF SILVER.—VOLHARD'S METHOD.

THE principle of this method of silver assaying depends upon the fact that when a solution of ammonium thiocyanate is added to silver nitrate a white insoluble precipitate is produced consisting of silver thiocyanate. If before this addition a small quantity of a ferric salt has been added to the silver solution, then at the instant when the whole of the silver is precipitated, the characteristic blood-red ferric thiocyanate forms, so that the end of the silver reaction is easily perceived.

A solution of ammonium thiocyanate known as deci-normal (containing 7·6 grams per litre) must first be prepared by weighing out 8 grams of the crystallised salt and dissolving in one litre of distilled water. This solution must now be standardised as follows: * Take 25 c.c. of a deci-normal solution of silver nitrate (16·966 grams of $AgNO_3$ per litre), transfer to a small flask and add 3 or 4 c.c. of a solution of ferric sulphate. This salt is made by dissolving a little ferrous sulphate (a few crystals) in water to which has been added half its volume of strong nitric acid, and boiling the mixture to expel all nitrous fumes. The thiocyanate solution is then carefully run in from a burette until a permanent red coloration appears. The experiment must be repeated several times until a close agreement of the various burette readings is obtained. From the volume used the exact strength of the thiocyanate solution is calculated, and therefore the amount of distilled water which must be added to make the solution the strength required, viz. 7·6 grams per litre.

Now 1 c.c. of the thiocyanate solution contains 0·0076 gram of the salt and is equivalent to 0·010766 gram of silver. The chemical reaction is shown in the following equation:—

$$AgNO_3 + (NH_4)CNS = AgCNS + NH_4NO_3$$

---

* See Newth's *Manual of Chemical Analysis* (Longmans), p. 165.

To carry out an assay dissolve the metal in nitric acid diluted with an equal bulk of water, and make up to a definite volume. Thoroughly shake and take a suitable proportion according to the amount of silver which the whole is supposed to contain.

The actual estimation is carried out exactly as directed above for standardising the thiocyanate solution, the ferric salt being added to the solution to be assayed before addition of the standard solution. Several readings should be taken until three successive ones are found to be in close agreement. The burette reading multiplied by 0·010766 (the weight of silver equivalent to 1 c.c. of thiocyanate) gives the weight of silver contained in the portion taken for assay.

Where standard silver and similar alloys have to be regularly assayed, and the approximate composition is therefore known, this method is particularly useful; the solution in which the sample is dissolved in such cases is diluted to a strength roughly corresponding to that of the standard thiocyanate solution.

The method is one of extreme accuracy in experienced hands, but some considerable practice is necessary to get the best results.

2. THE DETERMINATION OF WEIGHT OF DEPOSIT ON SILVER-PLATED ARTICLES.

This question is one which, during recent years, has assumed considerable commercial importance, due to the growing practice on the part of large buyers of such goods to specify the minimum weight of deposit which shall be given to each article. In many cases a guarantee is required from the manufacturer that such a weight actually obtains on the *finished* article when delivered. It is consequently often necessary to make determinations of the deposit on a sample article taken from the bulk, *e.g.* a spoon or fork.

Such determinations are often made in workshop practice by weighing a plated article carefully, then stripping the silver deposit by immersion in the stripping liquid described on page 213, then reweighing and ascertaining the difference, which is taken to represent the silver deposit. This method, however, is never quite accurate, under the most favourable conditions, as it is practically impossible to prevent a slight solution of the basis metal. The best practice is, therefore, to strip the silver deposit completely and then assay the stripping liquid to determine its resulting silver content.

A good method is to make up, in a vessel large enough to contain the article to be tested, a stripping liquid consisting of powdered potassium nitrate and strong sulphuric acid in the proportion of $\frac{1}{2}$ oz. of the salt to 1 pint of acid. The containing vessel is then placed in a bath of hot water, and the article completely immersed until every trace of silver is removed. On cooling, the liquid should be considerably diluted by adding to a larger volume of water, and the whole bulk made up to an exactly measured quantity by further addition of water as necessary. If the resulting volume is not too large to be reasonably handled, the *whole* may now be assayed by Volhard's method above described or by that advocated on page 210. If, on the other hand, the volume is very great some small but definite proportion, say $\frac{1}{10}$th or $\frac{1}{20}$th is taken, after thorough mixing, and assayed, the result being multiplied to give the exact weight of the total silver contents.

