PRINCIPLES OF ELECTROPLATING AND ELECTROFORMING
(ELECTROTYPING)

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by
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AND ELECTROFORMING (ELECTROTYPING)

PREFACE TO THE THIRD EDITION

During the past few decades there has been virtually a revolution in the electroplating industry. The rapid increase in the large-scale application of plating, notably in the automobile industry, has led to the employment of many chemists and engineers. These persons, as well as many platers, soon realized the need for more exact knowledge of the principles of electroplating and of methods for controlling the processes and products.

This need has been largely met through researches conducted in plant, government, and educational laboratories. During the period from 1930 to 1940, over 500 significant papers on electroplating were published in American and English journals and about an equal number in French, German, and Russian journals. During the Second World War fewer publications appeared, but extensive researches were conducted on military applications of plating, many of which are now being published and which will undoubtedly influence postwar plating practice.

Simultaneously, there was rapid progress in commercial plating, not so much in the development and application of entirely new methods as in the more intelligent and consistent use of existing knowledge. Electroplating engineering has come to be a recognized, important profession. The American Electroplaters' Society, the American Society for Testing Materials, and the Electrodepositors' Technical Society have developed numerous specifications for plated products and for materials used in plating. The net result has been a greatly increased use of plating of improved quality.

Among the important American developments were the publication of the authoritative summary "Modern Electroplating" by the Electrochemical Society in 1942 and the researches sponsored by the American Electroplaters' Society. These researches are still active and expanding and will no doubt furnish a sound factual and theoretical basis for still greater progress in this industry.

It is manifestly impossible to include in a single text of moderate length the details of all these developments. There is a field for more comprehensive texts on both the theory and the practice of electroplating. This book does not attempt to cover either of these exhaustively. Instead, an effort has been made to summarize and digest the available knowledge in both fields and to present it in a form that will benefit both platers and chemists. No attempt has been made to give exhaustive bibliographies or to cite references for each statement made. Sufficient references have been included, principally to papers in English that contain bibliographies, to permit the reader to become familiar with the extensive literature. All the papers that appeared in "Modern Electroplating" were also published in volume 80 of the *Transactions of the Electrochemical Society*. Because this volume is available in libraries and "Modern Electroplating" is now in process of revision, references have been given only to the *Transactions*.

Some important changes have been made in the scope and arrangement. Although numerous articles and books have been recently published on chemistry for electroplaters, the modest chapter on this subject has been retained for reference and review, especially by those without a formal scientific education. Such individuals should extend their knowledge of chemistry by study of appropriate texts, preferably in classes conducted for platers. Wherever new terms or those with special meanings in this field are introduced, explanatory notes are included throughout the text.

Instead of the analytical methods being distributed according to the specific baths, they have been assembled into one chapter, which will be more convenient for those persons engaged principally in analyses.

It has been pointed out by several authors in recent years that, through the periodic system of the elements, relations between the conditions for deposition of different metals can often be predicted. Therefore instead of treating the metals in the order of their apparent importance in electrodeposition (as in the previous editions), they have been discussed in groups according to the periodic system. This arrangement will permit the empirical use of any data presented and at the same time may stimulate new lines of thought by investigators in this field.

This edition is more scientific and technical than previous editions, for the obvious reason that the electroplating industry is becoming more scientific. By presenting new developments in simple terms, it is hoped that they can be more readily assimilated and applied by those directly engaged in plating operations.

The authors are indebted for helpful criticisms and suggestions received from many persons regarding the drafts of specific chapters and especially to G. Byron Hogaboom, Jr., Nathaniel Hall, J. Homer Winkler, Clarence L. Buck, John McLean, Arthur Logozzo, George Dubpernell, Karl Schumpelt, Walter R. Meyer, and Guerin Todd.

The cordial reception and wide use of the earlier editions of this text lead to the hope that this new edition will serve to meet the needs of an even greater number of individuals, firms, and institutions. If so, our efforts will have been fully rewarded.

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WASHINGTON, D.C.,
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June, 1949

PREFACE TO THE FIRST EDITION

During the past several years the authors have been associated with the investigation of electrotyping and electroplating processes at the Bureau of Standards. These studies have been carried out not alone to assist wherever possible other branches of the government service, but also to secure information useful to the manufacturing industries. In this field the Bureau has worked in close cooperation with the American Electroplaters' Society and the International Association of Electrotypers. In general, the results of specific investigations have been made public from time to time, through government publications and by presentation in appropriate journals.

Through the close association thus gained with persons connected with the above industries, the authors have become convinced that before there can be any extended industrial application of the results of research work, there must be a more general recognition and application of the established and fundamental principles of the related sciences. This book has therefore been prepared not so much for the purpose of presenting the results of research as of assisting those in the industry to understand and apply the results that have been or may be secured in various research and educational institutions.

A new word, *electroforming*, has been employed in this book. It may be defined as "the production or reproduction of articles by electrodeposition." It is suggested as a substitute for the term *galvanoplasty*, which has been occasionally used in English or American texts. It includes electrotyping, the reproduction of phonograph record matrices, and the manufacture of tubes and other objects by electrodeposition. The whole field of commercial electrodeposition is, then, covered by the four analogous terms, electrorefining, electrowinning,[1] electroplating, and electroforming.

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[1] Electrowinning is a term frequently used for the electrolytic recovery of metals from solutions obtained by leaching ores, *e.g.*, in the production of electrolytic zinc.

For the information regarding general principles and processes the authors have drawn freely from various texts and journal articles. No attempt has been made to give a specific reference for each statement made, but a few important references upon each subject have been cited for the benefit of those desiring to study the literature of electrodeposition.

The authors are especially indebted to the Bureau of Standards for the privilege of using subject matter and illustrations from articles that have appeared previously from that Bureau and of using in a few cases their unpublished data. The authors wish also to thank the American Electrochemical Society for the loan of cuts of illustrations that have appeared in their transactions.

For many of the facts and formulas of commercial processes, the authors are indebted to numerous electroplaters and electrotypers, especially the members of the American Electroplaters' Society and of the International Association of Electrotypers. To their colleagues at the Bureau of Standards they are indebted for helpful advice and suggestions.

William Blum
George B. Hogaboom

Washington, D.C.
January, 1924

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CHAPTER I

METHODS OF EXPRESSING CONDITIONS OF OPERATION

GENERAL PRINCIPLES

Reliable operation and control of any process, such as electrodeposition, that involves changes in the composition and form of matter depend upon the measurement and knowledge of certain conditions of operation, such as the composition, density, or temperature of the solutions; the capacity of the tanks; the current density and voltage employed; and the thickness of the deposited metal. In measuring or recording such data it is customary in most commercial work to employ the ordinary or English units, the Fahrenheit scale of temperature, and the Baumé scale of density. In scientific work, including most of that conducted in works' laboratories, the metric units, centigrade temperature scale, and specific gravity are generally used. It is highly desirable to bring about the general adoption of the more scientific units, which are much simpler to use. It is recognized, however, that, even if the metric system were actually adopted in the near future, a considerable period would elapse before it could come into common usage. In this book, therefore, all important values will be expressed in both units so as to be immediately useful both to chemists and to platers. The latter are urged to become as familiar as possible with the scientific units in order that they may be better able to make use of the results of scientific investigations and of such tests as may be conducted by chemists.

Before considering in detail the methods of expressing the results of any measurement, it is important to discuss at some length the principles of *relative accuracy* and *significant figures*, since a disregard of these principles often leads both practical and scientific persons to misconceptions and to waste of time and energy. The first principle depends upon the fact that the various measurements which enter directly into any final result should be made with approximately the same degree of relative accuracy. No measurements are absolutely accurate, owing to unavoidable errors in the calibration and use of any measuring instrument. Up to a certain point such errors can be reduced by definite precautions. The amount of care that is warranted depends entirely upon the use that will be made of the results. Thus, there is no advantage in measuring the dimensions of a plating tank to one-hundredth of an inch when we cannot adjust or maintain the height of the solution in the tank within one-quarter of an inch. Similarly, there is no advantage in measuring two of the tank dimensions with an accuracy of only 1 per cent and the third dimension with an accuracy of one-tenth of 1 per cent, since the final result desired, *i.e.*, the capacity of the tank, will be no more accurate than the least precise measurement.

For practical purposes we may assume that satisfactory results will be obtained if the composition of a plating solution is maintained constant to within 2 per cent (*i.e.*, 1 part in 50) of the actual concentration of each constituent. Any solutions requiring more accurate control than this are inapplicable for modern commercial plating. In the calculation of any actual result, such as the nickel content of a plating solution, a number of separate factors are involved, such as the volume of the solution (which in turn depends upon the length and width of the tank and the depth of the solution), the volume of the sample used in the analysis, and the weight of nickel obtained (or the number of milliliters[1] required for the titration). Since the accidental errors involved in some of these measurements may be in the same direction and therefore cumulative, it is desirable to make the individual measurements with somewhat greater accuracy than is required for the final result. If, for simplicity, we assume that we desire to adjust the composition of a plating solution to within 2 per cent, an accuracy of 1 per cent (of the value concerned) is usually adequate for the separate measurements involved in the determination of the composition.

In expressing the results of such measurements or of calculations based upon them, it is therefore useless to employ any more figures than are necessary to indicate an accuracy of about 1 per cent. Thus for the above purposes it is just as accurate and far more convenient to state that the volume of a plating solution is 235 gal as to call it 235.36 gal, even though the calculations might indicate the latter volume. In other words, no more significant figures should be employed than are justified by the accuracy of the

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[1] The term milliliter (ml) is now most commonly used in volumetric analysis. For all practical purposes the milliliter and cubic centimeter (cm^3) are equal.

measurements or by the use to which the results are to be put. By *significant figures* are meant those numerals which determine the relative accuracy of the value involved. Thus in the above illustration the value 235 gal has three significant figures, while 235.36 gal has five such figures. The first value indicates merely that the true volume is nearer to 235 gal than it is to 234 or 236 gal; the latter value would indicate (assuming that its use were justified) that the true volume is closer to 235.36 gal than to 235.35 or 235.37 gal. Similarly, a value of 28.7 oz/gal of nickel sulfate has three significant figures and is for practical purposes just as accurate as the value 28.676 oz/gal, which has five significant figures. In general, we may state that for this class of work it is sufficient to round off all the values involved to three significant figures. If in any given case a chemical analysis has shown that a solution contained (as based on the actual measurements involved) 214.47 g/l of nickel sulfate, it should be reported as 214 g/l. If, then, this value is converted to ounces per gallon (by multiplying by the factor 0.134), the actual result is 28.676 oz/gal, but the practical value is 28.7 oz/gal (not 28.6 oz/gal). Similarly, a statement that "10 ml of sulfuric acid is to be added to 10.0 ml of the plating solution" indicates that the measurement of the acid is only approximate while that of the plating solution is accurate to at least 1 per cent.

In general, in calculations of such data as the composition of plating solutions, the additions that may be required, the current density, the thickness of deposits, etc., the intelligent use of a slide rule not only will reduce the time required in making calculations but will also tend to eliminate the use of superfluous figures. Several platers who have been initiated into the use of a slide rule have found it of great assistance to them. A few minutes' instruction and some practice will enable any intelligent plater to use a slide rule.

METHODS OF EXPRESSING TEMPERATURE

The thermometer usually employed in scientific work is the centigrade thermometer, on the scale of which the freezing point of water is 0° and the boiling point of water (at a pressure of 1 atmosphere) is 100°, while on the Fahrenheit scale the corresponding points are 32 and 212°, respectively. In general, preference will be given to the centigrade scale, but in view of the prevalent use of the Fahrenheit scale, the values on the latter will also be included. The conversion of temperatures from one scale to the other can be readily accomplished by the use of simple formulas.

1. To convert centigrade to Fahrenheit temperatures, multiply the degrees centigrade by 9/5 and add 32°.

Example. To convert 20°C to Fahrenheit:

$$\left(\frac{9}{5} \times 20^\circ\right) + 32^\circ = 36 + 32 = 68^\circ\text{F}$$

2. To convert Fahrenheit to centigrade temperatures, subtract 32° from the degrees Fahrenheit and multiply the remainder by 5/9.

Example. To convert 77°F to centigrade:

$$(77^\circ - 32^\circ)\,\frac{5}{9} = 45^\circ \times \frac{5}{9} = 25^\circ\text{C}$$

The relation between the two scales can be readily seen from Tables 1 and 2 in the Appendix.

METHODS OF EXPRESSING DENSITY OF SOLUTIONS

For testing the density of solutions either a Baumé (B or Bé) or a specific gravity (sp gr) hydrometer can be used. By the specific gravity of a liquid is meant the ratio of the weight of a given volume of the liquid to the weight of an equal volume of pure water, both the liquid and the water being at a definitely stated temperature. Most of the hydrometers used for commercial work in this country are graduated for a temperature of 15.6°C (60°F) for both the liquid and water. Such hydrometers are said to be graduated for 60°/60°F. If, then, a certain solution has a specific gravity of 1.15, any definite volume of that solution at the above temperature weighs 1.15 times as much as does the same volume of water at that temperature. For the benefit of persons still using Baumé hydrometers, Tables 3 and 4 for the conversion of degrees Baumé to specific gravity and vice versa will be found in the Appendix.

To read a hydrometer, it should be floated in a glass cylinder or jar sufficiently wide that the hydrometer does not touch the sides. The true reading is the point at which the lower edge of the *meniscus* (*i.e.*, the curved surface of the liquid) crosses the hydrometer stem. This is best observed by looking through the solution, with the eye just level with the meniscus. As many of the plating solutions are too deeply colored to permit reading through the solution, it is sometimes necessary to take the reading from above the solution. For most purposes the results so obtained are sufficiently accurate, especially if the cylinder containing the solution is fairly wide. For greater accuracy a correction can be made, based upon the difference in the readings of the hydrometer as viewed from above and below when immersed in pure water or any colorless aqueous solution of suitable density in a similar-sized cylinder.

In the use of a hydrometer it should be borne in mind that the density should always be measured at approximately the same temperature (preferably that for which the hydrometer is graduated). It is also important to note that only in those cases where but one constituent (in addition to water) is present does the density of a solution indicate the composition. Thus for a solution containing only copper sulfate, the density at a certain temperature defines the concentration. If, however, one or more other constituents, such as sulfuric acid and aluminum sulfate, are present in the solution, the density indicates (and then only approximately) merely the total concentration of material dissolved in the water. The use of a hydrometer is therefore not adequate to determine the composition of any plating solution containing more than one dissolved constituent. Its use is very helpful in indicating the extent of the losses of solution that may occur either by mechanical withdrawal or by leakage, provided the solution is always adjusted to the same level in the tank before making the measurement. In some cases—as in an acid copper solution (page 172)—a density determination, together with a simple titration, may yield an accurate analysis of a solution containing two dissolved constituents.

METHODS OF EXPRESSING COMPOSITION OF SOLUTIONS

Among the numerous advantages of the metric system may be mentioned the following: (1) The fact that the units are related in multiples of 10 greatly simplifies calculations; (2) the simple relation between the units of capacity and volume (1 l is practically equal to 1 dm^3 or 1,000 cm^3) facilitates the calculation of the capacity of tanks or vats; (3) the simple relation between the units of weight, volume, and capacity (1 kg is equal to the weight of 1 dm^3 or 1 l of water at its maximum density) renders very convenient the calculation of the weight of a given volume of water or of any liquid of known specific gravity A complete list of the definitions and accurate tables of equivalents of the United States and metric units of weight and measure will be found in *Nat. Bur. Standards Circ.* 47. The relations between the values most commonly used in this work will be found in Table 5 in the Appendix.

Wherever practicable, it is highly desirable to use the metric system in the actual plating operations. By the use of a meter rule (or a 60-cm fourfold rule), a set of metric weights or a platform scale with metric graduations, and a suitable measure, holding, for example, 10 l, the metric system could be installed in a plant in a very short time.

In any case, if the plater is to make use of the results of analyses that may be made for him or of results of plating investigations, it is necessary for him to become familiar with some metric units, and the methods of converting them into ordinary units. Wherever such conversions are necessary, it is preferable to make an entire calculation in metric units and then to convert to ordinary units rather than to mix the units and calculations. Efforts toward short cuts, such as the use of an *assay gallon*[1] (*i.e.*, 13.4 ml of solution), so that the results can be obtained directly in terms of ounces per gallon, are likely to lead to confusion and are justified only when a large number of similar determinations are required, in which case they may be very convenient.

The use of *hybrid* expressions, such as *milligrams of zinc per square inch*, *grams of glue per gallon*, etc., is entirely unjustified. It is just as easy for a plater to obtain a conception of the magnitude of a square centimeter as of a milligram, and any use of hybrid units by chemists is a reflection upon the intelligence of the plater or an indication of mental laziness of the chemist.

In Table 6 in the Appendix will be found a number of simple conversion factors, by means of which results obtained in the metric system can be expressed in the ordinary units and vice versa. It will be noted that to convert the concentration (in grams per liter) to *percentage by weight*, we divide the concentration in grams per liter by ten times the specific gravity of the solution (or, more strictly speaking, the density of the solution, *i.e.*, the weight in grams of 1 ml). In this connection it is in place to call attention to the uncertainty that frequently arises through expressing concentrations in percentage. If a solution is stated to contain 20 per cent of copper sulfate, such an expression if correctly used

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[1] HALL, E. J., *Metal Ind.*, vol. 12, p. 466, 1914. The *assay gallon* for troy ounces per gallon is 12.2 ml.

means that the solution contains in each 100 g or 100 lb *of solution*, 20 g or 20 lb, respectively, of copper sulfate and 80 g or 80 lb of water. Even when the expression is used correctly, it is of little value to an electroplater, who rarely if ever weighs the water or the solutions used by him. The term *per cent* is often used incorrectly, even by persons engaged in scientific work, who sometimes state that a solution contains 20 per cent of copper sulfate when it has been prepared by dissolving 20 g of copper sulfate in 100 ml of water or else in sufficient water to make 100 ml of solution. To avoid any confusion, it is preferable to eliminate the expression per cent as applied to such solutions and in all cases to express the concentration in terms of the weight of substance present in a definite volume of solution, either in grams per liter or in ounces per gallon. In making use of such values the plater should bear in mind that in order to prepare 100 gal of a solution to contain 20 oz/gal of copper sulfate, the necessary amount of copper sulfate (*i.e.*, 2,000 oz, or 125 lb) should not be dissolved in 100 gal of water (which would produce slightly over 100 gal of solution) but in sufficient water to make 100 gal of solution. In other words, the copper sulfate should be dissolved in a volume of water slightly less than that required, and the solution should be finally diluted with water to a volume of 100 gal, as indicated by some convenient mark on the tank. It is important to remember that the British imperial gallon is about 20 per cent larger than the United States gallon.

For research and investigation work, it will usually be found preferable to express the concentrations in terms of *normality* (see page 23), *i.e.*, in terms of the chemical equivalents of the various substances present in the solution. Through failure to calculate the relative normalities of solutions used in investigations, erroneous conclusions may be drawn or important deductions may be overlooked. When, however, such researches lead to the recommendation of certain solutions in commercial work, it is necessary that the concentrations should be expressed in grams per liter or ounces per gallon.

CHAPTER II

PRINCIPLES OF CHEMISTRY

It is obviously impossible in a brief chapter of a book of this scope even to touch upon all the principles of chemistry that electroplaters may consciously or unconsciously apply in their industry. For such information, chemical texts should be consulted and, if possible, classes should be attended. Nevertheless, it is desirable to explain briefly the most important principles and terms likely to be employed. In doing so, the needs of electroplaters will be especially considered even though thereby the definitions or illustrations may be more restricted than would be otherwise desirable.

MATTER

Kinds of Matter. *Matter* may be defined as that which has weight (or mass) and occupies space. A *substance* is any specific kind of matter, such as wood, lead, water, or sodium carbonate. Substances are distinguished from each other and are hence identified by their *properties*, such as color, taste, odor, specific gravity, solubility (in water or other solvents), melting point, boiling point, and electrical conductivity. Whenever two samples have identical properties, the samples are of the identical substance. Actually, it is usually necessary to observe or determine only a few properties in order to identify a substance, although obviously the more properties are determined the more reliable is the identification.

Of those substances which are homogeneous, *i.e.*, uniform in composition throughout, we distinguish two classes, known respectively, as *elements* and *compounds*.

Elements may for convenience be defined as substances that have never been decomposed or separated into simpler substances by chemical methods. (The discovery of radium and the study of radioactive changes have shown that under certain circumstances some of the so-called "elements" may decompose, although the rate of such decomposition cannot at present be readily controlled.) Familiar examples of elements are oxygen and nitrogen, the gases that constitute the larger part of the atmosphere; carbon, sulfur, and phosphorus, all of which are nonmetallic; and the metallic elements, such as copper, silver, gold, lead, tin, and zinc.

Compounds are substances that are uniform in composition throughout and which contain two or more elements, which elements are always present in a definite and constant proportion by weight. Thus, for example, water is a compound that consists always of 88.9 per cent (by weight) of oxygen and 11.1 per cent of hydrogen. Similarly, sulfuric acid consists of hydrogen, sulfur, and oxygen, in definite proportions by weight. Invariably plating solutions contain one or more compounds in addition to water.

Mixtures may be distinguished from compounds by the fact that they consist of two or more substances (which may be either elements or compounds) which are present in many variable proportions and which retain their original properties in the mixture. The classic example of a mixture, given in many chemistry texts, is that produced by grinding together sulfur and iron filings. From such a mixture the iron can still be removed by a magnet and the sulfur by a suitable solvent for sulfur, such as carbon disulfide, showing that each substance has retained its original properties. If, however, such a mixture is heated, a chemical change or reaction occurs and a chemical compound, iron sulfide, is formed, which has the properties neither of iron nor of sulfur. Similarly, it is well known that the compound called *copper sulfate* has entirely different properties, such as color, density, solubility, and taste, from a mere mixture of copper, sulfur, oxygen, and water, all of which substances are present in definite proportions in the blue crystals of copper sulfate.

As is usually the case in attempts to classify nature, there is no sharp line of demarcation between compounds and mixtures. Some classes of substances, especially solutions and alloys, are on the border line, so that from one standpoint they may be considered as compounds and from another as mixtures. Certain properties of solutions will be discussed in detail (page 18), as solutions are the basis of all electroplating operations.

Structure of Matter. The various elements are considered to be made up of small particles called *atoms*. An atom of an element may conveniently be described as the smallest particle of that element that can enter into chemical combination. Modern theories of chemistry and physics indicate that atoms are in turn composed of much smaller particles, including *electrons* and *protons*. Electrons are the units of negative electricity, the movement and transfer of which are involved in the actual processes of electrodeposition. Protons are positively charged particles, derived by removing an electron from a hydrogen atom.