3. To Calculate Thickness of Electro-deposits.

When the electro-chemical-equivalent and the specific gravity of any metal are known (see page 393), the thickness of the metal deposited per hour with a given current density may readily be calculated, from which the thickness per hour for any current spread over a suitable area may be deduced.

Example.—Let us assume a current density of one ampere per square inch, and calculate the thickness of silver thus deposited per hour.

From page 63.

Weight of silver deposited by one ampere in one hour = 4·0245 grams. Assume this deposit to take place on one square inch area.

Let t = thickness of deposit in inches;

then volume of deposit = area × thickness.

$$= 1 \times 1 \times t \text{ cub. ins.}$$

$$= t \text{ cub. ins.}$$

But 1 cub. in. = 16·38 c.c., and 1 c.c. of silver weighs 10·5 grams (see Appendix 10).

∴ 1 cub. in. of silver weighs 10·5 × 16·38 grams, and t cub. ins. of silver weigh $10{\cdot}5 \times 16{\cdot}38 \times t$ grams.

But under the conditions assumed 4·0245 grams are deposited

$$\therefore 10{\cdot}5 \times 16{\cdot}38 \times t = 4{\cdot}0245$$

$$t = \frac{4{\cdot}0245}{10{\cdot}5 \times 16{\cdot}38} = 0{\cdot}0234 \text{ inch.}$$

Hence, with a current density of one ampere per square inch, the thickness per hour = 0·0234 inch, and it follows that if I is the current and A the area deposited upon, the current density would be $\frac{A}{I}$, and the thickness would be $\frac{A}{0{\cdot}0234 \times I}$ inch.

Similar calculations may be made for other metals.

4. To ascertain the Capacity of a Plating Vat in Gallons.

For rough estimations a fairly accurate method is to multiply the length, width, and depth together so obtaining the volume in cubic feet and to further multiply the result by 6¼, thus:—

Find the capacity of a vat measuring 6 feet in length × 2½ feet in width × 2 feet in depth.

6 × 2½ × 2 = 30 cubic feet.
30 × 6¼ = 187½ gallons.

More exact results are obtained by ascertaining the measurement of the vat in *inches*, multiplying the three factors, length, width, and depth together, and dividing the result by 277·27.

Thus, find the capacity of a vat measuring 6 feet 3 inches in length, 32 inches in width, and 21 inches in depth.

75 × 32 × 21 = 50,400 cubic inches.
50,400 ÷ 277·27 = 181¾ gallons.

5. Testing Polarity of Supply and Direction of Current.

The terminals of a dynamo are frequently marked + (positive) and − (negative), while the poles of primary and secondary cells may generally be distinguished by inspection.

In cases where no distinction can be made by inspection, one of the following tests may be applied:—

Test 1.—Remove about two inches of the insulation from the ends of two pieces of thin insulated copper wire, and clean the exposed copper.

Connect one end of each wire to the terminals of the source (if this be a dynamo it must be running), and dip the other ends into the coppering vat, or a little coppering solution in a bowl, *taking care that the wires do not at any time come into contact.* In a short time copper will be deposited on one of the wires; this wire is connected to the *negative* terminal of the source.

Test 2.—Take the wires prepared and connected to the source as described above, and place the free ends about half an inch apart on a strip of pole-finding paper which has been damped with water. A red spot will appear on the paper under the wire connected to the *negative* terminal.

A handy form of pole-finding paper is that known as Wilke's, which may be purchased in miniature books similar to litmus paper.

To determine the direction in which a current is flowing in a given conductor, (1) arrange the latter, if possible, in the magnetic meridian (approximately north and south). (2) Hold a compass needle directly over or under the conductor, and observe the direction in which the N. pole of the needle is deflected. (3) Grasp the conductor and needle with the right hand so that the former is next the palm, and the N. pole of the latter towards the wrist, then the outstretched thumb pointing along the conductor indicates the direction of the current.

6. Directions for First-Aid in Cases of Poisoning.

Plating shop chemicals are for the most part virulent poisons. Cases of poisoning therefore by any of them are usually serious, and no time should be lost in summoning medical aid. Meantime, however, the following information and simple outlines of treatment will be useful.

The usual course adopted in ordinary cases of poisoning is to administer immediately an emetic such as detailed in the table at the end of this section. In cases, however, when the poison is an acid or strong alkali such as are found in plating shops, the proper course is to neutralize the poison according to directions below, and not to attempt to remove it by giving emetics.