It is now known that many elements exist in the form of *isotopes*, the atomic weights of which are different, although they have identical chemical properties. Many of these isotopes are *radioactive; i.e.*, they decompose spontaneously into simpler atoms and simultaneously emit energy.

When a chemical compound is formed, we consider that a simple number of atoms of one element combine with a simple number of atoms of one or more other elements to form molecules of the compounds. A *molecule* of a compound is the smallest particle of that compound which can exist and retain the properties of the compound. Thus we consider that a molecule of water (represented as H_2O) is formed by the union of two atoms of hydrogen and one of oxygen. Elements may also exist in the form of molecules, which usually consist of two or more atoms. Thus a molecule of hydrogen is represented by H_2.

CHANGES IN MATTER

Physical Changes. Temporary changes in matter, such as a change in temperature or a change in physical state (as produced by melting or boiling), are known as *physical* changes.

Chemical Changes. Permanent changes that occur in matter are known as *chemical* changes. Typical examples of chemical changes are as follows: (1) the *combination* of elements to form compounds, as when iron combines with the oxygen of the air to form rust, or iron oxide, which is a compound of iron and oxygen; (2) the *decomposition* of compounds into elements or into simpler compounds. Thus, when a compound known as *mercuric oxide* is heated, it is readily decomposed into mercury (or quicksilver) and oxygen. A less simple decomposition occurs in every electroplating operation. Thus, when a direct current is passed through a solution containing copper sulfate, the latter is decomposed into copper (which deposits upon the cathode) and a residue (or radical) containing sulfur and oxygen (which residue recombines with the anode, if the latter is copper, and forms copper sulfate); (3) *double decomposition*, in which two compounds react with each other to form two different compounds. Thus, when sodium chloride is added to a solution of silver nitrate (such as is formed by dissolving silver in nitric acid), a white insoluble precipitate of silver chloride is formed, and there is also produced in the solution a soluble compound, sodium nitrate. Similarly, whenever an acid such as sulfuric acid is neutralized with a base or alkali, such as sodium hydroxide (caustic soda), a new compound (in this case sodium sulfate) and water are formed by double decomposition.

Conservation of Matter. Whenever the above chemical changes take place, the total weight or mass of all the products of the change or *reaction* is exactly equal to the weight of all the substances entering into the reaction. The law of conservation of matter, as formerly accepted, states that matter can be neither created nor destroyed. Modern science has shown that under certain conditions it is possible for matter to be converted into energy and vice versa. More strictly, it may be stated that the total amount of matter plus energy in the universe is constant.

ENERGY

Forms of Energy. All chemical changes are accompanied by some change in the form of *energy*. The various forms of energy, such as heat, light, electricity, magnetism, chemical energy, and mechanical energy, can under appropriate conditions be converted into each other, and just as with matter, the total amount of energy remains unchanged. Thus, for example, coal contains a certain amount of chemical energy (derived originally from the energy of the sun). When coal burns (*i.e.*, combines with the oxygen of the air), this chemical energy is converted into heat, which through the expansion of steam in a steam engine may be changed into mechanical energy. The engine may, in turn, be connected to a generator and thereby produce electrical energy, which can be reconverted to mechanical energy in an electric motor. Or the electrical energy can be applied to a storage cell, in which it is converted into chemical energy; *i.e.*, it produces new substances in the storage cell which, by reacting with each other, can again produce electricity. When a current of electricity is passed through a plating solution, most of the energy is converted into heat, although part may be used in decomposing the chemical compounds present. (In the ideal case, with anode and cathode of identical composition and physical properties, with no polarization, and with perfect anode and cathode efficiency, all the electrical energy is converted into heat.) A consideration of these relations between energy and chemical changes is essential to any understanding of electroplating operations.

CHEMICAL NOTATION

For convenience in writing and in calculations, there are assigned to each element an abbreviation or symbol and a number, known as its *atomic weight.* This number represents the proportion in which or in some simple multiple of which that element always enters into chemical combination (see Table 7, Appendix). These numbers are only relative and are at present based upon the atomic weight of oxygen as 16, though originally based upon hydrogen, the lightest of the elements, as 1. (Considering oxygen as 16, the atomic weight of hydrogen is 1.008, but for most practical purposes we may consider it as 1.) By the appropriate arrangement of the symbols of the elements it is possible to indicate very concisely the formula or composition of any chemical compound, and by the combination of such formulas into *equations*, the changes that take place in any reaction can be represented. It should be borne in mind that the use of symbols, formulas, and equations is simply a sort of chemical shorthand and, just as in shorthand, the symbols have no significance except in so far as they represent facts. There is no magic in chemical formulas or equations, and there is absolutely no justification for using them unless the underlying facts are understood and then only as a brief, explicit method of stating such facts.

If, as an illustration, we say that the chemical formula of water is H_2O, this formula states very explicitly certain facts, *viz.*, that water always consists of hydrogen and oxygen in the proportion of two atoms of hydrogen to one atom of oxygen or of 2 parts by weight of hydrogen to 16 parts by weight of oxygen in each 18 parts (*i.e.*, the *molecular weight*) of water. Every 18 g or 18 lb of water contains, therefore, 2 g or 2 lb, respectively, of hydrogen and 16 g or 16 lb of oxygen, or in other words, 1/9, or 11.1 per cent, of hydrogen, and 8/9, or 88.9 per cent, of oxygen.

CHEMICAL CALCULATIONS

The use of formulas to represent chemical compounds and of equations to represent chemical changes is the basis of all chemical calculations. As the name implies, an equation is correct only if the quantity (*i.e.*, number of atoms) of each element is the same on each side of the equation. But even such an equality is not evidence of the chemical correctness of the equation. Before an equation can be written, it is necessary to know what reaction, if any, occurs between the substances used and what substances are produced as a result of such a reaction. Thus, if it has been found experimentally that, when sodium cyanide, $NaCN$, is added to a solution of silver nitrate, $AgNO_3$, there are formed a white precipitate of silver cyanide, $AgCN$, and a solution of a salt, sodium nitrate, $NaNO_3$, these facts can be represented by an equation such as the following:

$$\begin{array}{ccccccc} \text{Sodium cyanide} & + & \text{silver nitrate} & = & \text{silver cyanide} & + & \text{sodium nitrate} \\ NaCN & + & AgNO_3 & = & AgCN & + & NaNO_3 \end{array}$$

If in this equation we introduce the atomic weights of the respective elements, we obtain the molecular weights of the various compounds:

$$\begin{array}{ccccccc} NaCN & + & AgNO_3 & = & AgCN & + & NaNO_3 \\ 23+12+14 & + & 108+14+(3\times 16) & = & 108+12+14 & + & 23+14+(3\times 16) \\ & & 48 & & & & 48 \\ 49 & & 170 & & 134 & & 85 \end{array}$$

In other words, 49 parts by weight (*e.g.*, grams or pounds) of sodium cyanide are required to react with 170 parts of silver nitrate, and there are formed 134 parts of silver cyanide and 85 parts of sodium nitrate. These substances react with each other always in *these proportions by weight.* With such information, it is possible to determine by simple calculations just how much of each substance will be required to react with a given amount of another substance or to produce a desired amount of some other substance.

Example. Thus, in the above illustration, suppose it is desired to know how much sodium cyanide is necessary to precipitate the silver from 100 oz of silver nitrate, to form silver cyanide, such as might be desired to prepare a cyanide silver-plating solution. Since, according to the above equation, 49 oz of sodium cyanide is needed for 170 oz of silver nitrate, it requires $\frac{49}{170}$ oz of sodium cyanide for each ounce of silver nitrate, and therefore for 100 oz of silver nitrate $\frac{49}{170} \times 100 = \frac{4{,}900}{170} = 28.7$ oz of sodium cyanide is required. Or again, suppose we wish to know how much silver cyanide can be prepared from 100 oz of silver nitrate. Since 170 oz of silver nitrate yields 134 oz of silver cyanide, 100 oz of silver nitrate will produce $\frac{134}{170} + 100 = \frac{13{,}400}{170} = 79$ oz of silver cyanide.

In short, all that is necessary to solve such problems is to determine from the equation in what proportion by weight the substances in question enter into the reaction and then to determine the unknown or desired quantity by the use of this same proportion.

As a precaution against confusion in such calculations, always check the result by *common-sense* methods. Thus, in the first of the above problems, simple inspection of the equation shows that 170 parts of silver nitrate require 49 parts of sodium cyanide, or slightly less than one-third of the weight of silver nitrate; hence it is evident that the result, 28.7 oz of sodium cyanide for 100 oz of silver nitrate, is at least approximately correct. If, on the other hand, the proportion had been accidentally reversed and written 170/49, the result obtained for 100 oz of silver nitrate would have been 347 oz of sodium cyanide, which is obviously incorrect. Similarly, in the second problem it is evident that the weight of silver cyanide must be somewhat less than that of the silver nitrate from which it is produced.

Example. As a further illustration of the use of such an equation let us solve the following problem. It is desired to prepare 100 gal of silver-plating solution to contain 3 oz/gal of silver cyanide. (1) How much metallic silver must be dissolved in nitric acid to form a solution from which the required amount of silver cyanide can be precipitated, and (2) how much sodium cyanide must be used in the precipitation? (1) 100 gal of solution will require 300 oz of silver cyanide. From the equation we note that 170 parts of silver nitrate (containing 108 parts of silver) are required to form 134 parts of silver cyanide; in other words, 108 parts of silver form 134 parts of silver cyanide. Therefore each ounce of silver cyanide will require $\frac{108}{134}$ oz of silver,[1] and 300 oz of silver cyanide will require $\frac{108}{134} \times 300 = \frac{32,400}{134} = 242$ oz of metallic silver. (2) Since to precipitate 134 parts of silver cyanide requires 49 parts of sodium cyanide, each ounce of silver cyanide will require $\frac{49}{134}$ oz of sodium cyanide, or 300 oz of silver cyanide will require for its precipitation $\frac{49}{134} \times 300 = \frac{14,700}{134} = 111$ oz of sodium cyanide.[2]

Confidence in such calculations can be gained only by practice. Platers are therefore urged to make such calculations frequently, in each case making sure from appropriate texts that the problems are based on correct equations.

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[1] For simplicity all these calculations are made in avoirdupois ounces. Actually the silver would be purchased in troy ounces (see Table 5).

[2] It will require an equal amount of sodium cyanide to redissolve the silver cyanide.

CLASSES OF CHEMICAL COMPOUNDS

In the study of chemistry it is convenient to make a distinction between organic and inorganic compounds. The original basis for such a distinction was the occurrence of the organic compounds in living organisms, *i.e.*, in animal and vegetable life. That distinction ceased to exist, however, when it was found possible to produce by artificial means many of such *organic* compounds. The present distinction is therefore an artificial one, and we may define *organic chemistry* as the chemistry of the compounds of carbon and *inorganic chemistry* as that of all other compounds. (For arbitrary reasons carbon itself, the oxides of carbon, and carbonic acid and carbonates are usually included in inorganic chemistry.) There are a great many classes of organic compounds, such as hydrocarbons, alcohols, organic acids, and carbohydrates. Many such compounds are used directly or indirectly in electroplating and electroforming, such as alcohol, benzene, plastics, and addition agents. Since, however, they only rarely enter into the actual composition of plating solutions and then usually in very small amounts, it will not be necessary to discuss them further, except as they may be involved in specific applications.

By far the greater number of compounds entering into plating solutions are inorganic. The simplest inorganic compounds are the *binary* compounds, *i.e.*, those which consist only of two elements. In general, binary compounds are designated by names ending in *ide*, as oxide, sulfide, chloride, etc., preceded by the name of the other element, usually the more metallic of the two. Thus, iron sulfide is a compound of iron and sulfur; sodium chloride, one of sodium and chlorine; etc. Although the names of such compounds usually indicate what elements are present in them, it is not possible to write formulas for such compounds without a knowledge of the relative proportions in which these particular elements combine—in other words, their *valence*.

Valence. By the *valence* of an element is meant the number of atoms of hydrogen with which one atom of the element will combine or which it will replace. Thus in water, H_2O, one atom of oxygen combines with two atoms of hydrogen; therefore the valence of oxygen is two. Similarly, in hydrochloric acid, HCl, one atom of chlorine combines with one of hydrogen, and therefore in this compound the valence of chlorine is one. In ammonia, NH_3, one atom of nitrogen combines with three of hydrogen; hence in this compound the valence of nitrogen is three. Some of the elements, especially the metals, do not readily combine with hydrogen, but under proper conditions they may replace hydrogen. Thus it is possible to replace one atom of hydrogen in hydrochloric acid, HCl, by one atom of sodium, Na, to form sodium chloride, $NaCl$; hence the valence of sodium is one. In sulfuric acid, H_2SO_4, it therefore requires two sodium atoms to replace the two hydrogen atoms, forming sodium sulfate, Na_2SO_4. If, however, instead of sodium, the metal calcium (or a suitable compound of calcium) is employed, it will be found that calcium sulfate, $CaSO_4$, is formed, in which one atom of calcium has replaced two atoms of hydrogen; in other words, the valence of calcium is two. Many of the elements exhibit several valences, according to the type of compound in which they are present. In each type of compound, however, the valence of the element remains the same. Thus iron has two principal valences, which are, respectively, two and three. All the compounds in which iron has a valence of two are designated as *ferrous* compounds, and those in which it has a valence of three are *ferric* compounds. Thus ferrous chloride is $FeCl_2$; *i.e.*, one atom of iron combines with two atoms of chlorine (each of which, as illustrated above, has a valence of one in hydrochloric acid and chlorides). Ferric chloride has the formula $FeCl_3$; *i.e.*, one atom of iron combines with three of chlorine. Copper has a valence of one in cuprous compounds such as cuprous chloride, $CuCl$, and of two in cupric compounds such as cupric chloride, $CuCl_2$.

It is sometimes convenient to designate as positive (+) the valence of those elements which either are metallic or in a particular case are able to replace hydrogen or to combine with oxygen and as negative (−) the valence of those elements which are able to combine with hydrogen or to replace oxygen. The valence of hydrogen is always considered as +I and that of oxygen as −II. (To avoid confusion, Roman numerals are used to indicate valence.) In every chemical compound the sum of the positive valences must always equal the sum of the negative valences; *i.e.*, the *algebraic sum* is always zero. Thus ferric chloride may be written $Fe^{+III}Cl_3^{-I}$, from which it can be seen that there are three positive valences and three negative valences. For convenience, we consider that a free element, such as carbon or sulfur or iron, existing as such, has a valence of zero. Therefore the valences assigned to the various elements apply only when those elements are present in compounds.

In Table 8 in the Appendix will be found a list of the valences of the common elements in their principal types of compounds. By the proper use of such tables the probable formulas of any binary compounds can be determined by using the simplest number of atoms of each element that will make the total valence of each element equal and of opposite sign.

Problem. What is the formula of calcium sulfide? Since from the table the valence of calcium is +II and that of sulfur *in sulfides* is −II, one atom of calcium is equivalent to one of sulfur, and the formula of calcium sulfide is CaS or $Ca^{+II}S^{-II}$.

Problem. What is the formula of sodium sulfide? Since the valence of sodium is +I and that of sulfur in sulfides is −II, it will require two atoms of sodium to combine with one of sulfur, and therefore the formula of sodium sulfide is Na_2S (*i.e.*, $Na_2^{+I}\ S^{-II}$).

Problem. What are the formulas of ferrous oxide and ferric oxide, respectively? As the valence of iron in ferrous compounds is +II and that of oxygen is −II, the formula of ferrous oxide is FeO. As the valence of iron in ferric compounds is +III and that of oxygen is −II, the simplest way to combine the two elements is to use two atoms of iron (having a total valence of +VI) and three atoms of oxygen (having a total valence of −VI). The formula is therefore Fe_2O_3.

Oxidation and Reduction. Whenever by means of a chemical reaction the valence of an element is increased (algebraically), the reaction is called an *oxidation*[1] (even though oxygen as such may not necessarily enter into the equation), and when the valence is decreased, *reduction* takes place. Thus if ferrous oxide, FeO, is changed to ferric oxide, Fe_2O_3, or if ferrous chloride, $FeCl_2$, is changed to ferric chloride, $FeCl_3$, in each case the iron has been *oxidized* from the ferrous to the ferric condition, *i.e.*, from a valence of +II to +III. In all chemical reactions involving oxidation of one element, there must be a corresponding reduction of some other element, and the total increase of valence of the one element must be equal to the decrease of valence of the other element. That compound in which the valence of the element is increased is (in the particular reaction involved) a *reducing agent*, and that in which the valence is decreased is an *oxidizing agent*. As a simple example of oxidation and reduction (which must always occur simultaneously) we may take the action of stannous (tin) chloride, $SnCl_2$, upon ferric chloride, $FeCl_3$, to produce stannic chloride, $SnCl_4$, and ferrous chloride, $FeCl_2$. This reaction is often em-

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[1] In a restricted sense the term *oxidation* is used to indicate the combination of a substance with oxygen.

ployed in the determination of the amount of iron in a solution. The above reaction may be written as follows:

$$Sn^{+II}Cl_2 + 2Fe^{+III}Cl_3 = Sn^{+IV}Cl_4 + 2Fe^{+II}Cl_2$$

From the numbers above the symbols Sn and Fe, indicating their respective valences, it will be noted that each atom of tin has increased in valence from +II to +IV, *i.e.*, it has been oxidized, while each atom of iron has decreased in valence from +III to +II, or has been reduced. (For simplicity only the valences of those elements which are actually oxidized or reduced are introduced into the above equation.) In this reaction, therefore, the stannous chloride serves as a reducing agent and the ferric chloride as an oxidizing agent. Most equations representing the reactions that occur during oxidation and reduction are much more complicated than the above example, but all are based on the same principles.

ELECTROLYTIC DISSOCIATION

Although a large variety of substances are soluble in water, it has been found that only certain aqueous solutions, *viz.*, those which contain acids, bases, or salts, will conduct electricity. From a study of other properties of these solutions, especially their boiling points and freezing points, we are led to the conclusion that, when acids, bases, or salts are dissolved in water, they are broken up or dissociated, to a certain extent at least, into particles called *ions*, which consist of atoms or groups of atoms. These ions are electrically charged, regardless of whether a current is passed through the solution or not. In general, when an atom is changed to a negatively charged ion, it has acquired one or more additional electrons. When an atom is changed to a positively charged ion, it has lost one or more electrons.

When a current is passed through the solution, the charged particles are carried by the current and discharged at the electrodes. The negatively charged particles, or *anions*, are carried to the positively charged pole or anode, and the positively charged particles, or *cations*, are carried to the negatively charged pole or cathode. By the discharge of the ions at the electrodes their charges are hence neutralized electrically.

If a substance such as hydrochloric acid (or, more strictly, hydrogen chloride), HCl, is dissolved in water, its dissociation may be represented as follows:

$$HCl \leftrightarrows H^+ + Cl^-$$

(In this form of expression the number of plus or minus signs is equal to the valence of the ion.)[1] In other words, each of the molecules of hydrochloric acid that dissociates forms a positively charged hydrogen ion and a negatively charged chloride ion. The double arrow indicates that this reaction (like all electrolytic dissociation) is reversible. If hydrochloric acid is dissolved in water, a part is dissociated or the reaction goes from left to right, but if, on the other hand, hydrogen ions and chloride ions are brought together in a solution, a certain proportion of them will combine to form hydrochloric acid, *i.e.*, the reaction proceeds from right to left.

With a more complex substance, such as sulfuric acid, H_2SO_4, the dissociation occurs as follows:

$$H_2SO_4 \leftrightarrows 2H^+ + SO_4^{--}$$

Actually the dissociation occurs in two stages, represented as follows:

$$H_2SO_4 \leftrightarrows H^+ + HSO_4^-$$
$$HSO_4^- \leftrightarrows H^+ + SO_4^{--}$$

The products of the second dissociation are known as hydrogen ions and sulfate ions. More details of the theory of electrolytic dissociation can be found in the regular texts on general and physical chemistry. With a knowledge of these simple principles of electrolytic dissociation, the relation of acids, bases, and salts may be more clearly understood.

ACIDS, BASES, AND SALTS

Acids. Acids are those substances which contain hydrogen, which hydrogen is replaceable by metals to form salts. Acids are also capable of neutralizing bases to form salts. When dissolved in water, acids are dissociated, to some extent at least, with the formation of hydrogen ions. Sulfuric acid, H_2SO_4, is a compound in which the two hydrogen atoms can be replaced by metals to form salts. When sulfuric acid acts upon zinc, a gas (hydrogen) is evolved and a salt (zinc sulfate) is formed in the solution. This may be shown by the equation

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

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[1] In many textbooks, the superscripts ′ and ˙ are used to designate positive and negative ions, respectively. The use of the + and − superscripts, as in the above equation, is less confusing and less subject to typographical errors.

from which it can be seen that the zinc has taken the place of the hydrogen.

When sulfuric acid is added to a base such as sodium hydroxide, NaOH, a reaction known as *neutralization* occurs, as a result of which there are formed water and a salt, in this case sodium sulfate, Na_2SO_4, according to the following equation:

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$

The extent to which an acid is dissociated when dissolved in water, or, in other words, the proportion of hydrogen ions formed, is an indication of the strength, or *acidity* of an acid. Thus, if in equivalent concentrations it is found that hydrochloric acid is dissociated to the extent of 95 per cent and sulfuric acid only 90 per cent, the hydrochloric acid is a stronger acid than the sulfuric acid, considered *as an acid, i.e.*, with respect to its power to neutralize bases. (The corrosive actions of concentrated sulfuric acid or nitric acid upon organic matter, such as wood, etc., or of hydrofluoric acid upon glass, are specific properties, not necessarily connected with the acidity of the acids, and are not an indication of the *strength* of the acids.) Hydrochloric, sulfuric, and nitric acids are the three principal *strong* acids, while acetic and citric acids are fairly weak acids, and boric and carbonic acids are very weak.[1] The degree of the sour taste of acids is roughly proportional to their strength as measured by their hydrogen-ion concentration.

In general, acids are formed from the nonmetallic elements, such as chlorine, sulfur, nitrogen, and phosphorus. Binary acids, such as hydrochloric acid, HCl, and hydrosulfuric acid or hydrogen sulfide, H_2S, may be considered as compounds of the element directly with hydrogen. The acids containing oxygen, such as sulfuric acid, H_2SO_4; nitric acid, HNO_3; phosphoric acid, H_3PO_4; and carbonic acid, H_2CO_3, may be conveniently considered as produced by the combination of water with the appropriate nonmetallic oxides, which oxides are then known as the *anhydrides* of the acids. Thus we may consider that

Sulfur trioxide, $SO_3 + H_2O = H_2SO_4$, sulfuric acid
Nitrogen pentoxide, $N_2O_5 + H_2O = 2HNO_3$, nitric acid
Phosphorus pentoxide, $P_2O_5 + 3H_2O = 2H_3PO_4$, phosphoric acid

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[1] The strong acids are often called *mineral* acids. This usage, in so far as it implies a distinction from *organic* acids, is inappropriate, as many inorganic acids are weaker than certain organic acids.

Carbon dioxide, $CO_2 + H_2O = H_2CO_3$, carbonic acid
Chromic anhydride,[1] $CrO_3 + H_2O = H_2CrO_4$, Chromic acid

Acids such as hydrochloric acid, HCl, and nitric acid, HNO_3, which contain only one replaceable atom of hydrogen in each molecule, are *monobasic;* those, such as sulfuric acid, H_2SO_4, with two replaceable hydrogen atoms, are *dibasic;* and with three replaceable hydrogen atoms, as phosphoric acid, H_3PO_4, are *tribasic.*

Bases. Bases are hydroxides of metallic elements, *i.e.*, compounds of a metal with hydrogen and oxygen, such as sodium hydroxide or caustic soda, NaOH; calcium hydroxide or hydrated lime, $Ca(OH)_2$; etc. In general, they have the power to combine with acids to form salts and water. They may be considered as made up of the oxide of a metal and water, thus:

Sodium oxide, $Na_2O + H_2O = 2NaOH$, sodium hydroxide
Calcium oxide (lime), $CaO + H_2O = Ca(OH)_2$, calcium hydroxide

When dissolved in water they usually have an *alkaline* taste and a soapy feeling. Those bases such as sodium hydroxide, NaOH, and potassium hydroxide, KOH, which are readily soluble in water are called *alkalies.* Ammonium hydroxide, NH_4OH, ordinary aqua ammonia, which is produced by dissolving ammonia gas, NH_3, in water, is also usually classed with the alkalies, since it has basic properties similar to them.

When a base is dissolved in water, it is dissociated, to some degree at least, with the formation of hydroxyl ions, OH^-, and the extent to which such dissociation occurs is a measure of the strength of the base. Thus sodium and potassium hydroxides are strong bases because in solution they are largely dissociated, while ammonium hydroxide is less dissociated and is hence a weaker base. (Owing to the very slight solubility of most of the metallic hydroxides, it is difficult to determine directly their relative strength as bases.) The dissociation of a strong base may be represented as follows:

$$NaOH \leftrightarrows Na^+ + OH^-$$

Salts. Salts may be considered as derived from acids, either through the replacement of the hydrogen of the acid by a metal or through the neutralization of the acid by a base. If the for-

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[1] The substance commonly sold as *chromic acid* is really chromic anhydride (CrO_3).

mer reaction takes place directly, hydrogen is given off, thus:

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

In the latter case, *i.e.*, whenever neutralization of an acid by a base occurs, water is always formed in addition to a salt, thus:

$$Zn(OH)_2\text{(zinc hydroxide)} + H_2SO_4 = ZnSO_4\text{(zinc sulfate)} + 2H_2O$$
$$2NaOH\text{(sodium hydroxide)} + H_2SO_4 = Na_2SO_4\text{(sodium sulfate)} + 2H_2O$$

The *names* of salts contain, in addition to the name of the metal, a term derived from the name of the corresponding acid according to the following simple rules:

Salts containing only two elements, *i.e.*, derived from acids containing only two elements, always end in *ide;* thus all salts of hydrochloric acid, HCl, are *chlorides.*

Salts of acids that contain oxygen and whose names end in *ic* always end in *ate;* thus salts of chloric acid, $HClO_3$, are chlorates; of nitric acid, HNO_3, are nitrates; of carbonic acid, H_2CO_3, are carbonates; etc.

Salts of acids that contain oxygen and whose names end in *ous* always end in *ite;* thus salts of chlorous acid, $HClO_2$, are chlorites; of nitrous acid, HNO_2, are nitrites; etc.

These principles can be illustrated by the following list of acids of sulfur and their corresponding sodium salts:

Acid		Salt	
Hydrosulfuric[1]	H_2S	Sodium sulfide	Na_2S
Hyposulfurous	H_2SO_2	Sodium hyposulfite[2]	Na_2SO_2
Sulfurous	H_2SO_3	Sodium sulfite	Na_2SO_3
Sulfuric	H_2SO_4	Sodium sulfate	Na_2SO_4
Persulfuric	$H_2S_2O_8$	Sodium persulfate	$Na_2S_2O_8$

The *formula* of a salt derived from a given acid and metal can be determined from the principles of valence discussed on page 15. If the formula of the acid and the valence of the metal are known, all that is necessary is to replace the hydrogen in the acid by the appropriate number of atoms of the metal.

Problem. What are the name and formula of the potassium salt of hydrochloric acid? Since hydrochloric acid contains only two elements, its salts are chlor*ides.* The formula of hydrochloric acid is HCl, and the valence of

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[1] More commonly named *hydrogen sulfide.*

[2] The salt usually called *hyposulfite* of soda, or *hypo,* is erroneously designated. Its formula is $Na_2S_2O_3$ and its correct name is sodium thiosulfate.

potassium, K, is +I; therefore one atom of potassium will replace one of hydrogen to form KCl, or potassium chloride.

Problem. What are the name and formula of the calcium salt of nitric acid? The formula of nitric acid is HNO_3, *i.e.*, it contains oxygen and the name ends in *ic;* therefore its salts are nitrates. The valence of calcium is +II. In order to secure the two atoms of hydrogen to be replaced with one atom of calcium, it is necessary to use two molecules of nitric acid. The formula of the salt is therefore $Ca(NO_3)_2$, or calcium nitrate.

When salts are dissolved in water they are dissociated to a large extent with the formation of *cations* (positively charged ions), containing the metal of the salts, and *anions* (negatively charged *ions*), containing the acid group present in the salt, in accordance with such equations as the following:

$$NaCl \leftrightarrows Na^+ + Cl^-$$
$$Na_2SO_4 \leftrightarrows 2Na^+ + SO_4^{--}$$
$$CuSO_4 \leftrightarrows Cu^{++} + SO_4^{--}$$

Normal Solutions. From a consideration of the following equations it may be noted that one molecule of hydrochloric acid will combine with one molecule of sodium hydroxide (in which the valence of sodium is one) and that it requires two molecules of hydrochloric acid for one molecule of cupric hydroxide (in which the valence of copper is two). On the other hand, one molecule of sulfuric acid combines with two of sodium hydroxide and with one of cupric hydroxide.

$$\begin{array}{llll} HCl & + NaOH & = NaCl & + H_2O \\ 36.5 & \quad 40 & & \\ 2HCl & + Cu(OH)_2 & = CuCl_2 & + 2H_2O \\ \ 73 & \quad 98 & & \\ H_2SO_4 & + 2NaOH & = Na_2SO_4 & + 2H_2O \\ \ 98 & \quad 80 & & \\ H_2SO_4 & + Cu(OH)_2 & = CuSO_4 & + 2H_2O \\ \ 98 & \quad 98 & & \end{array}$$

It is evident that a liter of sulfuric acid containing a weight in grams of sulfuric acid equal to the molecular weight of the sulfuric acid, *i.e.*, 98 g, would neutralize twice as much sodium hydroxide as would a liter of hydrochloric acid containing the molecular weight in grams of hydrochloric acid, *i.e.*, 36.5 g. In order, therefore, to obtain a solution of sulfuric acid that would be equivalent to that of hydrochloric acid containing 36.5 g/l, we should require, not 98, but one-half that amount, or 49 g of sulfuric acid per liter. Such a solution of sulfuric acid is a *normal solution.* A normal solution of any substance is a solution containing in each liter a weight in grams equal to the equivalent weight of that substance. The equivalent weight of an acid is the weight of the acid equivalent to one atom of replaceable hydrogen, or, in other words, the molecular weight of the acid divided by the number of replaceable hydrogen atoms. Therefore a normal solution of hydrochloric acid (HCl) contains 36.5 g/l; of sulfuric acid, H_2SO_4, 98/2 = 49 g/l; of phosphoric acid, H_3PO_4, 98/3 = 32.7 g/l. Similarly, the equivalent weight of a base is equal to its molecular weight divided by the number of replaceable hydroxyl groups. Therefore a normal solution of sodium hydroxide, NaOH, contains 40 g/l and of calcium hydroxide, $Ca(OH)_2$, 74/2 = 37 g/l. The equivalent weight of a salt is the molecular weight divided by the valence of either the total metal or acid groups in it. Thus a normal solution of sodium chloride, NaCl, will contain 58.5 g/l; of sodium sulfate, Na_2SO_4, 142/2 = 71 g/l; and of anhydrous copper sulfate, $CuSO_4$, 160/2 = 80 g/l. With respect to oxidation or reduction, the equivalent weight of a compound is equal to the molecular weight divided by the number of valences that it gains or loses in the reaction.

From these definitions it follows that equal volumes of all normal solutions are chemically equivalent to each other. Thus 100 ml of normal sodium hydroxide solution will exactly neutralize 100 ml of normal sulfuric acid or of any other normal acid. Solutions, instead of being always made normal (N), may have any definite fractional normality, thus half normal ($0.5N$ or $N/2$), tenth normal ($0.1N$ or $N/10$), etc., which indicates that they contain in each liter the corresponding fractional part of the equivalent weight.

Molar solutions are those which contain in one liter, one *gram molecule*, or one *mol* of the substance, *i.e.*, a weight in grams equal to the molecular weight of the substance. Thus a molar solution of sulfuric acid contains 98 g/l of H_2SO_4, or twice as much as a normal solution. Molar solutions are most commonly referred to when dealing with substances that are not dissociated, such as dextrose, $C_6H_{12}O_6$, of which a molar solution (M) contains 180 g/l. The term *molar* is also frequently applied to chromic acid (page 179) because for it the term *normal* may have two meanings.

Acid Salts. When an acid molecule is dibasic, *i.e.*, contains two replaceable hydrogen atoms, it is also possible to replace only one of the hydrogen atoms with a metal, forming an *acid* salt, *i.e.*, one that possesses some of the properties of an acid and some of a salt. Thus, if to a given amount of sulfuric acid there is added just half the amount of sodium hydroxide that would be required to neutralize the acid completely, the following reaction takes place:

$$H_2SO_4 + NaOH = NaHSO_4 + H_2O$$

The compound $NaHSO_4$ is an acid salt, known as sodium acid sulfate, sodium hydrogen sulfate, or sodium bisulfate (or commercially as niter cake, because it is formed as a by-product in the manufacture of nitric acid by the action of sulfuric acid upon sodium nitrate). That it still possesses acid properties is shown by its extensive use as a substitute for sulfuric acid in pickling. That it is not so strong as the original sulfuric acid is evident from the fact that when using it for pickling, it is necessary to use higher temperatures and longer periods than with sulfuric acid.

Basic Salts. Similarly compounds are sometimes formed in which only part of the hydroxyl, OH, groups in the base are replaced by the acid groups or radicals. Such compounds are designated as *basic* salts. Thus aluminum hydroxide is $Al(OH)_3$, and if all the hydroxyl, OH, groups are replaced with Cl (by reaction with hydrochloric acid), aluminum chloride, $AlCl_3$, is produced. If, however, only one of the hydroxyl groups is replaced, we obtain $Al(OH)_2Cl$, which is basic aluminum chloride. When nickel-plating solutions that contain iron become very nearly neutral, yellow basic compounds of iron usually separate. Such a compound as basic ferric sulfate might have the formula $Fe^{+III}(OH)SO_4$, although these compounds are usually more complicated in composition.

Indicators. In describing the properties of acids and bases, attention might have been called to the fact that they produced characteristic changes in the colors of certain organic dyes, which are therefore known as *indicators*. These substances can, however, best be considered with respect to the processes of neutralization and the formation and behavior of salts. For special purposes a great variety of indicators may be employed, but it will be sufficient at this time to consider three of the most common, *viz.*, litmus, methyl orange, and phenolphthalein, the colors of which are as follows:

	ACID	NEUTRAL	ALKALINE
Litmus	Red	Purple	Blue
Methyl orange	Red	Orange	Yellow
Phenolphthalein	Colorless	Colorless	Pink

Formerly the most common application of indicators was in the neutralization of acids or bases, for the purpose of determining the amount of acid or base in a given sample of solution. (Now they are extensively used for measuring pH, see page 74.) In the former operation, known as a *titration*, a measured amount, *e.g.*, 25 ml, of the solution to be tested is placed in a small flask or beaker and a very small amount of the indicator is added. If the sample contains free acid, an alkaline solution (*e.g.*, sodium hydroxide) of predetermined strength or concentration is run in from a burette or measuring tube until the indicator just changes color to the neutral tint. From the amount and concentration of the alkali added, the amount of acid present in the solution can be calculated. Suppose, that 25 ml of a sulfuric acid pickle required 30 ml of a normal sodium hydroxide solution (1 ml of which is equal to 0.049 g of sulfuric acid). Then the 25 ml sample titrated must contain $0.049 \times 30 = 1.47$ g of sulfuric acid, and therefore 1 l (or 1,000 ml) will contain $1.47 \times 1{,}000/25 = 1.47 \times 40 = 58.8$ g of sulfuric acid. Its strength is therefore 58.8 g/l, or 7.88 oz/gal, of sulfuric acid. The normality of the acid can be more conveniently calculated. If 25 ml of acid required 30 ml of normal alkali, the acid must be $30/25 = 1.2N$.

When relatively strong acids, such as sulfuric, nitric, and hydrochloric, are to be titrated with strong bases, such as sodium or potassium hydroxide, it is practically immaterial as to which of the above indicators is employed, since any of them will give a sufficiently sharp color change, or *end point*. When, however, a weak acid, such as acetic acid, or a weak base, such as ammonia, is to be titrated, it is necessary to choose the indicator that will give reliable results. Failure to do so may yield very erroneous results because of the hydrolysis of salts of weak acids or weak bases.

Hydrolysis. In the previous discussion it was pointed out that, as the result of the electrolytic dissociation of acids, hydrogen ions are formed, and of bases, hydroxyl ions, and also that whenever an acid is neutralized by a base, water is formed. The processes of dissociation and neutralization may therefore be represented as follows:

$$NaOH \leftrightarrows Na^+ + OH^-$$
$$HCl \leftrightarrows H^+ + Cl^-$$
$$NaOH + HCl \leftrightarrows NaCl + H_2O$$

or

$$(Na^+ + OH^-) + (H^+ + Cl^-) \leftrightarrows Na^+ + Cl^- + H_2O$$

Since in the last form the Na^+ and Cl^- ions are present on both sides of the equation, we may consider that the only change which has taken place as a result of neutralization is that hydrogen ions of the acid have combined with hydroxyl ions of the base to form water, a substance that is practically undissociated. With strong bases and acids, *i.e.*, those which are highly dissociated and whose salts are highly dissociated, the principal reaction that occurs during neutralization is therefore

$$H^+ + OH^- \leftrightarrows H_2O$$

As compared with strong acids or bases, water is practically undissociated. Actually, however, it has been found that pure water is dissociated to a very slight extent; *i.e.*, it contains a very small number of both hydrogen and hydroxyl ions. In pure (therefore neutral) water at 25°C (77°F) the concentration of hydrogen and hydroxyl ions is each equal to about 1/10,000,000 normal, usually written $10^{-7}N$. At any given temperature in water and in all aqueous solutions, the *product* of the hydrogen- and hydroxyl-ion concentrations is always the same; thus at 25°C it is $10^{-14}\left(\text{or, } \frac{1}{10{,}000{,}000} \times \frac{1}{10{,}000{,}000}\right)$. This value of 10^{-14} is the *dissociation constant* of water at 25°C. It therefore follows that if to pure water an acid containing hydrogen ions is added, the hydrogen-ion concentration is increased and the hydroxyl-ion concentration correspondingly decreased, but both kinds of ions are always present in some amount. Thus in a $0.01N$ solution of hydrochloric acid we may assume that the hydrogen-ion concentration $[H^+]$ is also $0.01N$, or 10^{-2}, and therefore the hydroxyl-ion concentration $[OH^-]$ must be $10^{-14}/10^{-2} = 10^{-12}N$.

Certain salts, such as sodium carbonate, Na_2CO_3, when dissolved in water have an alkaline reaction, which is evidence that the solution contains an excess of hydroxyl ions. In the above equations for neutralization the reversible sign was used, indicating that a salt may be decomposed, to a very slight extent at least, by the action of water. Such decomposition, which is known as *hydrolysis*, does not occur to any appreciable extent if the base and acid are both strong, since they would, if liberated, readily form hydrogen and hydroxyl ions, which would recombine and form water. However, with a salt, such as sodium carbonate, derived from a weak acid (carbonic acid), there are not so many hydrogen ions produced by hydrolysis from the carbonic acid as there are hydroxyl ions from the sodium hydroxide. Consequently, the solution of the salt contains an excess of hydroxyl ions; in other words, it is alkaline to indicators, slightly so to phenolphthalein, and greatly so to litmus or methyl orange.

Similarly, certain salts, such as ammonium chloride, NH_4Cl, formed from ammonium hydroxide, a weak base, and hydrochloric acid, a strong acid, have an acid reaction. This also is the result of hydrolysis and is an evidence that there are more hydrogen ions produced from the small amount of hydrochloric acid set free than there are hydroxyl ions from the (necessarily) equivalent amount of ammonium hydroxide. Most of the hydroxides of the *heavy metals*, such as copper, zinc, tin, lead, iron, and nickel, are weak bases; consequently their salts are slightly hydrolyzed with the formation of free acid. Hence we find that solutions of such salts as copper sulfate, zinc sulfate, tin chloride (stannous or stannic), lead fluoborate, ferric chloride, and nickel sulfate all have an acid reaction when tested with an indicator such as litmus, the color of which changes at approximately 10^{-7}, the true neutral point. This fact has an important bearing on the behavior of certain of these solutions upon electrolysis.

If, then, solutions of certain salts are alkaline because of hydrolysis and others are acid, it follows that in titrating an acid or alkali under conditions that will form such salts or in titrating the free acid or base present in solutions containing these salts, it is necessary to employ an indicator which will produce a definite color change or end point when the base and acid are equivalent to each other and not at the true neutral point, $[H^+] = 10^{-7}$. For simplicity we may state that titrations of the total acidity of a weak acid or in the presence of a weak acid, such as acetic or carbonic acid, should be made with an indicator such as phenolphthalein, which changes to pink only when the solution is appreciably alkaline, *i.e.*, contains a slight excess of hydroxyl ions. For titrations of a weak base, such as ammonium hydroxide, or of an acid in the presence of ammonium salts or in the presence of salts such as copper sulfate, zinc sulfate, etc., an indicator such as methyl orange should be employed, which changes color when the solution is appreciably acid. Consideration of these principles will explain the failure to get reliable results when the wrong indicator is used. Unfortunately the colors of many plating solutions may mask those of the indicators, but in such cases, with some care, an approximate end point may often be obtained. Thus it is possible to titrate the free sulfuric acid in a copper sulfate solution by using methyl orange, in the presence of which the solution undergoes, at the end point, a color change from purple to green instead of the customary red to yellow (page 172).

CHAPTER III

PRINCIPLES OF ELECTRICITY AND ELECTROCHEMISTRY

ELECTRICAL UNITS AND TERMS

In spite of certain limitations, the time-honored analogy of the flow of water and of d-c electricity may be helpful, especially to beginners in this field. The following brief discussion applies primarily to direct current, which is normally employed in electrodeposition. Because, however, alternating current is applied to operate most motor-generator sets and all rectifiers, and because in recent years there have been numerous proposals to *superimpose* alternating current (ac) on direct current (dc) in certain plating processes, brief references will be made to the principles of alternating current.

In any hydraulic system the rate of flow of water depends upon (1) the pressure, or *head* that is produced either by a difference in elevation of the two parts of the system or by means of a pump and (2) the resistance of the pipes, which, in turn, depends upon their diameter and length and to some extent upon the inner surface of the pipes. These relations may be expressed by a simple equation.

$$\text{Rate of flow is proportional to } \frac{\text{pressure}}{\text{resistance}}$$

$$\text{Gallons per minute} = \frac{\text{feet (head)}}{\text{resistance}^1}$$

The rate of flow, *e.g.*, in gallons per minute, is *directly* proportional to the pressure; *i.e.*, twice the pressure will produce twice the flow. The rate of flow is inversely proportional to the resistance of the system; hence if the resistance is doubled, the rate of flow is reduced to one-half. The resistance of a pipe can be increased by increasing its length or by reducing its cross section. The *quantity* of water (in gallons) that flows will be equal to the product of the rate and the time of flow. Thus a flow of 10 gal/min for 10 min will yield 100 gal of water.

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[1] There is no simple unit for expressing the hydraulic resistance of a pipe.

Direct Current (dc). In a d-c circuit, the *potential* or *electromotive force* (*emf*, or voltage), usually expressed in volts, corresponds to the pressure. The obstruction that a wire or other conductor introduces to the flow of current is known as the *resistance* of that part of the circuit and is measured in *ohms*. The rate of flow of electricity is defined as the *current* and is expressed in amperes. The same relations exist as in hydraulic systems; hence

$$\text{Current is proportional to } \frac{\text{potential}}{\text{resistance}}$$

$$I^* = \frac{E}{R}$$

$$\text{Amperes} = \frac{\text{volts}}{\text{ohms}}$$

This relation, known as *Ohm's law,* is the fundamental expression of current flow; *i.e.* in any circuit or part of a circuit the current is directly proportional to the potential and inversely proportional to the resistance. This law may be expressed in three equivalent equations, which can be used to solve specific problems.

$$I = \frac{E}{R} \tag{1}$$

Problem. If a potential of 6 volts is applied to a plating tank having a total resistance of 0.02 ohm, what current will flow?

$$I = \frac{E}{R} = \frac{6}{0.02} = 300 \text{ amp}$$

$$E = IR \tag{2}$$

Problem. If a current of 600 amp passes through a bus bar having a resistance of 0.003 ohm, what will be the potential drop (or IR drop) through the bar?

$$E = IR = 600 \times 0.003 = 1.8 \text{ volts}$$

$$R = \frac{E}{I} \tag{3}$$

Problem. If a potential drop of 0.1 volt is observed across a contact through which 500 amp is flowing, what is the resistance of the contact?

$$R = \frac{E}{I} = \frac{0.1}{500} = 0.0002 \text{ ohm}$$

It is important to distinguish between the current, *i.e.* the rate of flow of electricity, and the quantity of electricity, just as in

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* The symbol I, commonly used for current, is derived from *intensity* of the current flow.

hydraulic systems. The unit of current is the *ampere,* while the unit of quantity is the *coulomb,* which is the quantity of electricity delivered when one ampere flows for one second.