Poisoning by Hydrochloric, Sulphuric, or Nitric Acids.

1. Neutralize the acid by giving any one of the following—
    - (*a*) Chalk or whiting (calcium carbonate).
    - (*b*) Sodium or potassium carbonate dissolved in plenty of water.
    - (*c*) Half to one ounce of magnesium carbonate in a glass of water.
    - (*d*) Soap and water in large draughts.
2. Afterwards give the patient milk and egg, or thick gruel.

Olive oil ($\frac{1}{4}$ pint in 1 pint of water) is also very useful in such cases.

Poisoning by Oxalic Acid or by Salt of Lemons.

Treatment as above, and after neutralizing administer a full dose of castor oil and give milk freely.

Poisoning by Cyanides or Hydrocyanic Acid.

1. Place the patient in the open air, and if the poison has only just been taken administer an emetic (if not, this may be omitted), then proceed to give a cold water douche. Let the water fall from a height on to the head and spine, or dash cold water on continuously.

2. Artificial respiration may also be necessary, and the patient should be allowed to inhale ammonia by the nostrils.

3. Administer any of the following stimulants:—

Sal volatile; brandy; hot coffee or tea.

The following is a very useful draught in such cases if a chemist is at hand:—

Sulphate of iron	15 grains.
Tincture of iron perchloride . .	20 minims.

Dissolve in a wine-glassful of water, and add 1 to 2 drachms of magnesium carbonate previously made into a thin cream with water. Repeat if necessary.

Poisoning by Caustic Alkalies (Caustic Potash, Caustic Soda, or Strong Ammonia).

1. Do not give emetics, but neutralize the alkali by administering any one of the following:—

(*a*) Vinegar well diluted with water.
(*b*) Lemon juice in water.
(*c*) Tartaric acid, ½ drachm in ½ pint of water.
Repeat as necessary.

2. Afterwards give the patient either plenty of milk, or ¼ pint of olive oil in 1 pint of water, or the white of an egg.

3. Give stimulants, sal volatile, hot coffee or tea.

Poisoning by Antimony or Arsenic Compounds.

1. Incessant vomiting usually follows antimony or arsenic poisoning, and this should be encouraged by giving tepid water. If vomiting does not occur, give an emetic.

2. Strong tea should be given as often as vomiting occurs.

3. Afterwards, milk or white of an egg, the former freely.

4. In cases of collapse, give stimulants and apply hot-water bottles to extremities.

Poisoning by Copper Salts.

1. If vomiting does not occur, administer an emetic, but *before* doing so give large quantities of milk.

2. Then an emetic.

3. Afterwards, milk and egg, thick gruel, or barley water.

Poisoning by Mercury or Mercury Salts.

1. Give large quantities of white of egg mixed with milk or water, or both.

2. Then an emetic.

3. If much pain, give the following:—

Opium tincture	20 minims.
Water	1 oz.

4. Milk and eggs, gruel, or barley water.

Poisoning by Silver Nitrate.

1. First and immediately give:—

   One ounce of common salt in a tumblerful of water, and repeat if deemed necessary.

2. Then an emetic to remove the silver chloride formed by the above treatment.

3. Give white of egg in water, freely.

Poisoning by Zinc Salts.

1. Do not give emetics, but large draughts of white of egg and milk.

2. Good doses of sodium carbonate dissolved in warm water.

3. Strong tea, and afterwards thick gruel or barley water.

4. For acute pain give the opium tincture prescribed above. (See Mercury poisoning.)

Emetics.

1. Mustard powder, 1 table-spoonful in a tumblerful of warm water.

2. Common salt, 2 table-spoonfuls in a tumblerful of tepid water.

3. Zinc sulphate, 30 grains in half a tumblerful of warm water.

4. Ammonium carbonate, 30 grains in half a tumblerful of warm water.

5. Powdered ipecacuanha, 30 grains in half a tumblerful of warm water.

6. Copper sulphate, 5 to 10 grains in half a tumblerful of warm water.

7. THE METRIC SYSTEM OF WEIGHTS AND MEASURES.

On this system, the multiples and submultiples are arranged on a decimal basis. The multiples are designated by the Greek prefixes:—*deka* = 10, *hecto* = 100, *kilo* = 1000. For the subdivisions Latin prefixes are employed:—*deci* = $\frac{1}{10}$, *centi* = $\frac{1}{100}$, *milli* = $\frac{1}{1000}$.