Both for scientific and for industrial applications, the numerical values of the electrical units must be accurately defined. Because the three primary units are related by Ohm's law, it is necessary to define only two primary units, from which the other one is derived.

Until recently the so-called "international" units were employed, which were defined in terms of material standards. Since Jan. 1, 1948, the "absolute" units of electricity have been adopted internationally.[1]

These two sets of standards differ by less than 1 part in 2,000; hence this change in standards has no effect on measurements made in connection with commercial plating.

The absolute units are defined in terms of the centimeter-gram-second system of electromagnetic units. The primary absolute units are the ampere and the ohm, and the volt is defined by their relation.

For practical measurements it is also desirable to employ concrete standards of reference, which may then be defined as follows:

Ampere. An absolute ampere is equivalent to that unvarying current which, when passed through a solution of silver nitrate under specified conditions, deposits 0.0011182 g of silver per second.

Volt. An absolute volt is equivalent to the potential difference derived from the potential of a Weston normal cell of 20°C, of which the assigned value is 1.0186 volts.

Ohm. An absolute ohm is equivalent to the resistance through which a potential of one volt produces a current of one ampere. (As noted above, the ohm is now legally defined as one of the two primary standards, but for practical purposes, it may be defined in terms of standard resistances, the values of which are determined by comparison with absolute standards.)

Coulomb. A coulomb is that quantity of electricity which flows when a current of one ampere is passed for one second. An instrument that is used to measure the quantity of electricity and, accurate form, used for work of high precision, is the silver coulometer, in which the weight of silver deposited from a silver nitrate solution under specified conditions is a direct measure of the quantity of electricity passed. In practice, an acid copper solution is often used in a coulometer, and the weight of copper deposited is used as a measure of the quantity of electricity. To measure and to control the quantity of electricity in plating processes, *e.g.*, in silver plating, an *ampere-hour meter* is used. This is a form of coulometer.

The *power* involved in the flow of electricity is equal to the product of the emf and the current, *i.e.*, to the number of volts multiplied by the number of amperes. The unit is the *watt*, which is the power involved when a current of one ampere is passed through a circuit by the application of one volt. The commercial unit is the *kilowatt* (kw), equal to 1,000 watts. One horsepower is equal to 746 watts, or 1 kw equals 1.34 hp.

The *energy* consumed in the passage of current is equal to the product of the power and the time, *e.g.*, watts multiplied by seconds. One *joule* is the energy involved in applying one watt for one second. The commercial units are the *watt-hour* (3,600 joules) and the *kilowatt-hour* (1,000 watt-hours). The kilowatt-hour is the usual basis of payment for electrical energy.

Alternating Current (ac). In the passage of alternating current, the electricity flows first in one direction and then, after a short interval of time, in the other direction. The number of reversals per second is known as the *frequency*. In the 60-cycle a-c circuit that is commonly used for lighting, 60 complete cycles occur per second. Much higher frequencies are involved in radio circuits. During each cycle the current increases from zero to a maximum in one direction, then decreases to zero, and again increases to the same maximum in the other direction. The variation of current with time is usually expressed by a *sine wave* (Fig. 1).

A d-c ammeter cannot be used to measure alternating current, because it merely indicates the algebraic average of the current in the two directions, which is zero. An a-c ammeter is deflected according to the actual current regardless of its direction and hence yields the *average* value of the current, which varies from zero to a maximum. If the current follows a sine wave, the average value of an alternating current is equal to 0.707 times its maximum value.

If the only obstacle to the flow of alternating current was the resistance of the circuit, Ohm's law would still apply. However, two other factors, known as *inductance* and *capacity*, enter into the flow of alternating current.

The *inductance* is the result of the fact that, when current flows at a varying rate (as in alternating current), it produces a potential in any adjacent circuit or part of a circuit, which potential hinders the flow of alternating current in the primary circuit and thus acts as an increased resistance.

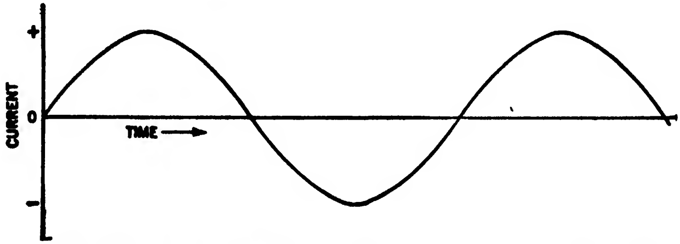


Fig. 1. Sine wave. This represents the usual variation of the current with time in an a-c circuit. Two successive loops, *i.e.*, 360 deg, constitute 1 *cycle*. In the United States, commercial alternating current usually involves 60 cycles/sec.

The *capacity* of a circuit is related to the fact that a condenser, consisting of two separated plates, may be so charged as to store electrical energy according to their capacity. In an a-c circuit some part may act momentarily as a condenser; *i.e.*, it stores up energy. In general, the presence of a condenser effect, *i.e.*, a capacity, in an a-c circuit assists the flow of current or is equivalent to a reduced resistance.

The net effect of the inductance and capacity in an a-c circuit is known as the *reactance*, which represents an increased resistance. The combined effect of the resistance and the reactance is known as the *impedance* of the circuit.

The ratio of the resistance to the impedance is known as the *power factor*. A circuit containing resistance and no reactance has a power factor of 1, which represents the most economical use of alternating current. In practice the power factor is always less than 1 but is kept as high as possible in a given operation.

The presence of inductance or capacity in an a-c circuit causes a delay in the production of current by the applied potential. This is illustrated in Fig. 2, in which it is seen that the maximum current flows, not when the potential is at a maximum, but at a shortly later interval of time. The whole distance on the sine curve corresponding to one complete cycle is considered as 360 deg. The difference in *phase*, *i.e.*, in the corresponding points for maximum potential and maximum current, is defined in terms of the portion of a cycle. For example, in Fig. 2(*a*) the current and potential are in phase, *i.e.*, they coincide, and the phase angle is zero. In Fig. 2(*b*) the difference of phase is one-eighth of a cycle, hence is 45 deg. In Fig. 2(*c*) the emf and current phases differ by 180 deg.

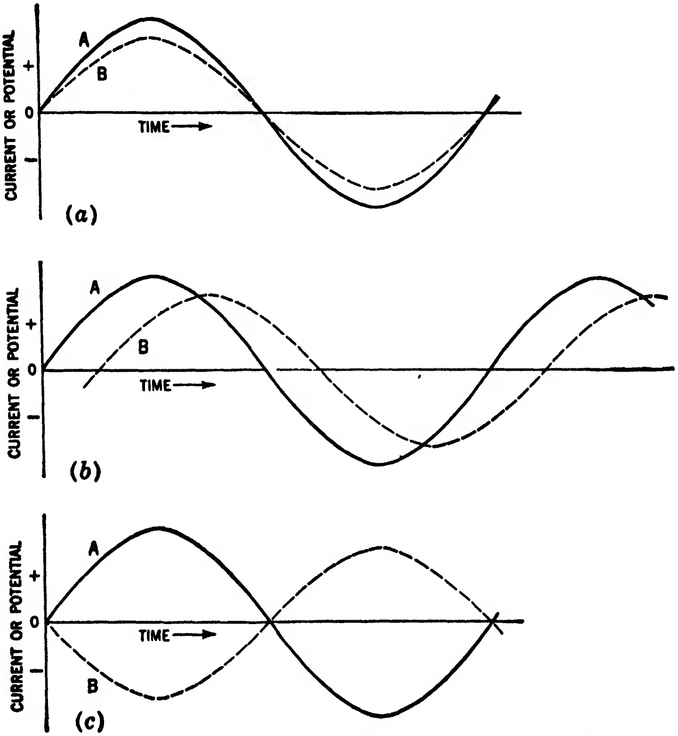


FIG. 2. Relation of current *A* and potential *B* in a-c circuits. (*a*) The current and potential are *in phase*; *i.e.*, the maximum values of each occur at the same time. (*b*) The current and potential are *out of phase* by 45 deg; *i.e.*, the *phase angle* is 45 deg. (*c*) The current and potential are out of phase by 180 deg; *i.e.*, the phase angle is 180 deg. In this case the maximum value of the current occurs when the potential is a minimum, and vice versa.

In recent years various electroplating processes have been proposed in which an alternating current is ***superimposed*** on a direct current, *e.g.*, in order to decrease the anode or cathode polarization. This method, known as the ***Wohlwill process***, has long been employed in the refining of gold. In such an arrangement several types of curves that represent the relation of time to current or potential may result, as shown in Fig. 3.

The potential of the direct current is represented as a straight line, even though there are always some slight fluctuations in the voltage derived from a generator or a rectifier. If, as in Fig. 3(*a*), the maximum potential of the alternating current is less than that of the direct current, the current always flows in the direction of the direct current but its value fluctuates because in part of the cycle the a-c potential is added to the d-c potential and part of the time it is substracted. The net result is essentially the same as if the direct current had been interrupted or reduced at small intervals.

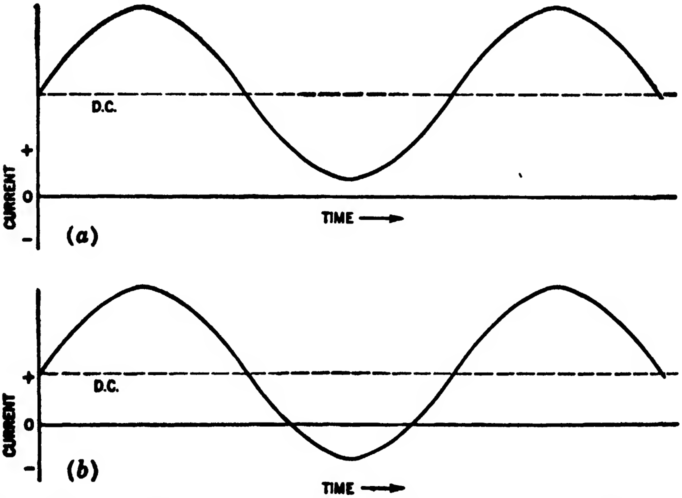
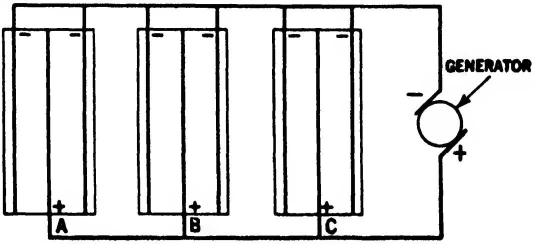


FIG. 3. Effect of superimposing an alternating current on a direct current. (*a*) The maximum value of the alternating current is less than the value of the direct current. Hence, the current always flows in the same direction, but its intensity fluctuates with time. (*b*) The maximum value of the alternating current exceeds the value of the direct current. Hence, during less than one-half the time, the direction of the current is reversed.

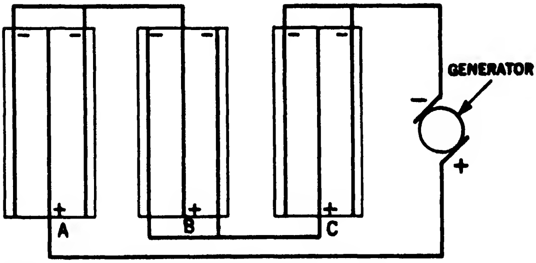
If, as in Fig. 3(*b*), the potential of the alternating current exceeds that of the direct current, an *unbalanced* alternating current results, in which, for example, a larger current may flow in one direction than in the other. In effect, the article to be plated, instead of being continuously cathodic, is alternately anodic and cathodic, but the cathodic current exceeds the anodic; otherwise no deposition would usually occur. It should be noted that any advantage gained by the use of an alternating current in deposition must be sought in some change in the resultant polarization, which may influence the anode or cathode efficiencies. Apart from such changes the use of alternating current cannot result in increased deposition, since the two portions of the a-c cycle neutralize each other electrically.

The shapes and positions of the curve for potential and current when alternating current is involved are most conveniently studied by means of a cathode-ray *oscillograph,* in which many advances have been made in recent years.

ARRANGEMENTS OF TANKS AND ELECTRICAL SOURCES



(*a*) PARALLEL ARRANGEMENT OF TANKS



(*b*) SERIES ARRANGEMENT OF TANKS

FIG. 4. Arrangement of tanks. (*a*) Parallel arrangement of tanks. (*b*) Series arrangement of tanks.

It is possible to connect two or more plating tanks to a source such as a generator so that electrically the tanks are in *parallel* or in *series,* represented in Fig. 4(*a*) and (*b*), respectively.

In the parallel arrangement, most commonly used in plating, the anode and cathode bars of each tank are connected directly to the source or to the bus bars leading from the source. Under these conditions the current that flows in each tank depends simply upon the total resistance of the existing circuit in that tank, and provided the potential on the bus bars remains constant, the current in a given tank is independent of that in other tanks that are in parallel.

Problem. If in Fig. 4(*a*) a potential of 6 volts is maintained on the bus bars and the total resistances of tanks *A*, *B*, and *C* are, respectively, 0.01, 0.02, and 0.03 ohm, what current will pass through each tank?

$$A.\quad \frac{6\text{ volts}}{0.01\text{ ohm}} = 600\text{ amp}$$

$$B.\quad \frac{6\text{ volts}}{0.02\text{ ohm}} = 300\text{ amp}$$

$$C.\quad \frac{6\text{ volts}}{0.03\text{ ohm}} = 200\text{ amp}$$

The total current drawn from the generator will be 600 + 300 + 200 = 1,100 amp. If in each tank the cathode area is 20 ft², the current densities will be

$$A.\quad \frac{600}{20} = 30\text{ amp/ft}^2$$

$$B.\quad \frac{300}{20} = 15\text{ amp/ft}^2$$

$$C.\quad \frac{200}{20} = 10\text{ amp/ft}^2$$

If, as in Fig. 4(*b*), the tanks are arranged in series, the anodes of one tank are connected to the cathodes of the next tank and only the first anode and the last cathode are connected to the generator. In this case no current can pass unless the anodes and cathodes in each tank are so connected. The same current flows through all the tanks, and the value of this current is determined by the sum of the resistances.

Problem. If a potential of 6 volts is applied and the series tank resistances are 0.01, 0.02, and 0.03 ohm, what current will flow?

$$\frac{6\text{ volts}}{0.01 + 0.02 + 0.03\text{ ohm}} = \frac{6}{0.06} = 100\text{ amp}$$

If the cathode area in each tank is 20 ft², the current density in each will be the same; *i.e.*

$$\frac{100}{20} = 5\text{ amp/ft}^2$$

If, however, the cathode areas in each tank are different, the current densities and hence the rates of deposition will be different.

The potential drop in each tank will be proportional to its resistance. In the above case, the total drop of 6 volts is the sum of the *IR* drop of 1, 2, and 3 volts in tanks *A*, *B*, and *C*, in which the resistances are 0.01, 0.02, and 0.03 ohm.

In copper electrotyping, two tanks are often connected in series to a 6-volt generator. This is practicable because the cathode plates have about the same areas, and it is convenient to keep the same total cathode areas in each tank. In electroplating, especially with articles of various shapes, it is not practicable to use tanks in series.

The same principles apply to the arrangement of electrical sources, such as generators, rectifiers, or batteries, either in series or in parallel. In such cases the potentials are added together if they are connected in series, while the current capacities are added if they are in parallel. Arrangements of generator circuits are discussed in Chap. IX.

FARADAY'S LAW

In electrolysis, such as occurs in electrodeposition, current is passed through a solution known as the *electrolyte*[1] between two conducting electrodes known as the *anode* and *cathode*. The changes occur principally at the electrodes. In electrolysis of aqueous plating solutions, metal is dissolved from anodes or oxygen is liberated upon them and metal or hydrogen is deposited upon the cathodes.

The fundamental principle of electrolysis is known as *Faraday's law*, which is commonly expressed in the following statements.

1. The quantity of any element (or radical, *i.e.*, group of elements) liberated at either the anode or cathode during electrolysis is proportional to the quantity of electricity that passes through the solution.
2. The quantities of different elements or radicals liberated by the same quantity of electricity are proportional to their equivalent weights.

In a more general statement of this law, the *change in valence* may be substituted for the *quantity of an element*. This then includes electrolysis in which no elements are discharged at the electrodes but oxidation or reduction of ions occurs there.

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[1] The term *electrolyte* is now used in two senses, *viz.*, (1) as the conducting medium, *e.g.*, a solution of copper sulfate, and (2) as the *solute* or dissolved substance, *e.g.*, the salt copper sulfate. The term *ionogen* has been suggested for the latter usage but is not extensively applied. In this text the term *electrolyte* will be used to define the solution through which current is

If 1 coulomb (1 amp-sec) deposits 1.118 mg of silver, then 10 coulombs will deposit 10 × 1.118 = 11.18 mg of silver. It is immaterial whether a current of 1 amp flows for 10 sec or of 2 amp for 5 sec, or any other current and time that yield 10 coulombs.

The *equivalent weight* of an element is its atomic weight divided by its valence in the compound present. For several common elements the values are given in Table 9 (Appendix).

Since 1 coulomb deposits 0.0011182 g of silver, it requires 107.88/0.0011182 = 96,488 coulombs to deposit the equivalent weight in grams of silver or of any other element. This quantity of electricity (often rounded off to 96,500 coulombs) is known as one *Faraday*. It is equivalent to about 26.8 amp-hr or about 1.1 amp-days. It is sometimes convenient to remember that the equivalent weight in grams of an element is deposited in about 1.1 amp-days.

Current Efficiency. Any aqueous solution of a metal salt contains positively charged ions of the metal and also of hydrogen. If the solution is acid, it contains a larger concentration of hydrogen ions. Thus an acid copper solution made from copper sulfate and sulfuric acid contains cupric ions, Cu^{++}, and hydrogen ions, H^+, and also sulfate, SO_4^{--}, ions and OH^- ions. These result from the dissociation of copper sulfate, sulfuric acid, and water.

$$CuSO_4 \rightleftarrows Cu^{++} + SO_4^{--}$$
$$H_2SO_4 \rightleftarrows 2H^+ + SO_4^{--}$$
$$H_2O \rightleftarrows H^+ + OH^-$$

When a current is passed through such a solution, the positively charged ions, or *cations*, in this case Cu^{++} and H^+, move toward the cathode where they may be discharged, and the negative ions, or *anions*, in this case SO_4^{--} and OH^-, move toward the anode. There the SO_4^{--} may combine with copper from the anode to form copper sulfate or may be discharged and react with water to form oxygen and sulfuric acid.

$$Cu + SO_4^{--} - 2\ominus \rightarrow CuSO_4{}^*$$
$$SO_4^{--} - 2\ominus + H_2O \rightarrow H_2SO_4 + O$$

At either the cathode or anode the total reaction, *i.e.*, the sum of all possible reactions, corresponds to the quantity of electricity passed, in accordance with Faraday's law. If, however, as in copper plating, we are concerned primarily with dissolving copper from the anode and depositing copper at the cathode, any current

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* The sign $\ominus$ represents an electron, or unit negative charge.

used in other reactions may be considered as wasted. From this standpoint the *efficiency* of the current is defined as the proportion of the current that is used in a specified reaction. (With respect to the sum of all possible reactions the anode or cathode efficiency is always 100 per cent.)

For example, if in the electrolysis of a copper sulfate bath 90 per cent of the current were used to deposit copper and the balance to liberate hydrogen, the cathode efficiency of copper deposition would be 90 per cent. Similarly if at the anode 80 per cent of the current served to dissolve copper and 20 per cent to liberate oxygen, the anode efficiency would be 80 per cent.

In order to determine the *cathode efficiency* of a given electrolysis it is necessary to measure accurately the quantity of electricity that is passed. If this is done by merely measuring the current with an ammeter and the time with, for example, a stop watch, errors may arise from the fact that the current is likely to vary during the electrolysis. It is therefore preferable to measure the total quantity of electricity by means of a silver or copper coulometer (page 32) in series with the cell studied. The cathode efficiency of the process studied is then the ratio of the weight of metal actually deposited to the maximum that could be deposited by that quantity of electricity in accordance with Faraday's law.

Problem. Suppose that a certain current was passed for a given time through three baths connected in series, *viz.*, (1) an acid copper bath, used as a coulometer and assumed to have an efficiency of 100 per cent, (2) a nickel bath, and (3) a zinc bath. The respective weights of the three metals deposited were 35.6 g of copper, 29.2 g of nickel, and 34.8 g of zinc. What are the cathode efficiencies of the nickel and zinc deposition?

According to Table 9 (Appendix) 1 amp-hr deposits 1.186 g of copper. Hence in this experiment, the quantity of electricity that passed was 35.6/1.186 = 30 amp-hr. At 100 per cent cathode efficiency 30 amp-hr will deposit 30 × 1.095 = 32.8 g of nickel. If, therefore, in this test only 29.2 g of nickel was deposited, the cathode efficiency was

$$\frac{29.2}{32.8} = 89 \text{ per cent}$$

Similarly, 30 amp-hr at 100 per cent efficiency will deposit

$$30 \times 1.22 = 36.6 \text{ g of zinc}$$

If only 34.8 g was deposited, the cathode efficiency was

$$\frac{34.8}{36.6} = 95 \text{ per cent}$$

In principle, the *anode efficiency* can be determined by weighing the anode at the beginning and end of electrolysis to determine the loss in weight and comparing this value with that corresponding to 100 per cent anode efficiency for that quantity of electricity.

Practically, it is difficult to employ this direct method, because even when pure metals are used as anodes, some metal particles or metal compounds may be detached and carried into suspension. If the anodes contain insoluble impurities, such as carbon or nickel oxide in nickel anodes, these particles may be detached and lead to erroneous results.

For this reason it is more practical to estimate the anode efficiency by indirect means, usually involving a comparison with the cathode efficiency, which can be determined directly. If the anode and cathode efficiencies are exactly equal and no solution is lost by drag out or other causes, the metal content of the solution will remain constant. If, however, the anode efficiency exceeds the cathode efficiency, the metal content of the solution will increase and vice versa. From the change in metal concentration of a given volume of bath produced by a definite quantity of electricity, the relative anode and cathode efficiencies can be computed. Then if the cathode efficiency is known, the anode efficiency can be computed.

An even more sensitive indication of any difference between anode and cathode efficiencies in nearly neutral solutions is the pH of the solution (page 74), which is not directly affected by drag out. If the anode efficiency is greater than the cathode efficiency, the pH of the solution will increase and vice versa. In order to compute the actual anode efficiency from the change in pH, it is necessary to have available a titration curve of that solution, which indicates the amount of acid or alkali (or of metal) that is necessary to produce a given change in pH. Therefore although the direction of change of pH is a valuable means for determining whether the anode efficiency is greater or less than the cathode efficiency, it is seldom used to estimate the anode efficiency.

The total weight of metal lost by an anode during electrolysis may consist of (1) metal actually dissolved to form soluble salts, (2) metal attacked to form insoluble basic compounds that may adhere to the anode or may pass into suspension, and (3) particles of metal or of impurities in the anode that become detached but remain insoluble. From a practical standpoint only the metal represented by (1) represents true anode efficiency.

ELECTRODE POTENTIALS

In electrolysis it is necessary to know not only the effects of passing current through a bath, such as the dissolving and deposition of metal, but also what potential is required to cause the current to pass through the bath. As previously noted, the resistance of a bath determines the current that flows when a certain potential is applied, in accordance with Ohm's law. In an ideal electrolysis, in which exactly the same (but reversed) process takes place at the anode and cathode, respectively, the passage of current takes place in accordance with Ohm's law. However, in all electrolysis carried out at an appreciable current density, the potentials of the anodes and cathodes change as a result of *polarization* and hence affect the passage of current apart from Ohm's law.

Single Potentials. Before attempting to explain polarization, it is necessary to discuss the potential existing between a metal and the adjacent solution when no current is passed. Whenever a metal is dipped into a solution that contains salts and ions of that metal, *e.g.*, a piece of copper into a copper sulfate solution, a certain potential difference is set up, known as the *single potential* or *solution potential* of that metal in that solution. This potential can be measured in relation to some accepted reference potential by means of a potentiometer.

The practical reference potential is that of a *calomel electrode*, but for purposes of record, the potential of a hydrogen electrode in a solution that is normal in hydrogen ions (*i.e.*, has a pH of 0) is employed as the basis of reference, to which a value of *zero* potential is assigned.

Now if different metals such as copper and zinc are immersed in their respective salt solutions and their potentials are measured (directly or indirectly) against the potential of a standard hydrogen electrode, it will be found that the metal zinc is more negative than the adjacent zinc sulfate solution, while the copper is more positive than the copper sulfate solution. Study of the behavior of these metals shows that the zinc has become negative because a small amount of it has dissolved to produce positively charged zinc ions. Conversely, the copper has become positive because some of the positively charged copper ions in the solution have deposited on the copper.

According to this very simple view of the electrode potentials, these serve to measure the relative tendencies of the various metals to pass into solution to form positively charged ions of each metal. It is well known that zinc is much more readily dissolved by dilute acids, such as sulfuric or hydrochloric acid, than is copper.

When the zinc dissolves, it displaces hydrogen from the acid, thus

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

or

$$Zn + 2H^+ + SO_4^{--} = Zn^{++} + SO_4^{--} + H_2$$

(The solution of a metal by a strongly oxidizing acid, such as of copper by nitric acid, depends on its oxidizing action, and not on direct replacement of hydrogen by the metal.)

Any given metal will have a greater tendency to pass into a solution that contains very few ions of that metal than into one with a high concentration of those metal ions, just as a salt dissolves more readily in a dilute than in a concentrated solution of that salt. The potential of any metal in a solution containing ions of that metal is therefore a measure of the concentration (or more strictly the activity) of the metal ions in that solution, just as the potential of a hydrogen electrode is a measure of the hydrogen-ion concentration or pH of the adjacent solution. In general, the potential of a metal electrode becomes more positive when the concentration of the ions of that metal increases and vice versa.

In order to compare directly the potentials of different metals, it is convenient to express them in terms of the *normal* or *standard* potential, *i.e.*, the potential of that metal in a solution of a metal salt that contains one equivalent of the ions of that metal. Because most metal salts are incompletely dissociated, it would require a high (or impossible) concentration of the salt to yield a normal solution of the metal ions. For this reason, the normal ion solutions are usually hypothetical, and the values of the normal potentials are computed from measurements made in less concentrated salt solutions.

When the normal potentials of metals are arranged in order as in Table 10 (Appendix), we obtain what is commonly known as the *electrochemical* or *electromotive* series of the metals or, more strictly, of the specified reactions. In such an arrangement each metal will displace from solutions of equal ion concentration any metal that is lower down in the series. Thus, as is well known, zinc or iron will displace copper, silver, or gold from their simple salt solutions. Correspondingly, it is easier to dissolve zinc or iron anodically than copper, silver, or gold, while it is easier to deposit copper, silver, and gold than to deposit zinc or iron. The metals above hydrogen in this series are commonly referred to as *base* metals, while those below hydrogen are *noble* metals.

In Table 10 it will be noted that the upper metals such as zinc and iron have negative potentials while copper, silver, and gold have positive potentials. Unfortunately, exactly the opposite signs have been used in many books on physical chemistry, and much confusion has resulted. The system used in this text, *i.e.*, the negative sign for zinc and the positive for copper, has been adopted by many scientific organizations.

It should be emphasized that the order of replacement of metals shown in Table 10 applies only in solutions having at least approximately equal ion concentrations, *e.g.*, in solutions of sulfates and chlorides. In solutions containing complex ions, *e.g.*, the cyanide baths, the metal-ion concentrations are very low and may differ enough to reverse the order in simple salt solutions. Thus it is possible in a suitable cyanide bath to make copper displace zinc. For many purposes, however, the electromotive series is a valuable guide to the behavior of metals in electrodeposition.

Polarization. Before electrolysis starts in a solution such as copper sulfate between a copper anode and a copper cathode, the single potentials of the two copper electrodes are alike, having a value that depends upon the copper-ion concentration of the electrolyte. As electrolysis proceeds, it will be observed that the potential of the anode becomes more positive and that of the cathode more negative than the initial, or *equilibrium*, potential. The change in potential of an electrode as a result of electrolysis is known as the *polarization* of that electrode. One obvious explanation of such a change in potential is the change in concentration that occurs near an electrode as a result of electrolysis.

In the bath considered, copper is dissolved from the anode, and hence the solution next to the anode tends to become more concentrated in copper salts and copper ions than the body of solution. Conversely, at the cathode, copper is deposited, and the adjacent solution tends to become less concentrated in copper sulfate and copper ions. Certain processes such as diffusion, ion migration, and convection (natural or through agitation) tend to equalize the concentration at the electrodes and in the bath but never produce entirely uniform concentrations.

The polarization at either electrode that is caused by the changes in local concentration of metal salts and ions is known as *concentration polarization.* Such a change in potential corresponds to the change in concentration of the film of solution at the electrode surface. For example, a cathode polarization of 0.029 volt in an acid copper bath corresponds to a decrease of the cupric (Cu^{++}) copper-ion concentration to one-tenth of its original value, while in a cyanide bath, in which the copper is cuprous (Cu^{+}), a polarization of 0.059 volt corresponds to a decrease to one-tenth the original cuprous-ion concentration.

A special form of concentration polarization occurs when insoluble products are formed on the anode. These may consist of normally soluble compounds, such as copper sulfate crystals on a copper anode when the anode film is saturated, or of insoluble compounds, such as cuprous cyanide in a cyanide bath. The presence of the latter compound results from an inadequate local supply of the alkali cyanide to dissolve the cuprous cyanide. In either case the polarization and also the resistance at the anode surface are increased; hence a higher voltage is required for passage of a given current.

Although some concentration polarization is always present when electrolysis is conducted at an appreciable rate, it usually is not sufficient to account for the entire polarization, which in some baths, *e.g.*, nickel, may be relatively large. The term *chemical polarization* has been used to cover all forms of polarization that cannot be adequately explained by changes in metal-ion concentration. In general, the chemical polarization is believed to result from the differences in the rates of the various processes that may occur at an electrode, including hydration or dehydration of ions, their discharge at the electrodes, and the combination of the atoms to form crystals or molecular gases.

MEASUREMENT OF POLARIZATION. As previously noted, the static potential of an electrode with respect to the adjacent solution is commonly measured against a standard electrode, or *half cell*, usually a calomel electrode. The potential when current is flowing and hence the change in potential or polarization can be similarly measured. In that case it is necessary to have the tip of the calomel electrode as close as possible to the surface of the cathode in order to minimize the *IR* drop between the two. On the other hand, the reference electrode should be so constructed and inserted that it does not interfere with the passage of the electrolyzing current to that part of the electrode surface. At best there are certain limitations to this method of measurement that may reduce the accuracy of individual measurements. As will be shown, however, we are usually more concerned with the shapes of the resulting curves than with their exact values or positions.

One ingenious approximate method of measuring polarizations during electrodeposition was devised by H. E. Haring.[1] A box or cell is constructed (Fig. 5), which is divided into three parts by means of intermediate gauze electrodes. It has been shown that, in general, there is a negligible polarization upon such electrodes.

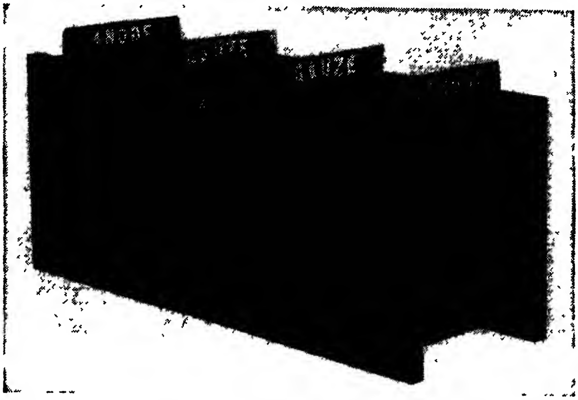

FIG. 5. Haring cell developed for polarization and resistivity measurements.

If, then, during passage of current, the total potential drop in each of the three compartments is measured with a potentiometer (or a very high resistance voltmeter), the polarizations at the anode and cathode can be computed as follows, based on Fig. 5.

The total potential drop in the section A consists of the IR drop plus the anode polarization. In M there is an equal IR drop with no polarization. The potential in C includes the same IR drop plus the cathode polarization. Hence,

$$\text{Potential } A - M = \text{anode polarization}$$
$$\text{Potential } C - M = \text{cathode polarization}$$

Example. Suppose that a current of 1 amp/dm^2 was passed through the cell and the measured potentials were, respectively,

	VOLTS
In A, anode section	1.15
In M, middle section	0.95
In C, cathode section	1.25

Then

$$A - M = 1.15 - 0.95 = 0.20 \text{ volt, anode polarization}$$

and

$$C - M = 1.25 - 0.95 = 0.30 \text{ volt, cathode polarization}$$

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[1] *Trans. Am. Electrochem. Soc.*, vol. 49, p. 417, 1926.

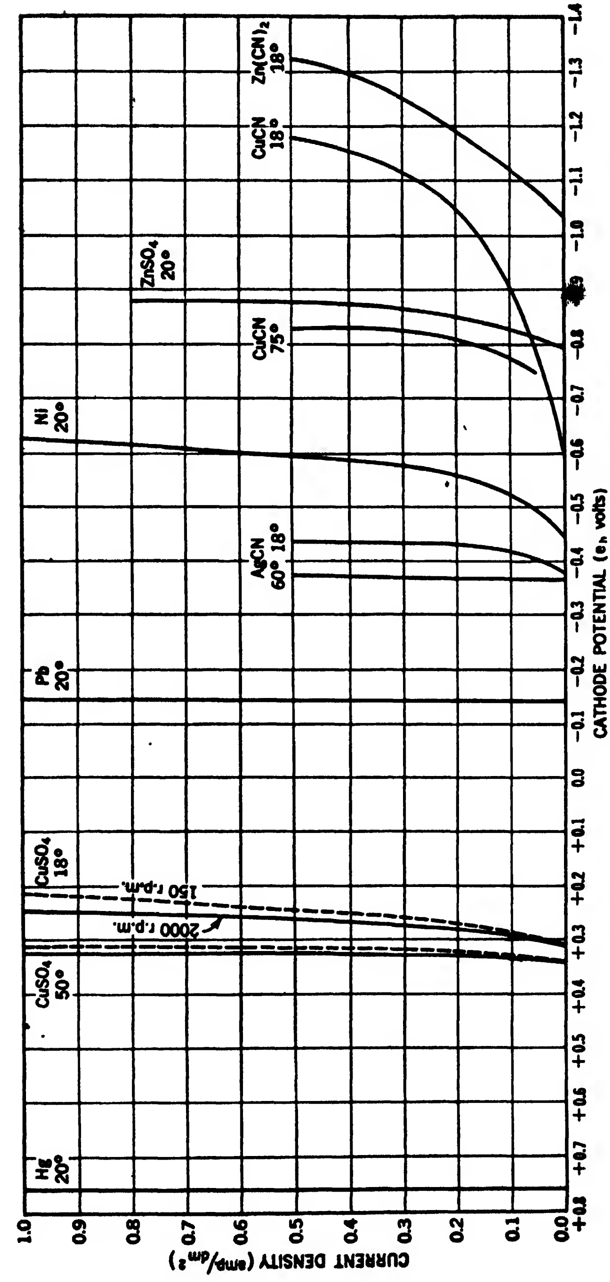

FIG. 6. Typical cathode polarization curves. (*Derived from F. Foerster, "Electrochemie Wässeriger Lösungun," 3d ed., 1922.*)

This method has been shown to yield results that closely approximate those obtained with a reference electrode. There is a need for a more critical study of this and other methods for measuring polarization during electrolysis.

If the polarization at the cathode is plotted against the current density (as in Fig. 6), it will be observed that the resultant curves fall roughly into three classes. In all cases the cathode polarization increases with an increase in current density. In certain simple baths, such as lead nitrate and silver nitrate, the curves are nearly vertical; *i.e.*, the polarization increases but slightly with the current density. In such baths the polarization is principally the result of concentration changes. In salts of this type the relatively large decrease in specific gravity of the bath when the

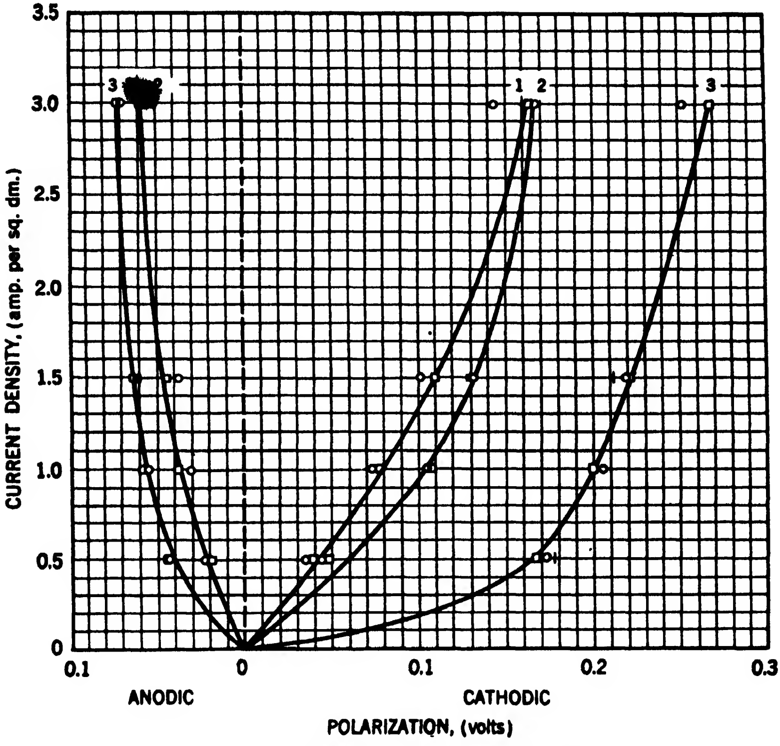

FIG. 7. Anode and cathode polarizations in copper sulfate. Curve 1: Solution *A*, 1.5*N* $CuSO_4$ + 1.5*N* H_2SO_4. Curve 2: Solution *A* + 0.002 g/l of glue. Curve 3: Solution *A* + 0.02 g/l of glue. (*Derived from H. E. Haring, Trans. Am. Electrochem. Soc.*, vol. 49, p. 417, 1926).

metal is deposited causes a rapid upward movement of solution on the cathode face, which tends to reduce the change in concentration and hence in polarization that would otherwise occur.

In baths with an intermediate cathode polarization such as an acid copper sulfate bath, the change in potential probably results from a combination of concentration and chemical polarization.

In cyanide baths the polarization is relatively large and is caused principally by chemical polarization, probably associated with the slowness of dissociation of the complex metal cyanide ions to produce metal ions (or other cations containing metal).

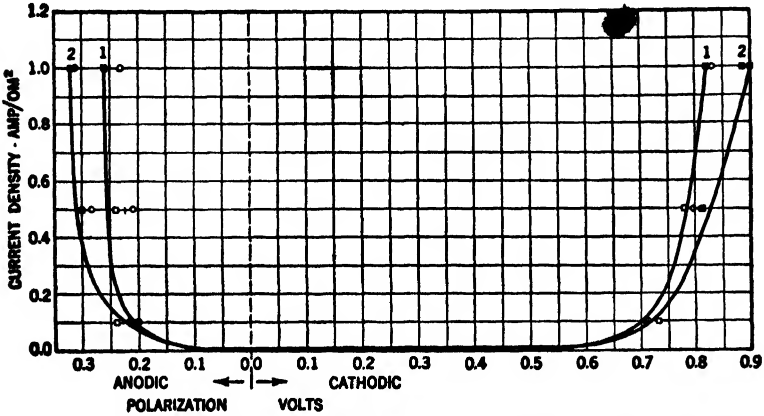

FIG. 8. Anode and cathode polarizations in a nickel bath. Curve 1: Solution *D*, *N* $NiSO_4$, $0.25N$ NH_4Cl and $0.25M$ H_3BO_3. Curve 2: Solution *D* + $2N$ Na_2SO_4. (*Derived from H. E. Haring, Trans. Am. Electrochem. Soc., vol.* 49, *p.* 417, 1926.)

At the anode there are also several types of polarization (Figs. 7 and 8). With a soluble anode that dissolves readily, *e.g.*, a copper anode in an acid copper bath, the polarization curve is similar to the cathode polarization in such a solution. If, however, the anode tends to become *passive,* as does nickel in a sulfate bath free from chlorides, the anode potential rapidly increases (becomes more positive) and tends to approach the curve for evolution of oxygen in that solution. If an entirely insoluble anode is employed, *e.g.*, a platinum anode in an acid copper bath, the resultant curve represents the anode polarization for oxygen evolution on such a surface.

Overvoltage. When hydrogen is evolved at a cathode or oxygen at an anode, the potential required is almost always greater than that corresponding to the pH of the solution, *i.e.*, to the equilibrium potential of a hydrogen or oxygen electrode in that solution. This difference in potential, known as the *overvoltage* for the evolution of hydrogen or oxygen, varies with the composition and structure of the electrode surface and increases with the current density. Overvoltage, as most commonly defined, is simply the polarization involved in the evolution of a gas, such as hydrogen, upon a specified electrode surface. A more restricted use of the term overvoltage refers to the minimum polarization, *i.e.*, the excess potential (above the equilibrium potential) at which visible gas evolution first occurs. In this sense the overvoltage corresponds to a specific but not always well-defined point on the polarization curve, approximately the point where there is a sharp upward break in the curve. (The total potential required to initiate gas evolution or any other process is designated as the *decomposition potential.*) Less confusion would result if the term *overvoltage* were used only in the latter sense and the term *polarization* were used to cover the whole curve for gas evolution.

Typical hydrogen overvoltages, or, more strictly, hydrogen polarizations at specified current densities on various metals, are listed in Table 11, Appendix. Most of the polarization or overvoltage in gas evolution may be designated as chemical polarization, although the exact causes have not been clearly defined. It involves such factors as the potential necessary to initiate discharge of hydrogen ions on a surface having a particular composition and space lattice, and a smooth or rough surface, the time necessary for the initially discharged hydrogen atoms to form hydrogen molecules (H_2), and the time required for bubbles to form and to be released from the surface. Similarly, the overvoltage of chlorine on nickel determines if it is evolved on a nickel anode.

Effects of Polarization and Overvoltage on Electrodeposition. 1. In all cases, polarization at an anode or cathode represents an *increase* in the potential required for the passage of a given current. This is illustrated in Fig. 9, in which the total voltage required in electrodeposition is plotted against the current density. As there illustrated, this total voltage may consist of three parts.

a. The reaction potential, *i.e.*, the difference in the equilibrium potentials of the anode and cathode when no current is flowing. In a cell for electrolysis of water, discharging only hydrogen and oxygen, this difference in the potentials of an oxygen and a hydrogen electrode in any aqueous solution is 1.23 volts. If a lead anode is used in an acid copper bath, the products are oxygen at the anode and copper at the cathode, and the minimum theoretical potential for electrolysis is the difference between the equilibrium potentials of a copper electrode and an oxygen electrode in that solution. The actual or decomposition potential will be greater than the equilibrium potential by the sum of the minimum anode and cathode overvoltages. If, as is usual in copper plating, both the anode and cathode are of copper, they have the same equilibrium potentials and no difference in potential is required to start electrolysis.

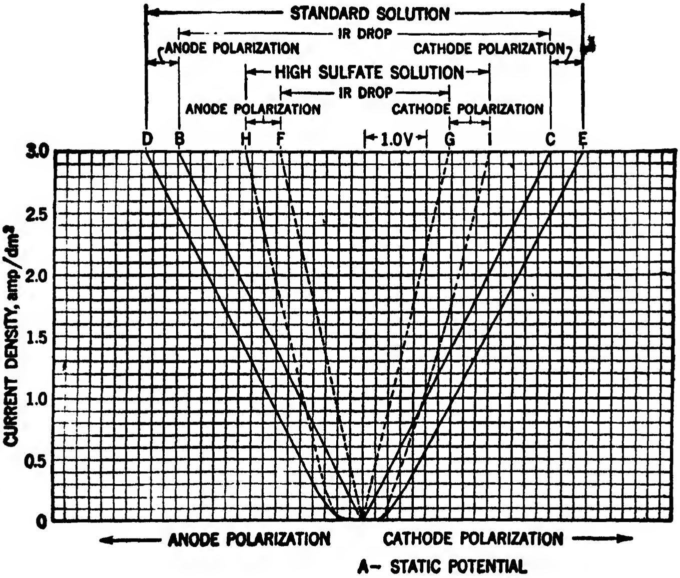

FIG. 9. Total potential drop of cell during nickel deposition. Solid lines represent a *standard* solution containing N $NiSO_4$, $0.25N$ NH_4Cl, and $0.25N$ H_3BO_3. Dotted lines for *standard* plus $3N$ Na_2SO_4. (*Derived from H. E. Haring, Trans. Am. Electrochem. Soc., vol.* 49, *p.* 417, 1926.)

b. The *IR* drop through the solution. This depends upon the shapes and positions of the electrodes, *e.g.*, the distance between them, and the resistivity of the solution. This potential drop is proportional to the current density; hence the lines representing its magnitude are straight lines whose slope is determined by the above factors.

c. The sum of the anode and cathode polarization. In Fig. 9 these curves are plotted beyond the sides of the *IR* lines.