LENGTH.—The unit of length is the *metre.* The British standard, kept at the Board of Trade in London, is a bar of a platinum-iridium alloy, the measurement being represented by the distance between two fine lines marked on the bar when the metal is at a temperature of 0° C.

1 kilometre	=	1000 metres	=	0·6214 mile.
1 hectometre	=	100 ,,	=	109·361 yards.
1 dekametre	=	10 ,,	=	32·8 feet.
1 metre	=	1 ,,	=	39·37 inches.
1 decimetre	=	0·1 ,,	=	3·937 ,,
1 centimetre	=	0·01 ,,	=	0·3937 ,,
1 millimetre	=	0·001 ,,	=	0·0394 ,,

MASS.—The unit of mass, the *gram,* was derived from the metre, and represents very nearly the mass of one cubic centimetre of water at its temperature of maximum density, 4° C. A standard weight of 1000 grams or 1 kilogram is now kept at the Board of Trade.

1 kilogram	=	1000 grams	=	2·2046 lbs.
1 hectogram	=	100 ,,	=	3·5274 ozs. (avoir.).
1 dekagram	=	10 ,,	=	154·3236 grains.
1 gram	=	1 ,,	=	15·4324 ,,
1 decigram	=	0·1 ,,	=	1·5432 ,,
1 centigram	=	0·01 ,,	=	0·1543 ,,
1 milligram	=	0·001 ,,	=	0·0154 ,,

VOLUME.—The unit of volume, the *litre,* is derived from the unit of length. The litre is a cubic decimetre, or 1000 c.c. It is therefore also the volume of 1000 grams (1 kilogram) of distilled water at 4° C. A standard litre is also kept at the Board of Trade, London.

1 kilolitre = 1000 litres = 220·4 imp. galls.
1 hectolitre = 100 ,, = 22·04 ,, ,,
1 dekalitre = 10 ,, = 2·20 ,, ,,
1 litre = 1 ,, = 1·76 imp. pints.
1 decilitre = 0·1 ,, = 3·52 Brit. fluid ozs.
1 centilitre = 0·01 ,, = 0·352 ,, ,,
[*] 1 millilitre = 0·001 ,, = 16·894 ,, minims.

8. Weights and Measures.

Fluid Measure (British).

60 minims = 1 fluid drachm.
8 fluid drachms = 1 ,, ounce.[†]
20 ,, ounces = 1 imp. pint.[‡]
2 pints = 1 ,, quart.
4 quarts = 1 ,, gall.[§]

Avoirdupois Weight (British and U.S.A.).

16 drachms = 1 ounce (437·5 grains) = 28·35 grams.
16 ounces = 1 pound (7000 ,,).
28 pounds = 1 quarter.
4 quarters = 1 hundredweight (cwt.).
20 hundredweights = 1 ton.

Troy Weight (British and U.S.A.).

24 grains = 1 pennyweight (dwt.) = 1·555 grams.
20 pennyweights = 1 ounce (480 grains) = 31·1 ,,
12 ounces = 1 pound (5760 grains).

Apothecaries' Weight (British and U.S.A.).

3 scruples = 1 drachm (60 grains).
8 drachms = 1 ounce (480 ,,).
12 ounces = 1 pound (5760 ,,).

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[*] Commonly known as a cubic centimetre (c.c.).

[†] 1 British fluid oz. = volume of a weight of 437·5 grains (*i.e.* 1 oz. Av.) of water = 1·73 cub. in.

1 U.S.A. fluid oz. = volume of a weight of 455·6 grains of water = 1·8 cub. in.

[‡] 1 imperial pint = 20 fl. oz. = 567 c.c.
1 U.S.A. ,, = 16 fl. oz. = 473·15 c.c.

[§] 1 imperial gallon = 277·274 cub. in.
1 U.S.A. ,, = 231 ,, ,,

9. Useful Data.

1 gallon of water weighs 10 lbs. and occupies 0·1605 cubic feet.
1 cubic foot of water contains 6·232 gallons.
1 pint = 0·567 litres. 1 litre = 1·76 pints.
1 imp. gall. = 4·54 litres.
1 oz. per gallon = 6·25 grams per litre.
1 lb. „ „ = 100 „ „ „

To convert Fahrenheit degrees (F.) to Centigrade degrees (C.), first subtract 32, then multiply by 5, and divide by 9.

$$\text{C.} = \frac{5(\text{F.} - 32)}{9}$$

To convert Centigrade degrees to Fahrenheit degrees, multiply by 9, divide by 5, then add 32.

$$\text{F.} = \frac{9\text{C.}}{5} + 32$$

Useful Factors.