For any given current density the required bath potential is represented by the length of a horizontal line that includes the three factors listed. The equilibrium potential is fixed by the process. The *IR* drop is determined by the size, shape, and position of the electrodes and is proportional to the current density. The polarization curves at the anode or cathode may vary widely, according to the type of bath and the surface of the electrodes.

2. In general, the polarization affects the throwing power of the bath (page 89) in such a way that the greater the slope of the polarization curve (*i.e.*, the more nearly horizontal) the better is the throwing power. This difference is illustrated by comparison of acid copper and cyanide copper bath (Fig. 6).

3. An increase in cathode polarization tends to produce finer grained deposits (page 65).

4. An increase in hydrogen overvoltage retards evolution of hydrogen and thus fosters metal deposition. The most familiar illustration of this effect is the fact that zinc can be deposited with good efficiency from acidified baths. If the hydrogen were discharged at its equilibrium potential, the current would be used principally in depositing hydrogen. Because of the high overvoltage of hydrogen on zinc, the latter is deposited along with some hydrogen. In general, the overvoltage curves for hydrogen and oxygen in a given bath influence the anode and cathode efficiencies, especially of metals less noble than hydrogen.

These few illustrations show that polarization and overvoltage are important factors in all metal deposition. More study is required to understand polarization and the possibility of controlling it to achieve desired results in electrodeposition.

The above principles explain the relation of the voltage used in electrodeposition to the quantity and quality of the deposit obtained. Strictly speaking, these results are determined largely by the cathode polarization. If a convenient means existed for measuring and controlling the cathode polarization, regardless of the *IR* drop and the anode polarization, such measurements might serve better to control the product than the present control of current density.

In practice, a plater can adequately control his processes by means of the voltage only, without reference to current density, provided that such factors as the arrangement and spacing of the electrodes and the composition and temperature of the bath are nearly constant, because then the *IR* drop and the anode polarization either are nearly constant or are directly related to the overall bath potential. In effect, the plater who controls his operations by regulating the bath voltage is really controlling the cathode polarization, which, in turn, governs the cathode current density and efficiency. The principal advantage of controlling plating directly by means of the current density is that this is more closely related to the cathode polarization and is not much influenced by large changes in electrode shape and spacing, such as may occur in plating widely different articles. With experience it is possible to achieve equally good results, whether the current density or the bath voltage is controlled, provided that the results with a particular setup have shown that the two are closely related.

RESISTANCE OF SOLUTIONS

Definitions. Frequent reference has been made to the resistance offered to the passage of current through a conductor such as an electrolyte. The resistance of a given conductor with a uniform cross section, *e.g.*, a length of wire or a portion of a plating solution, depends upon (1) the *resistivity* of the material, which is a property of that substance, and (2) the dimensions, *e.g.*, the length and cross section of the conductor. It should be emphasized that *resistivity* and its reciprocal *conductivity* are properties of a material while *resistance* and *conductance* are properties of a particular portion or assembly of materials.[1] The resistance of any portion of a homogeneous substance with a uniform cross section is directly proportional to the resistivity of that substance, and to the length and is inversely proportional to the cross section. This relation may be expressed thus:

$$\text{Resistance } (R) = \frac{\text{resistivity } (r) \times \text{length}}{\text{area of cross section}}$$

In the metric system, the usual units are

$$\text{Ohms} = \frac{\text{ohm-cm} \times \text{cm}}{\text{cm}^2}$$

In all such expressions the terms resistance and conductance and resistivity and conductivity can be used reciprocally. An increase in resistance or resistivity corresponds to a decrease in conductance or conductivity. In this text the terms resistance and resistivity

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[1] In some texts the terms *specific resistance* and *specific conductance* are used for *resistivity* and *conductivity* as here defined.

will be principally used because they are more directly related to Ohm's law and to practical computations.

The resistivities of most metals are low, especially those of silver, copper, and aluminum, which are hence used as conductors, *e.g.*, as bus bars. Alloys usually have higher resistivities, and certain alloys, such as those of nickel and chromium (ni-chrome), are used as *resistors*, *e.g.*, in rheostats, when it is desired to interpose resistance or to produce heat by passage of current.

The resistivities of aqueous solutions of strong acids and bases are relatively low (but much higher than those of most metals). The resistivities of salt solutions such as may be used in plating (Table 12) are fairly high, and hence when feasible, acids or alkalies are added to decrease their resistivities.

The resistivity of a solution is usually expressed in *ohm-centimeters*, or in *ohms per centimeter cube*. (Occasionally the unit *ohms per inch cube* is employed.) The meaning of the metric unit can be illustrated by a simple diagram such as Fig. 10. If two metal electrodes, each 1 by 1 cm, are placed at opposite faces of a cube and the space between is filled with the medium whose resistivity is unity, the resistance R of the cell will be *one ohm per centimeter cube*, or one ohm-centimeter. The latter expression is derived from the equation

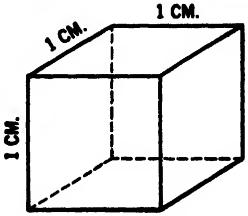

FIG. 10. Unit of resistivity, 1 cm cube, *i.e.*, a cube 1 cm on each side.

$$R = r \times \frac{1\text{ cm}}{1\text{ cm}^2} = \frac{r}{1\text{ cm}}$$

hence

$$r = R \times \frac{1\text{ cm}^2}{1\text{ cm}} = R \times \text{cm}$$

The same relation exists if the English units are employed, in which case the unit is *one ohm per inch cube* or *one ohm-inch*. In these expressions it should be emphasized that the unit of resistivity is *one ohm per centimeter cube*, *i.e.*, the resistance of a cube one centimeter on a side, and not *one ohm per cubic centimeter* (which volume might have any shape).

Measurement of Resistivity. In principle, all that is necessary to measure the resistivity of a solution is to observe the relation between the voltage and current when a direct current is passed through the solution contained between two plane parallel electrodes that completely fill the cross section and on which there is no polarization. Such an arrangement is involved in the Haring cell (page 47). In this apparatus the resistance R of the body of solution between the two gauze electrodes is equal to

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

$$\text{Ohms} = \frac{\text{volts}}{\text{amperes}}$$

The resistivity r of the solution is then calculated:

$$r = \frac{R \times \text{area}}{\text{length}}$$

If in a cubical compartment 5 cm on a side a current of 2 amp passes when a potential of 5 volts is applied,

$$R = \frac{5}{2} = 2.5 \text{ ohms}$$

and

$$r = \frac{2.5 \times (5 \times 5)}{5}$$

$$= 2.5 \times \frac{25}{5} = 2.5 \times 5 = 12.5 \text{ ohm-cm}$$

Practically, if plane electrodes are used, this method is subject to errors caused by polarization at the electrodes. In the Haring cell this polarization is reduced to nearly zero by the use of the two center gauze electrodes, and approximately correct values are obtained for the resistivity.

For more accurate measurements of resistivity an alternating current is used, preferably with a high frequency such as 500 to 1,000 cycles, although fairly accurate results can be obtained with 60-cycle alternating current. By the use of alternating current the polarization at the electrodes is practically eliminated. Platinum electrodes coated with black spongy platinum are employed because they further reduce polarization, especially of hydrogen and oxygen evolution. Instead of using a cell with exactly defined dimensions, a cell of any convenient size and shape is used, and the *cell constant* is determined by measuring its resistance when filled with a solution of accurately known resistivity, *e.g.*, a normal solution of potassium chloride.

Such measurements are usually made by means of a *Wheatstone bridge*, shown diagrammatically in Fig. 11. By means of a suitable battery *E* a definite emf is maintained between *F* and *H*. Part of the current will then flow through the path *FIH* and part through *FKH*. A galvanometer *G* is then connected from a point *I* on *FIH* to some point *K* on *FKH*, so adjusted that no current flows through the galvanometer. The resistances in the two parts of each branch are then proportional, *i.e.*,

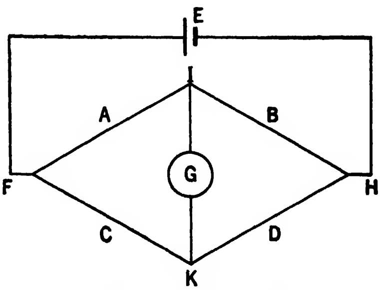

FIG. 11. Diagram of Wheatstone bridge.

$$\frac{A}{B} = \frac{C}{D}$$

If the unknown resistance to be measured is placed in branch *A*, the resistance of *A* may be computed because

$$A = \frac{BC}{D}$$

With alternating current, a d-c galvanometer cannot be used. Instead, a sensitive telephone receiver is used to detect the point at which no current flows, *i.e.*, when the bridge is *balanced*.

A form of cell that is convenient for taking a sample of a plating bath and measuring its resistivity is shown in Fig. 12. The cell should be immersed in a constant-temperature bath, *e.g.*, at 25°C (77°F).

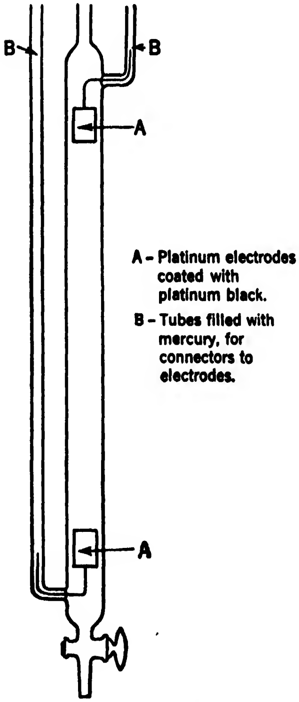

FIG. 12. Simple conductivity cell.

If the resistance of the cell when filled with *N* KCl solution was 210 ohms and when filled with an acid copper solution was 150 ohms, the resistivity of the latter is computed as follows: The resistivity of *N* KCl at 25°C is 8.94 ohm-cm. Hence the *cell constant* (*i.e.*, the resistance of the cell when filled with a solution of unit resistivity) is $210/8.94 = 23.5$ ohms. The resistivity of the copper solution is $150/23.5 = 6.4$ ohm-cm.

In Table 12 in the Appendix are listed the approximate resistivities of solutions related to electroplating. The strong acids and alkalies have the lowest resistivities; next are the salts of sodium, potassium, and ammonium; and then of the heavy metals. These values permit one to estimate the relative resistivities of typical plating baths. They do not, however, permit computations of the actual current densities produced by a given voltage, because the total resistances of the plating baths depend also upon the sizes, shapes, and positions of the electrodes and of the plating tanks.

In general, the resistivity of most aqueous solutions decreases by about 2 per cent for an increase of 1°C or about 1 per cent for each degree Fahrenheit. Hence a lower voltage is required to produce the same current density at a higher temperature.

Heat Produced by Electrolysis. In an ideal electrodeposition cell, with identical but reversed processes at the anode and cathode, no evolution of hydrogen or oxygen, and no polarization, all the energy consumed by the passage of current would be converted into heat.

$$\begin{aligned}\text{Energy (joules)} &= \text{electromotive force (volts)} \times \text{current (amp)} \times \\ &\quad \text{time (sec)} \\ &= EIt\end{aligned}$$

Since $E = IR$,

$$EIt = I^2Rt$$

As 1 joule = 0.239 cal,

$$\text{Heat produced in calories} = 0.239I^2Rt$$

Hence the rate of heating, *i.e.*, the heat produced per second, is proportional to the resistance and to the square of the current. This relation permits computation of the relative quantities of heat produced under specified conditions.

Problem. A certain bath A has a resistance R of 0.1 ohm, so that when a potential of 5 volts is applied, the current $= 5/0.1 = 50$ amp. By the addition of some substance, such as an acid, the resistance of the bath (now bath B) is reduced to 0.05 ohm; *i.e.*, the conductance is doubled. What will be the relative heating effects in the two baths if (1) the potential is kept at 5 volts or (2) the current is kept at 50 amp?

In A, the heat produced $= I^2R = 50^2 \times 0.1 = 250$ joules/sec.

In B, (1) with 5 volts

$$I = \frac{E}{R} = \frac{5}{0.05} = 100 \text{ amp}$$

$$\text{Heat} = 100^2 \times 0.05 = 500 \text{ joules/sec}$$

(2) with 50 amp (which will require only 2.5 volts)

$$\text{Heat} = 50^2 \times 0.05 = 125 \text{ joules/sec}$$

Therefore, decreasing the resistance of a bath, *e.g.*, by adding more sulfuric acid to an acid copper solution, *increases* the evolution of heat if the same voltage is applied, but *decreases* the heating if the same current is passed.

The increase in temperature produced in the bath by a given evolution of heat cannot be readily calculated. It depends on the volume of the bath and the rate at which heat is carried away. The latter rate depends upon (1) the relative temperature of the room and the bath; (2) the thermal conductivity of the tank walls (metal is a better conductor than stoneware, and metal is better than wood); the use of rubber or plastic linings, which decrease the thermal conductivity; (3) the rate of evaporation, which depends on the temperature and humidity of the air; and (4) the heat introduced or carried away by heating or cooling coils, bus bars, and racks.

CHAPTER IV

FACTORS THAT GOVERN THE CHARACTER AND DISTRIBUTION OF ELECTRODEPOSITS

INTRODUCTION

In commercial electroplating it is not sufficient merely to coat the object completely or even with relative uniformity. In addition it is necessary to produce deposits of a given metal that have those properties, such as smoothness, brightness, hardness, or ductility, which may be required for a particular purpose. The successful application of electroplated coatings depends largely upon the ability of the plater to control the character of the deposits by making appropriate changes in the composition of the baths or in the conditions of operation. To do so, it is not necessary that the causes of all such effects be understood, desirable as that may be, or even that the exact magnitude of a given effect be predictable. The most important consideration is to know the direction of the effect produced by a change in a certain variable. Most of these directions are fairly well known, although it may be difficult to predict the change that will occur when two or more factors are varied simultaneously.

MECHANISM OF ELECTRODEPOSITION

If the actual process by which a dissolved metal ion is converted into a solid crystalline deposit were more fully understood, the effects of various changes could be more reliably predicted. It is not yet possible to explain this process in terms of the modern theories of physics and chemistry, although progress is being made in that direction.[1] The following very elementary description merely gives a picture of the process in terms of the accepted simple theories. Only the reactions at the cathode will be discussed. In general, the reactions at a soluble anode will be the reverse of those at the cathode. In a solution of a metal salt such as copper sulfate, the salt is dissociated to a considerable extent to form positively charged cations, in this case Cu^{++}, and nega-

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[1] Hunt, L. B., *J. Phys. Chem.*, vol. 36, p. 1006, 1932, and *Trans. Electrochem. Soc.*, vol. 65, p. 413, 1934. Also Symposium, Electrode Processes, *Trans. Faraday Soc.*, No. 1, 1947.

tively charged anions, SO_4^{--}. The water present is slightly dissociated to form hydrogen ions, H^+, and hydroxyl ions, OH^-. Any sulfuric acid present is dissociated into hydrogen ions, H^+, and sulfate ions, either HSO_4^- or SO_4^{--}. Most of these ions are *hydrated; i.e.*, they are combined with one or more molecules of water.

When a potential is applied between two electrodes in such a solution, the positively charged cations. in this case Cu^{++} and H^+, "migrate" toward the cathode and the negatively charged anions, OH^- and SO_4^{--}, move toward the anode. In an acidified solution the concentration of hydrogen ions is relatively high and of hydroxyl ions is very low. Because the hydrogen ions move more rapidly than the copper ions, most of the current is carried to the cathode by the hydrogen ions. As, however, it is easier to discharge copper ions than hydrogen ions at the cathode, practically all the current is used at the cathode in depositing copper. Consequently, the cathode efficiency of copper deposition from an acid bath is close to 100 per cent. Because less copper is brought to the cathode by migration than is deposited, the layer of solution at the cathode surface, known as the *cathode film*, becomes weaker in copper ions. This is one cause of the cathode polarization, *i.e.*, of the increased potential required to deposit the copper at a higher current density.

However, as soon as the concentration of copper in the cathode film decreases, copper ions start to diffuse into this film from the adjacent, more concentrated body of solution. If the solution is agitated, fresh solution is brought mechanically toward the cathode surface. This process reduces the thickness of the cathode film and thereby facilitates diffusion to the cathode surface. In general, the reduction in the metal content of the cathode film lowers its specific gravity, and the depleted solution tends to rise along the cathode surface. Hence there is some upward movement (convection) even in solutions not otherwise agitated.

It is difficult to picture the process involved in the actual deposition of metal at the cathode. The cathode is negatively charged; *i.e.*, it has a relatively high concentration of electrons. When these have an opportunity to combine with positively charged ions, neutral (uncharged) metal atoms are formed, thus:

$$Cu^{++} + 2\ominus = Cu$$

The crystals of which all electrodeposited metals consist are made up of atoms arranged in a *lattice* consisting of geometrical forms, most commonly cubes. Many of the deposited metals are in the form of *face-centered cubes.* Each of these cubes has a total of 14 atoms, of which 8 are located at the corners of the cube and 6 are located at the center of each side of the cube. The smallest crystal unit therefore consists of 14 atoms, the distances between which are very small and are characteristic for each metal. The actual crystals in a deposit are made up of large numbers of these lattice units, usually in layers.

When there is a sufficient difference in potential between the negatively charged cathode and the adjacent positively charged ions, some of the latter are discharged to form metal atoms. According to certain theories these atoms are discharged in haphazard order, *i.e.*, amorphous or without orientation, and afterward rearrange themselves into crystals. According to another theory they are preferentially discharged at those points on the cathode where they are needed to make up a crystal. There is also evidence that in certain cases the potential builds up until suddenly one whole layer of atoms is deposited, each in its proper orientation with respect to existing crystals. Regardless of the exact procedure, the net result is that metal atoms are produced and are arranged in the geometrical forms characteristic of that metal.

THE COMPOSITION OF CATHODE FILMS

Because deposition of metal takes place from a film of solution whose composition is different from the body of solution, increased knowledge of the composition and properties of that film may throw light on the actual processes involved in deposition. Three methods have been proposed for sampling this cathode film prior to its analysis.

Drainage Method. This method was suggested by H. E. Haring[1] and used by him to show that in nickel deposition the cathode film has a higher pH than the body of solution. It merely involves the quick removal of a vertical plane cathode during electrolysis and analysis of the solution that adheres to the surface after a short period of drainage. This residual film is about 0.001 in. thick, and has approximately the composition of the cathode film up to that thickness.

Pinhole Method. This procedure was used by A. K. Graham and associates.[2] It depends upon drawing a sample of the solution

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[1] *Trans. Am. Electrochem. Soc.*, vol. 41, p. 351, 1922.

[2] Graham, A. K., Heiman, S., and Read, H. J., *Am. Electroplaters' Soc., Proc.*, p. 95, 1939. Read, H. J., and Graham, A. K., *Trans. Electrochem. Soc.*, vol. 78, p. 279, 1940.

through a small hole in the cathode during electrolysis into an appropriate container.

Freezing Method. This method, devised by A. Brenner,[1] depends upon the use of a hollow cylinder as the cathode, into which, during electrolysis, a freezing mixture is suddenly introduced. This freezes the film of solution on the cathode surface. The cylinder, still filled with a freezing mixture, is then placed on a lathe, and successive thin layers are turned off, collected, and analyzed.

Too few data have yet been published to evaluate fully the advantages and limitations of these methods. The results obtained by Brenner indicate that the freezing method gives the most complete information for those solutions to which it is applicable. It yields not only the solution composition very close to the cathode but also the concentration *gradient*, *i.e.*, the rate at which the concentration changes in passing from the cathode to the body of solution. The drainage method yields, for the film composition very close to the cathode, results that are in fair agreement with those by the freezing method. The pinhole method, however, yields much lower changes in film concentration than are obtained by the other two methods. This discrepancy is to be expected because it is not possible to withdraw through a hole a sample of the cathode film without removing with it considerable of the body of solution.

Typical results by the freezing method for an acid copper solution are shown in Fig. 13(*a*) and (*b*). Figure 13(*a*) shows that the effective thickness of the cathode film is from 0.006 to 0.010 in. (0.15 to 0.25 mm). The copper content at the cathode surface is about 25 per cent lower than in the body of solution. Figure 13(*b*) shows that in this bath the content of sulfuric acid in the cathode film is higher than in the rest of the solution. In a more nearly neutral nickel bath, the pH of the cathode film is higher than the body of solution.

STRUCTURE OF ELECTRODEPOSITS

As previously indicated, electrodeposited metals consist of crystals, each of which, in turn, is made up of a large number of lattice units. The properties of metal deposits are determined principally by the size and arrangement of the individual crystals

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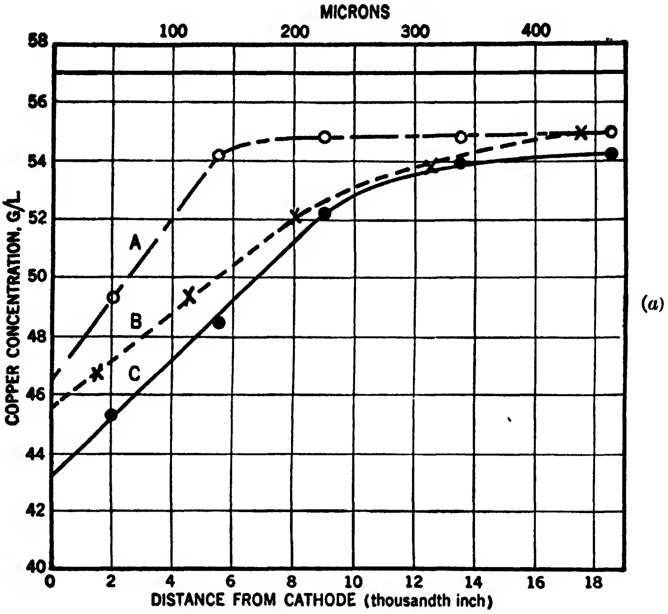
[1] *Proc. Am. Electroplaters' Soc.*, p. 95, 1940.



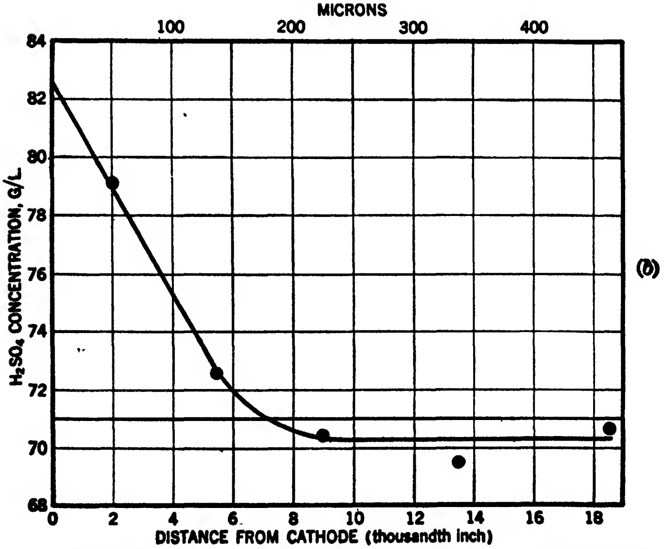
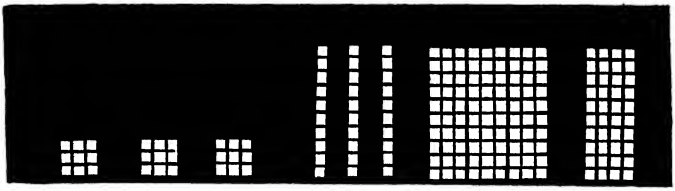
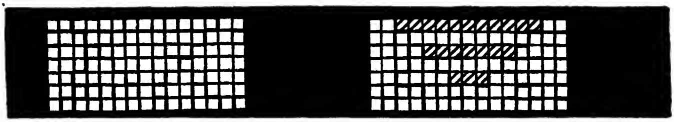


Fig. 13. Concentration gradients in the cathode film in an acid copper bath. Measured by the freezing method. (*a*) Copper concentrations at different distances from the cathode. (*b*) Concentrations of sulfuric acid at different distances from the cathode (*A. Brenner.*)

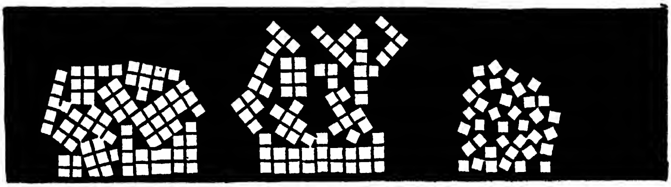
or in some cases of the still larger crystal aggregates that make up the deposits. It has frequently been pointed out that the type of crystal structure produced under given conditions depends largely upon the relative rates of (1) formation of nuclei, from which new crystals proceed, and (2) growth of existing crystals. In general, conditions that favor (1) will yield finer grained deposits, which contain more but smaller crystals, while conditions that favor (2) will result in fewer but larger crystals. Some of the simple types of crystals are represented diagrammatically in Fig. 14. As a rough (but not infallible) guide, it has been found that any factors which increase the cathode polarization tend to decrease the crystal size and to change the type of deposit from those of Group I to those of Groups II and III. These and many of the other



(1) Symmetrical (2) Acicular (1) Columnar (2) Fibrous
(a) Isolated (b) Contiguous
GROUP I



(a) Conical (b) Twinned
GROUP II



(a) Broken (b) Arboreal (c) Powdery
GROUP III

Fig. 14. Diagrammatic representation of principal crystal types.

principles of crystal structure were predicted by W. D. Bancroft[1] in his "axioms" of electroplating.

It will require much more extensive research to determine fully the relation between (1) the structure and properties of deposits and (2) the operating conditions and the types of structure produced. In the following summary only the important and well-defined conclusions will be considered.

RELATIONS BETWEEN THE STRUCTURE AND PROPERTIES OF DEPOSITS

The normal range of values of such properties as hardness, strength, and ductility for a given metal (Chap. V) is characteristic of that metal. For example, lead is always softer than copper, and copper is usually softer than nickel, in spite of the fact that the hardness of each of these metals may vary over a wide range with the conditions of deposition. In general, for a given metal, fine-grained deposits are smoother, brighter, harder, stronger, but less ductile than coarse-grained deposits. Some of the apparent exceptions can be explained. For example, treed (arboreal) deposits, produced at high current densities, are really very fine grained, *i.e.*, they consist of small individual crystals, but these are united to form coarse aggregates, which are rough and usually dull. Specific effects, such as the brightness of certain nickel deposits, may be caused by the arrangement as well as by the size of the crystals and especially by the formation of successive bands or layers of crystals.[2]

EFFECTS OF OPERATING CONDITIONS UPON THE STRUCTURE OF DEPOSITS

The two obvious methods by which an operator can change the structure of deposits are (1) by altering the bath composition and (2) by changing the conditions of deposition. As the latter procedure is usually more convenient, it may well be considered first.

The three principal changes that can be made in the operation of a given bath are (1) in the current density, *i.e.*, the rate of deposition; (2) in the method or degree of agitation; and (3) in the temperature. In the following discussion, reference is made to the effect of a change in that particular variable while all other conditions are kept constant.

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[1] *Trans. Am. Electrochem. Soc.*, vol. 6, p. 27. 1904, and vol. 23, p. 266, 1913.

[2] For X-ray evidence, see READ, H. J., *Plating*, vol. 36, p. 355, 1949.

Current Density. In general, it is desirable to use as high current densities as practicable and thereby to increase the rate of production from a given unit. Within certain limits an increase in current density decreases the crystal size, as illustrated in Fig. 15, in which *a* has a typical conical structure (Group II*a*) and *b* has a broken structure (Group III*a*). When, however, the current density exceeds the *limiting* value for that bath and temperature, there is a tendency to produce rough or treed deposits. A still further increase in current density yields spongy or burnt deposits, which usually contain inclusions of hydroxides or basic salts.

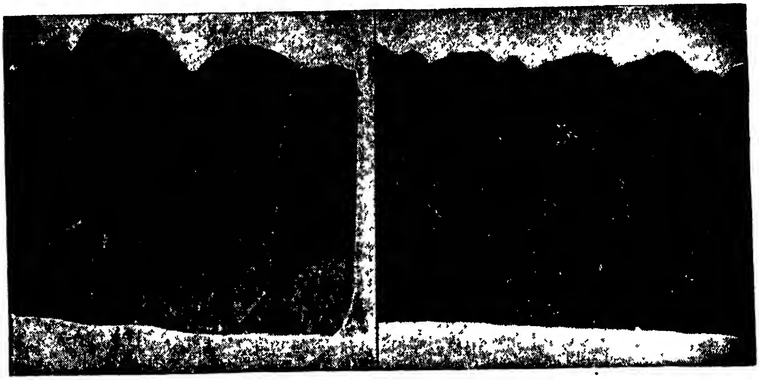
(*a*) (*b*)

FIG. 15. Effect of current density on copper deposits (300 diam.). (*a*) 4 amp/dm^2 (37 amp/ft^2). (*b*) 10 amp/dm^2 (93 amp/ft^2).

All these changes are consistent with the fact that, when the current density is increased, the concentration of metal (and of metal ions) in the cathode film decreases and the polarization increases. The limiting current density in a given solution has been used to compute the composition and thickness of the cathode film and vice versa.

Agitation. In general, agitation of the solution brings up a fresh supply of metal salts or ions to the cathode, reduces the thickness of the cathode film, and thus facilitates replenishment of the metal ions or compounds at the cathode surface. Another advantage of agitation is that it sweeps away gas bubbles, which may cause pits. Agitation is also desirable because it mixes the solution and prevents stratification of heavier solution toward the bottom of the tank. The net result is that agitation permits a higher current density to be used to produce a deposit with a given structure and it increases the limiting current density for dense deposits. W. M. Phillips[1] showed how the current density in acid copper baths can be increased by vertical movement of the cathodes. A. C. Simon and J. T. Lumley[2] used current densities up to 200 amp/ft^2 (20 amp/dm^2) in rapidly circulated silver baths, which were later exceeded in the commercial silver plating of airplane engine bearings (page 299). These and other studies show that, to permit an appreciable increase in current density, it is necessary to have a relative motion of the cathode and solution equal to at least 10 ft (3 meters) per minute and preferably much higher. Conveyor tanks usually produce a relatively slow movement of the cathodes and do not greatly increase the permissible current density, unless a transverse or rotary movement is also provided.

In principle it is immaterial whether the relative motion is obtained by horizontal, vertical, or rotary movement of the cathodes or by moving the solution by a stirrer, a pump, or a jet of air. Two general types of agitation are possible, in which, respectively, the resultant flow of solution is (1) *lamellar*, *i.e.*, in layers, or (2) *turbulent*, *i.e.*, in all directions. The former type, sometimes designated as *mass flow*, has been found to yield the most beneficial and consistent method of agitating plating baths. It is especially adapted to regular shapes, such as strips, wires, and cylinders.

Air agitation is universally used in America in copper and nickel electrotyping baths and in England in many nickel-plating baths. One reason that rapid agitation is not more extensively used is because it detaches particles from the anode and stirs up sludge and hence causes rough and porous deposits. The use of anode bags and of frequent or continuous filtration permits an increase in agitation. Agitation of cyanide baths, especially by air, increases their decomposition with the formation of carbonates. Rapid agitation decreases the polarization and may reduce the throwing power.

Temperature. In general, an increase in the temperature of deposition causes an increase in the crystal size. This is illustrated in Fig. 16. In this figure *a* illustrates twinned crystals (Group II*b*), which are often intermediate between the conical and broken

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[1] *Proc. Am. Electroplaters' Soc.*, p. 87, 1940.

[2] *Proc. Am. Electroplaters' Soc.*, p. 91, 1940.

types. The importance of such a change in structure, especially in electrotyping, is shown by the fact that the deposit in *a* had a tensile strength of 2,800 kg/cm² (40,000 lb/in²) while that in *b* had a strength of only 1,400 kg/cm² (20,000 lb/in²) and was much softer and more easily abraded. This increase in crystal size corresponds to a decrease in polarization at the higher temperature.

That fine-grained, smooth deposits are often produced in intentionally heated solutions is caused by the fact that, at higher temperatures, higher current densities are possible and customary. The higher current density counteracts the effect of the higher temperature. The influence of temperature is caused by a greater solubility and dissociation of the metal salt, which, in turn, leads to a higher conductivity of the solution. A high temperature increases the mobility of the metal ions and decreases the viscosity of the solution, so that the cathode film is more rapidly replenished. This reduces the tendency toward treeing and also increases the current density obtained with a given voltage. Another advantage of high temperatures is that there is usually less absorption of hydrogen in the deposits and less stress and tendency toward cracking, especially of iron, nickel, or cobalt.


(*a*) (*b*)

FIG. 16. Effect of temperature on copper deposits (300 diam.). (*a*) 25°C (77°F). (*b*) 40°C (104°F).

EFFECTS OF THE BATH COMPOSITION AND PROPERTIES

Most of the metals that are used in plating can be deposited from more than one type of bath, each of which may be best suited for certain applications. In each type of bath there is a fairly wide range of composition and concentration. The task of the plater is to select (1) the type of bath and (2) the composition best suited for his purpose. After that it may be necessary to decide what additions or changes should be made to modify the character of the deposits or to correct some defect. In the following presentation, an effort is made to indicate the direction of the effects of such changes.

Bath Composition. *Metal Concentration.* Because metal can be deposited only from solutions that contain some dissolved compound of that metal, it might appear advisable to have the highest possible concentration of that salt, *e.g.*, a saturated solution. Among the advantages of using a strong solution are (1) a higher conductivity, (2) a higher permissible current density, and (3) a higher cathode efficiency. Its disadvantages include (1) its increased cost, both for initial preparation and to replace the drag out (which is relatively greater in stronger and more viscous solutions); (2) the tendency to crystallize out if evaporation occurs or the temperature is lowered; and (3) a probable decrease in anode efficiency. In practice, intermediate concentrations are used, but the present tendency is to employ as strong solutions as feasible. An increase in metal concentration under given conditions decreases the cathode polarization and, as predicted, increases the crystal size. Just as with an increase in temperature, the higher current density that can be used with more concentrated solutions may effectively counteract the effect of concentration on the crystal size.

For any given operating conditions, certain concentrations of the bath constituents represent the *optimum* for obtaining results. When such optimum conditions have been defined, they should be maintained as closely as feasible. It is entirely possible, however, especially for other conditions of operation, that other concentrations may be superior. When, *e.g.*, in this text, a certain range of concentration is stated for a given bath, this does not justify a variation of that magnitude during its operation. It means merely that within that range a specific composition can be selected which will meet the requirements. In most cases, the concentrations of the different bath constituents should be varied proportionally.

Metal-ion Concentration. Because metal deposition is the result of discharge of the metal ions, the concentration of the latter is more important than that of the metal compounds from which they are derived. In general, a decrease in metal-ion concentration increases the cathode polarization, decreases the crystal size, and improves the throwing power. If the desired low metal-ion concentration were obtained by merely using a dilute solution of a simple metal salt, the supply of metal at the cathode would be very quickly exhausted and the limiting current density would be so low as to be impractical. This difficulty can be overcome by using solutions that have a high concentration of metal compounds but a low metal-ion concentration. The metal compound then serves as a reservoir that replenishes the supply of ions as they are discharged.

The two principal ways of reducing the metal-ion concentration are (1) addition of a compound with a *common ion* and (2) formation of complex compounds and ions. The first effect is illustrated by the addition of sulfuric acid to a copper sulfate solution, of sodium sulfate to a nickel solution (as in the *high-sulfate* bath), and of calcium chloride to a ferrous chloride bath. By this means it may be possible to reduce the effective metal-ion concentration to about 10 per cent of that present in that concentration of the metal salt alone. While the resultant effects on polarization and crystal size are appreciable, they are much less than those obtainable by the formation of complex compounds.

The most important complex compounds used in plating are the double cyanides of sodium or potassium with such metals as copper, silver, gold, zinc, and cadmium. In general, these are formed by dissolving the metal cyanide (which is nearly insoluble in water) in a solution containing sodium or potassium cyanide. (Except for silver and gold plating, sodium cyanide was always used, but recently potassium cyanide has been used in copper baths.) The formation of the soluble double cyanides may be represented by such equations as the following:

$$\begin{array}{ll} \text{AgCN} + \text{KCN} & = \text{KAg(CN)}_2 \\ \text{silver cyanide} + \text{potassium cyanide} & = \text{potassium argentocyanide} \end{array}$$

$$\begin{array}{ll} \text{CuCN} + 2\text{NaCN} & = \text{Na}_2\text{Cu(CN)}_3 \\ \text{cuprous cyanide} + \text{sodium cyanide} & = \text{sodium cuprocyanide} \end{array}$$

In solutions of these compounds the principal dissociation is as follows:

$$\text{KAg(CN)}_2 \rightleftarrows \text{K}^+ + \text{Ag(CN)}_2^-$$
$$\text{Na}_2\text{Cu(CN)}_3 \leftrightarrows 2\text{Na}^+ + \text{Cu(CN)}_3^{--}$$

It is important to note that, as a result of such dissociation, the heavy metal (silver or copper) is in the negatively charged anion and not in a positively charged cation, such as is formed by the dissociation of a simple metal salt. Consequently, upon electrolysis these complex ions which contain the metal move toward the anode and not toward the cathode. No entirely satisfactory explanation has been proposed to account for the deposition of metal on the cathode from such solutions. The constitution and behavior of complex cyanide baths is further complicated by the fact that ammonia may be formed in them or intentionally added, thereby giving rise to other complex compounds.

In a summary of the constitution of cyanide plating baths[1] the following theories are discussed, as illustrated with silver deposition:

1. The sodium is first discharged at the cathode, and the resulting metallic sodium reduces the complex silver compounds or ions to form metallic silver by secondary displacement. This theory is not very plausible because the potentials employed are too low to cause discharge of sodium.

2. The complex ion dissociates to a very slight extent to form positive silver ions, thus

$$Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^-$$

These silver ions are then discharged in the usual way. Potential measurements with a silver electrode indicate that there are some silver ions in a cyanide solution, but their concentration (or activity) is so very low that it is improbable that they can account for the deposition of the silver at appreciable current densities.

3. The complex anions may split up to form complex cations that are then reduced to silver at the cathode.

$$2Ag(CN)_2^- \rightleftharpoons Ag_2CN^+ + 3CN^-$$
$$Ag_2CN^+ + \ominus = Ag + AgCN$$

4. Direct reduction of anions may occur at the cathode.

$$Ag(CN)_2^- + \ominus = Ag + 2CN^-$$

The latter two processes are plausible, but it is difficult at present to demonstrate what is the actual mechanism. This situation shows that it is not uncommon for platers to make extensive successful use of processes which are not at present understood.

Other complexes may exist in certain plating baths. For example, in an ammoniacal nickel bath, sometimes used to plate on zinc die castings,[2] the nickel is present in complex ions with

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[1] THOMPSON, M. R., *Trans. Electrochem. Soc.*, vol. 79, p. 417, 1941.

[2] HIRSCH, A., *Trans. Electrochem. Soc.*, vol. 63, p. 135, 1933.

ammonia. Citrates and tartrates are likely to form complex ions in certain metal baths. Rochelle salt (sodium potassium tartrate), used in the Rochelle salt copper bath (page 296), probably forms certain complexes in addition to those already present in the cyanide. The recent increased use of fluoborates and pyrophosphates in plating baths probably involves the presence of complex salts and ions.

Nature of the Anions and Cations. In almost all plating solutions the metal is introduced as a salt, *i.e.*, a compound of the metal with some acid. (One of the few exceptions is the use of chromic acid, CrO_3 or H_2CrO_4, as the source of metal in chromium plating.) Salts of other metals than that to be deposited are often added and thereby introduce other cations. The common additions are the chlorides and sulfates of sodium, potassium, ammonium, and magnesium. While specific advantages are often found for a particular cation, such as ammonium salts in a nickel bath or potassium cyanide instead of sodium cyanide, there is at present no clear basis for predicting their relative behavior. It is possible that these cations migrate into the cathode film to different degrees and that they influence the behavior of any colloidal materials there present. The soluble salts of the simple strong acids, sulfuric, hydrochloric, and nitric acid, are usually similar in many properties. Sulfates and chlorides are the most commonly used in plating baths. Nitrates are seldom used because the nitrate ion, NO_3^-, may be reduced at the cathode to form ammonia, NH_3, and thus change the composition and pH of the bath. [The use of a nitrate in a silver cyanide bath (page 299) depends upon the fact that silver is more readily reduced than nitrate.]

If the metal-ion concentration were the only consideration, we should expect to get very similar results with chlorides and sulfates of a given metal such as iron, nickel, or tin. Actually it is found that there are often marked differences in the behavior of chloride and sulfate baths, *e.g.*, of nickel, which cannot be accounted for by their solubilities or their dissociations and resultant metal-ion concentrations. These differences are especially marked when certain addition agents are used. It is necessary, therefore, to conclude that the anions in a bath may affect its operation, *e.g.*, by affecting the form of colloids in the cathode film. Little knowledge is available regarding the behavior and effects of either foreign cations or of any anions in the cathode film, and no sound predictions can be made.

This lack of knowledge regarding effects of specific ions is illustrated by the introduction in recent years of new types of plating baths. For example, fluoborates, formerly confined to lead and tin baths, are now used for copper, nickel, and other metals. Sulfamate lead baths and pyrophosphate copper and zinc baths are now in commercial use. Until much more knowledge is gained regarding the constitution and mechanism of such baths, their use for any given purpose must depend upon demonstrable advantages and not on predictions of their performance.

Hydrogen-ion Concentration (pH). PRINCIPLES. All aqueous solutions contain some hydrogen ions. Perfectly pure water dissociates to a slight degree to form hydrogen ions and hydroxyl ions.

$$H_2O \rightleftharpoons H^+ + OH^-$$

If an acid is added, the concentration of hydrogen ions increases, and if an alkali is added, the concentration of hydroxyl ions increases. Because the hydrogen ions are positively charged, on electrolysis they migrate toward the cathode, where they may be discharged to form hydrogen gas. The cathode efficiency (page 40) depends principally upon what proportions of the current are used, respectively, in depositing metal and hydrogen. A 100 per cent cathode efficiency (for metal deposition) means that no hydrogen is discharged, while a zero efficiency may mean that only hydrogen is discharged. Because this efficiency is partly determined by the concentration of hydrogen ions, it is important to know and control these concentrations, especially in the nearly neutral baths, such as those of nickel.

In water and aqueous solutions the product of the concentrations of hydrogen and hydroxyl ions is constant and is equal to about 1×10^{-14} N, read as "one times ten to the minus fourteenth normal," *i.e.*, $0.000,000,000,000,01N$. In pure water or a neutral solution the concentrations of hydrogen and hydroxyl ions are alike, and each is equal to $10^{-7}N$. If sufficient acid is added to make the hydrogen-ion concentration $[H^+]$ equal, for example, to $10^{-3}N$, the hydroxyl-ion concentration $[OH^-]$ automatically becomes $10^{-11}N$.

In order to avoid the use of cumbersome decimal fractions to express hydrogen-ion concentrations, a simple method known as the *pH system* was devised and is now in nearly universal use. The pH of a solution is equal to the numerical value of the exponent in the denominator of the fraction that expresses the hydrogen-ion concentration. (In more mathematical language the pH is the negative logarithm of the concentration of hydrogen ions; *i.e.*, $\text{pH} = -\log c_{\text{H}^+}$.) For example, in a *neutral* aqueous solution, in which the hydrogen-ion concentration is $10^{-7}N$ or $1/10^7N$, the pH is 7. The relations between these different forms of expression is illustrated in the following table.