To convert	grams into grains	multiply by	15·432
„	„ ozs. (avoir.)	„	0·03527
„	kilograms into pounds	„	2·2046
„	grains into grams	„	0·0648
„	(avoir.) ozs. into grams	„	28·35
„	(Troy) „ „	„	31·10
„	cubic centimetres into (British) fluid ozs.	„	0·0352
„	litres „ „ „ „	„	35·2
„	British fluid ozs. into cubic centimetres	„	28·42
„	pints into litres	„	0·567
„	metres into inches	„	39·37
„	inches into metres	„	0·0254

The following information will enable coins to be used as makeshift weights:—

One	sovereign .	weighs	123·274	grains,	or approximately	5	dwts. (Troy).
„	half-sovereign	„	61·637	„	„	$2\frac{1}{2}$	„
„	five-shilling piece	„	436·363	„	„	1	oz. (avoir.).
„	half-crown „	„	218·181	„	„	$\frac{1}{2}$	„
„	florin . . .	„	174·543	„	„	$\frac{2}{5}$	„
„	shilling . .	„	87·2727	„	„	$\frac{1}{5}$	„
„	sixpence .	„	43·6363	„	„	$\frac{1}{10}$	„
„	threepenny piece	„	21·8181	„	„	$\frac{1}{20}$	„
„	penny . .	„	145·83	„	„	$\frac{1}{3}$	„
„	halfpenny .	„	87·5	„	„	$\frac{1}{5}$	„

10. SPECIFIC GRAVITIES OF METALS AT ORDINARY TEMPERATURES. (Water = 1.)

Name.	*Sp. gr.*	*Name.*	*Sp. gr.*
Aluminium	2·60	Manganese	7·40
Antimony	6·62	Mercury	13·55
Cadmium	8·64	Nickel	8·80
Cobalt	8·70	Palladium	11·40
Copper	8·95	Platinum	21·50
Gold	19·30	Silver	10·50
Iron	7·86	Tin	7·29
Lead	11·38	Zinc	6·92

11. SOLUBILITIES OF VARIOUS COMMON SUBSTANCES IN WATER AT ORDINARY TEMPERATURES.

One part of	is soluble in	One part of	is soluble in
Citric acid	0·75 parts	Boric acid	30 pts.
Ammonium carbonate	4 ,,	Mercuric chloride	16 ,,
,, chloride	3 ,,	Potassium iodide	0·75 ,,
,, phosphate	4 ,,	,, nitrate	4 ,,
Silver nitrate	0·54 ,,	Sodium chloride	2·8 ,,
Copper sulphate	3·5 ,,	,, phosphate	6 ,,
Ferrous ,,	0·9 ,,	Zinc sulphate	0·53 ,,
Magnesium sulphate	1 ,,	Antimony tartate	17 ,,
Lead acetate	0·5 ,,		

12. PROPERTIES OF SOLID COPPER CONDUCTORS.

Diameter in inches.	Area, sq. ins.	Weight in lbs. (avoirdupois) per foot.*	Approximate Resistance at 60° F. per 1000 yds. ohms.†	Current		Length in yards giving 1 volt drop.
				at 1000 amps. per sq. in.	at 800 amps. per sq. in.	
⅜″ or 0·375	0·1104	0·425	0·2178	110	88	With 1000 amps. per sq. in. the length is approx. 40 yds., *i.e.* 20 yds. lead, 20 yds. return.
½″ ,, 0·500	0·1963	0·757	0·1225	196	157	
⅝″ ,, 0·625	0·3068	1·182	0·0784	307	246	
¾″ ,, 0·750	0·4418	1·703	0·0544	442	354	
⅞″ ,, 0·875	0·6013	2·317	0·0400	601	480	
1″ ,, 1·000	0·7854	3·027	0·0306	785	628	
1¼″ ,, 1·250	1·2272	4·730	0·0196	1223	980	
1½″ ,, 1·500	1·7671	6·811	0·0136	1767	1410	

* Taking copper to weigh 555 lbs. per cubic foot.

† Calculated from data derived from the "Report of the Committee on Copper Conductors" (1899).

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