METHODS OF EXPRESSING HYDROGEN-ION CONCENTRATION IN TERMS OF NORMALITY

Fraction	Decimal	Exponential	pH
1	1	$1/10^0 = 10^0$	0
1/10	0.1	$1/10^1 = 10^{-1}$	1
1/100	0.01	$1/10^2 = 10^{-2}$	2
1/1000	0.001	$1/10^3 = 10^{-3}$	3
1/10,000	0.000,1	$1/10^4 = 10^{-4}$	4
1/100,000	0.000,01	$1/10^5 = 10^{-5}$	5
1/1,000,000	0.000,001	$1/10^6 = 10^{-6}$	6
1/10,000,000	0.000,000,1	$1/10^7 = 10^{-7}$	7
1/100,000,000	0.000,000,01	$1/10^8 = 10^{-8}$	8
....	....	....	..
1/100,000,000,000,000	0.000,000,000,000,01	$1/10^{14} = 10^{-14}$	14

In the pH system, used throughout this book, an increase in pH represents a decrease in acidity and vice versa. Actually the scale represents both acidity and alkalinity, the customary dividing line between which is a neutral solution, having a pH of 7. Solutions with a lower pH than 7 are said to be acid, and those with a higher pH than 7 are alkaline. The acid copper, chromic acid, acid zinc and acid tin baths and most nickel baths have pH values below 7, and all cyanide baths are alkaline, *i.e.*, have pH values above 7.

It is important to distinguish between the concentration of acid in a solution and the concentration of hydrogen ions. The latter, measured in terms of pH, expresses the degree of acidity. (A closely analogous relation is that between the quantity of heat, *e.g.*, in calories, in a given volume of solution and the temperature or degree of heat of that solution.) This distinction is illustrated by the properties of two normal solutions containing, respectively, hydrochloric acid, HCl, and acetic acid, $HC_2H_3O_2$. A given volume of each solution will neutralize the same volume of a normal solution of sodium hydroxide to form, respectively, sodium chloride, NaCl, and sodium acetate, $NaC_2H_3O_2$. In that sense the solutions are equal in their concentrations of acid. If, however, the pH of each of these solutions is measured, the *N* HCl will have a pH of approximately 0 corresponding to a normal hydrogen-ion concentration, while the *N* acetic acid will have a pH of about 3. In other words, the hydrochloric acid is a much stronger acid than the acetic acid of equivalent concentration. Most organic acids, including hydrocyanic acid, are weak acids.

METHODS OF MEASUREMENT. 1. Hydrogen electrode. The primary standard for measuring pH is the *hydrogen electrode,* which usually consists of platinum coated with spongy platinum black, which is saturated with hydrogen gas that bubbles over it. The potential of this electrode, measured, for example, against a saturated calomel electrode, serves as a direct measure of the pH, or hydrogen-ion concentration. This method is generally used to determine the pH values of standard buffer solutions that serve to check other electrodes. The hydrogen electrode is not commonly used to measure the pH of plating solutions because it is troublesome to use and is likely to be "poisoned" by oxidizing agents and by cyanides.

2. Quinhydrone electrode. This involves measuring the potential of a gold electrode in a sample of the solution to which quinhydrone has been added. It is more easily applied than the hydrogen electrode and is used to some extent for measuring the pH of nickel baths.

3. Glass electrode. This consists of a thin-walled glass tube within which is a reference electrode such as a calomel electrode. This is immersed in the solution sample, and its potential is measured against another reference electrode. This potential is a measure of the pH. The glass electrode is not much affected by metallic salts or oxidizing agents and can therefore be used in almost all types of plating solutions. Corrections must be made, however, for the effects of alkaline solutions, in which the direct readings are too low. By the use of a special glass in the electrode this error is so reduced as to be negligible for pH values up to about 12. Because of the wide applicability of the glass electrode, it is the most generally used electrometric method for measuring pH.

4. Colorimetric methods. The colorimetric methods for measuring pH all involve the use of *indicators, i.e.,* substances whose colors change with the pH. It is therefore necessary to

standardize the colors of a particular indicator by means of *buffered* solutions (page 78) whose pH has been measured electrometrically. Color standards corresponding to definite pH values are then prepared and used to compare with the color of the solution to be tested.

These color standards may consist of (1) sealed tubes containing buffer solutions and the appropriate indicator, (2) colored glass that reproduces the indicator colors, or (3) colored papers with which the color produced on a similar strip of indicator paper can be compared.

One objection to colorimetric measurements is that they are affected by *salt errors*, depending on the concentrations of the salts in the solution. For most nickel-plating baths this error amounts to about 0.5 pH, which should be subtracted from the observed value to get the true pH. (In certain commercial pH sets for use with nickel baths this average correction has been applied to the pH values of the standards.)

The most common colorimetric method for pH involves the use of sealed standard tubes whose colors correspond to successive pH values for a given indicator (usually at intervals of 0.2 pH). In a suitable device the colors are compared in such a way that any color of the plating bath is compensated. For example, in some procedures the comparison involves six tubes, arranged as follows:

$$\begin{tikzcd}
A & B & C \\
D \arrow[u] & E \arrow[u] & F \arrow[u]
\end{tikzcd}$$

A and C = standard indicator pH tubes
D and F = bath sample with no indicator
B = bath sample plus indicator
E = water

The total color in each pair of tubes represents the sum of equal thicknesses of water, bath sample, and indicator. When the color of $B + E$ matches $A + D$ or $C + F$, the pH is equal to that of the standard tube A or D. If the color is intermediate, the pH is usually reported as the mean of the two standards. The standard color tubes are usually stable for considerable periods, especially if kept away from direct sunlight.

The choice of indicator depends upon the pH range to be measured. Most of the pH indicators have a useful range of about two units, as shown in Table 13 (Appendix). When observed values come near the extremes of a given indicator, they are less accurate and should be checked with another indicator. With care, colorimetric measurements can be made to ±0.1 pH, while electrometric measurements can easily be made to ±0.05 pH.

CONTROL OF pH. When experience has shown that a certain pH value (or range) yields the desired performance and a measurement of the pH shows that it is too high or too low, it can readily be adjusted to the desired value. This is accomplished by adding acid if the pH is too high and alkali if it is too low. In general, these additions should be selected so as to make no other marked change in the composition of the bath. If the latter contains chlorides or sulfates, addition of hydrochloric or sulfuric acid, respectively, will merely change slightly the content of chloride or sulfate; hence these acids are most commonly used, for example, in nickel baths. If the bath contains sodium or ammonium salts, additions of sodium or ammonium hydroxide are logical. In many cases a basic compound of the principal metal salt, *e.g.*, nickel carbonate or hydroxide, is used to raise the pH, as thereby no new salts are formed. In such cases it is preferable to use freshly precipitated compounds, which should be kept moist till used, as these dissolve more rapidly and completely than the dried compounds.

The amount of acid or alkali required to produce a given change in pH depends upon the bath composition and especially upon its buffer properties. A buffered solution is one in which a relatively small change in pH is caused by a given addition of acid or alkali. In general, this condition exists if a salt of a weak acid or base is present. For most baths, especially those operated between pH 3 and 10, a buffer salt is advantageous because then the pH of the bath remains more nearly constant if there is a small difference in the anode and cathode efficiency. (Whenever the anode efficiency exceeds the cathode efficiency, the pH tends to rise and vice versa.)

The use of boric acid (a very weak acid) in nickel baths operated around pH 5 illustrates the behavior of a buffered solution (Fig. 17). It can be seen that between pH 4 and 6, more acid (or alkali) is required to make a given change in pH in a solution containing boric acid than in one containing only nickel sulfate. By making a titration curve for a given type and composition of bath, it is possible to compute the amount of acid necessary to bring the pH to the desired value. If, however, much suspended basic material (such as ferric hydroxide in a nickel bath) is present, it will dissolve in and hence consume some of the acid that is added to reduce the pH. Either dissolved or suspended iron compounds may interfere with colorimetic pH determinations. For these and many other reasons it is desirable to have all plating baths frequently purified and filtered.

Effects of pH. The effects of pH in acid baths, *i.e.*, below pH 7, are more definite and better understood than in alkaline baths, in which pH control is more recent. As previously noted, the pH of the cathode film tends to be higher than that of the body of solution if the cathode efficiency is less than 100 per cent. This and related changes in the composition and structure of the cathode film have a direct effect upon the cathode efficiency and the composition and properties of the deposit.

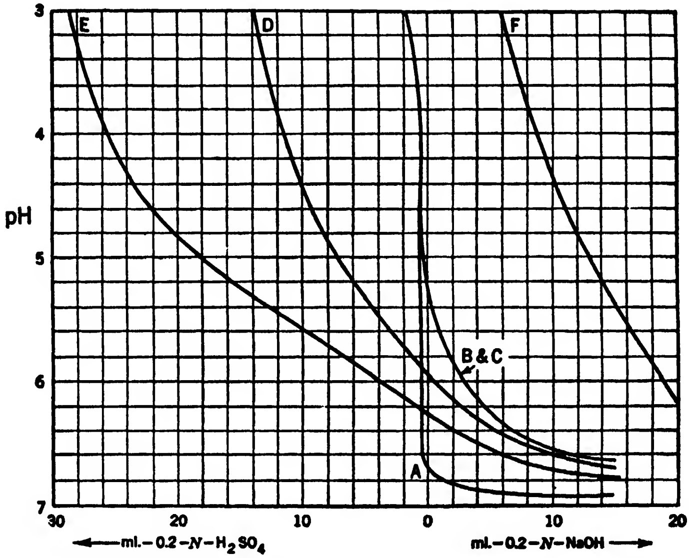

Fig. 17. Buffer action in nickel solutions.[1] Titration curves for 50 ml. Curve *A*: *N* $NiSO_4$. Curve *B*: *N* $NiSO_4$; 0.5*M* H_3BO_3. Curve *C*: *N* $NiSO_4$; 0.5*M* H_3BO_3; 0.2*N* NaCl. Curve *D*: *N* $NiSO_4$; 0.5*M* H_3BO_3; 0.1*N* NaF. Curve *E*: *N* $NiSO_4$; 0.5*M* H_3BO_3; 0.2*N* NaF. Curve *F*: *N* $NiSO_4$; 0.5*M* H_3BO_3; 0.1*N* HF.

The pH reached in the cathode film under otherwise uniform conditions depends upon the pH in the body of solution. In

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[1] The pH values on these curves are uncorrected colorimetric readings and are probably about 0.5 pH too high. They should therefore be used merely to illustrate the relative buffer properties and not the exact pH of the specified solutions.

general the use of a low pH in the bath will result in a lower pH in the cathode film than in a bath with higher pH. This will result in a lower cathode efficiency and in less tendency for basic material to be included in the deposit, which will hence tend to be softer. A low pH in the bath permits the use of higher current densities in the bath to produce a sound deposit at a relatively high efficiency. These principles are illustrated by the *low pH* nickel baths used in the last fifteen years, for both plain and bright nickel deposits (page 372). For the latter type of bath the pH also affects the form and behavior of the organic addition agents or brighteners, especially if these are colloidal or give rise to the formation of colloids in the cathode film. Qualitatively it may be concluded that the use of low pH baths, especially of metals less noble than hydrogen, *e.g.*, nickel and zinc, results in purer, softer deposits and permits use of higher current densities. In the more acid baths, such as the copper sulfate, lead fluoborate, and chromic acid baths, the pH (usually less than 1) is not critical and has less marked effects on the bath performance or the deposits.

All cyanide baths are alkaline, with pH values from about 9 for those like silver which do not contain much free cyanide to about 13 for those like cadmium and zinc which contain both free cyanide and free alkali. All cyanide baths contain sodium carbonate, formed by decomposition of the cyanide. Carbonates also hydrolyze to form alkaline solutions. Measurement of the pH of cyanide baths indicates the concentration of hydroxyl ions. For example, in a bath with a pH of 10 the concentration of hydroxyl ions is about $10^{-4}N$, and in one with a pH of 14 the hydroxyl-ion concentration is about normal, N. Since the cyanides and carbonates do not yield pH values much above 11, any higher pH values indicate the presence of actual free alkali, *i.e.*, NaOH or KOH.

In one of the few papers[1] on the pH of cyanide baths, exploratory tests on copper, zinc, cadmium, silver, and brass baths showed that the effects of pH, *e.g.*, on anode and cathode efficiency, are highly specific. In brass plating, the pH also affects the ratio of copper and zinc in the deposits. Control of cyanide plating baths by pH measurements is practicable and useful, but much more study is required to explain, much less predict, the effects of pH in a particular bath. Much less is known about the solubility and

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[1] HOGABOOM, G. B., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 24, p. 713, 1937.

equilibrium relations of the compounds, such as cyanides, carbonates, and hydroxides, that are present in alkaline baths than about the common constitutents of acid baths.

Addition Agents. Early in the development of electrodeposition it was learned that addition of small quantities of certain organic substances, *e.g.*, to acid copper baths, resulted in smoother, finer grained, and harder deposits. The most effective of these early addition agents were colloidal proteins, such as glue, gelatin, and albumen. Glue is still the principal addition agent used in copper-refining baths. These addition agents are most useful in acid baths of those metals, such as copper, lead, zinc, and tin, which in the absence of such substances tend to form very coarsely crystalline deposits.

During the period up to about 1930 a very large number of these addition agents were employed or proposed, usually on a purely empirical basis. No complete or satisfactory explanation of their behavior was developed, although it was generally assumed that the addition agents or products derived from them were colloidal and hence (under favorable conditions) migrated to the cathode, where they increased the polarization and were adsorbed into the deposits. This theory of migration and adsorption is supported by the fact that almost all metals deposited in the presence of addition agents contain appreciable quantities of organic matter.

Colloidal solutions, or, more strictly, colloidal suspensions, contain very fine particles of matter, which are, however, larger than the molecules and ions present in *true* solutions. Milk illustrates both types of medium, as it contains truly dissolved substances, such as milk sugar and certain salts, and materials in colloidal suspension, such as the casein and the fat particles. Colloidal particles have an electrical charge, owing to their adsorption of charged ions from the surrounding medium. If the colloids are positively charged, they move toward the cathode when a potential is applied and vice versa. The sign of their charge may depend on the pH of the solution.

While this very simple theory of addition agents accounts qualitatively for some of their principal effects, it does not explain the specific action of a particular agent, which may have widely different effects in somewhat similar solutions of two different metals or even of two salts of the same metal. One possible explanation is that the presence of particular cations or anions may determine the form and charge of the colloids and their behavior, including their coagulation and tendency to be adsorbed in a metal deposit. Another theory is that the organic substances or products derived from them form complex ions with the metals present, and when these ions are discharged at the cathode, the organic material is automatically included in the deposit.

The rapid development of organic addition agents during recent years, especially for bright-nickel plating, has, for the time being, complicated rather than clarified the picture. Many of the brighteners now used are specific chemical compounds, and therefore in time we may expect to correlate their composition and behavior. One difficulty is that in bright-nickel baths several types of additions may be made for specific purposes and each may affect the behavior of the other.

The types of addition agents used in bright-nickel plating will be discussed briefly, not so much with reference to their value in nickel plating as to illustrate the principles involved.

METALLIC COMPOUNDS. Additions of salts of cobalt, zinc, or cadmium are known to yield brighter nickel deposits. Those with zinc or cadmium tend to be brittle. The principal advantage of such additions, especially of cobalt, is that they increase the effectiveness of certain of the organic addition agents.

ORGANIC SUBSTANCES. Compounds such as aryl sulfonic acids may not themselves produce bright deposits, but they increase the solubility and brightening power of other organic compounds.

OTHER ORGANIC COMPOUNDS. Such compounds as formates, aldehydes, and ketones and amino polyaryl amines may yield bright but brittle deposits unless they are accompanied by compounds of the second class.

WETTING AGENTS. Hydrogen peroxide, which is commonly used to prevent pitting of nickel baths, is likely to oxidize some of the organic additions and thereby be reduced and rendered ineffective. In bright-nickel-plating baths, wetting agents are often added, *i.e.*, substances that reduce the surface tension of the solution and hence decrease the tendency for hydrogen bubbles to stick to a surface (page 85).

It is obvious that with so many possible types of additions (each of which has many examples) to a nickel bath, no simple theory will account for their effects. One property observed in many bright-nickel deposits (and in bright deposits of some other metals) is that they consist of a large number of very thin layers parallel to the surface of the deposits. These layers indicate that in such baths deposition does not take place continuously but in steps, alternated by some other process that prevents or retards metal deposition. The latter process probably involves migration, precipitation, and adsorption of organic material upon the just previously deposited metal layer. Especially in the presence of an excessive amount of an organic addition it has been found that the cathode potential fluctuates in cycles approaching the periods corresponding to the deposition of each layer.

The above simplified and inadequate explanation of addition agents emphasizes the fact that their selection and use are still empirical and that much more fundamental research is required in this field.

Physical Properties of the Bath. Apart from but closely related to the chemical composition of the plating solutions are certain measurable physical properties, which may affect the behavior of the bath. Among these are the following:

Electrical Resistivity. It is obvious that, in order for a metal to be electrodeposited from a solution, the latter must be a conductor of electricity. The most direct effect of the resistivity of the solution is upon the voltage required to produce a desired current density. Assuming that other conditions remain constant, the required bath voltage will be inversely proportional to the conductivity of the solution (or directly proportional to its resistivity). This relation is most important in large-scale operations, where the cost of electrical energy is significant, and in those cases where the available potential, *e.g.*, 6 volts, is barely sufficient to yield the desired current density. On general principles the best conducting solution that is otherwise suitable should be used.

There are, however, practical limitations to the conductivity of many baths. Increasing the concentration of the metal salt usually causes the conductivity to approach a maximum; *i.e.*, there is not so much proportional increase in conductivity in changing from 2 to $4N$ nickel sulfate, for example, as from 1 to $2N$. Hence there is no great advantage, from the standpoint of conductivity, in greatly increasing the metal salt concentration.

Among the common heavy metal salts, the chlorides are better conductors than the sulfates (Table 12, Appendix). For example, an N solution of nickel chloride has over twice the conductivity of N nickel sulfate. Because the solutions of most of the heavy metal salts are not very good conductors, it is customary to add some better conducting substances to the bath. When very acid solutions are employed, addition of a strong acid is desirable, *e.g.*, sulfuric acid to an acid copper bath. Similarly the conductivity of cyanide baths can be greatly increased by the addition of sodium or potassium hydroxide. When it is necessary to employ nearly neutral solutions, well-conducting salts are commonly added. Chlorides are better conductors than sulfates, and ammonium salts are better conductors than sodium salts.

Apart from the effect on the required voltage, there are not many direct benefits from increasing the bath conductivity. However, the same additions that increase the conductivity usually also change other properties. For example, the addition of a strong acid decreases the pH and may decrease the metal-ion concentration. The latter effect is also produced by adding a salt with a common ion, *e.g.*, sodium sulfate to a nickel sulfate bath. As will be discussed shortly, an increase in bath conductivity does not increase the throwing power unless there is also a large cathode polarization. Good conductivity is desirable, but it may not be considered apart from associated factors.

Viscosity of the Solution. A solution of almost any salt has a higher viscosity, *i.e.*, flows less readily, than does pure water, and the viscosity of most solutions increases with their concentration. For example, a nickel sulfate bath with a high content of sodium sulfate is more viscous than is the nickel sulfate solution alone. Few measurements have been made on the viscosity of actual plating baths.

The most obvious effect of a high viscosity is that it increases the *drag out* of the solution, because in a given period of drainage the solution does not flow off so completely. This may represent a serious economic loss, especially in barrel plating, where the drainage is poor.

Another, more profound effect of viscosity is upon the composition and behavior of the cathode film. The rate at which this rises along the cathode is retarded by an increase in viscosity, and hence the cathode film becomes more depleted, and the polarization increases. The viscosity also influences the rate of diffusion of salts (or ions) to the cathode film but does not usually affect the rate of their migration. To the extent that an increase in polarization may be desired, *e.g.*, to improve the throwing power or to produce finer crystals, an increase in viscosity may be desirable. It is, however, difficult to predict the exact effects of a change in viscosity produced by a given addition of salts or of an organic compound or by a change in temperature, because each of these changes may produce either additive or compensating effects. In short, there is no basis for changing or controlling the viscosity of a bath unless a definite benefit has been established.

Surface Tension. On all surfaces, especially of liquids, there are certain attractive forces that set up a tension at the surface. The magnitude of this force, known as *surface tension,* for a given liquid influences its behavior when in contact with gases, solids, or other liquids. One of the most common evidences of differences in surface tension is the behavior of liquids in capillary tubes. If two similar open glass capillary tubes are immersed, respectively, in mercury and in water, it will be found that the level of mercury inside the tube is *below* that outside while the level of the water inside is *above* that outside. This difference results from the facts that the surface tension of the mercury is much greater than that of the water, and that the mercury is pulled away from the glass and does not wet it as does the water.

If now, *e.g.*, by the addition of a substance like soap to the water, its surface tension is made lower, the resultant solution will not rise as high in the capillary as does pure water. This behavior is made use of directly in all cleaning solutions that contain alkalies, soaps, or other *wetting agents.* For present purposes a wetting agent, or *surface-active material,* may be defined as any substance whose addition to a solution reduces its surface tension.

The principal applications of wetting agents in the plating industry are (1) in alkaline cleaning solutions to increase or accelerate their cleansing action, (2) in pickling solutions for the same purpose and to cut down spray by producing a foam blanket, and (3) in plating solutions to reduce or prevent pitting. The last application depends upon the fact that a bubble of gas, either of hydrogen or of air, will have less tendency to stick to a surface in a liquid of low surface tension than in one with high surface tension.

Most commercial wetting agents are salts of organic sulfonic acids. Literally hundreds of these substances are used for such purposes as the application of insecticides, in which they facilitate wetting of the leaves. A much more limited number have been used in bright-nickel-plating baths and cyanide copper baths to reduce pitting. Because they are commonly added in low concentrations and their content is difficult to determine by analytical methods, it is customary to control their addition by measurements of surface tension of the solution.

The principal methods for measuring the surface tension of a liquid are as follows:

1. Measuring the rise of the liquid in a capillary tube.
2. Measuring the size of a drop of the liquid when it just detaches from a horizontal glass tip. This is done by measuring the total volume of a given number of drops, such as 100, or conversely by measuring the number of drops corresponding to a measured volume. This method is called the *drop-weight* method, and the apparatus is a *stalagmometer.*
3. Measuring the force necessary to pull a ring of fine platinum wire from the surface of the liquid in an apparatus known as a *tensiometer.*

In all three of these methods it is customary to standardize the apparatus with pure water, the surface tension of which is 73 dynes/cm at 20°C (68°F). Method 2, using a stalagmometer, is most convenient for plating solutions.

EFFECTS OF THE BASIS METAL UPON THE DEPOSITS

The metal to which the deposit is applied may affect the deposit in numerous ways. The most obvious effect is that of the surface finish of the basis metal on the contours of the deposit. In practically all cases a given deposit produced on a rough surface will be less smooth than that on a finer grained surface. Hence, if a final bright deposit is desired, it is usually more economical to apply a fairly fine finish to the basis metal than to use a rough surface and to increase the amount of buffing or polishing of the deposit. The latter operations represent not only a buffing cost but also a reduction in the thickness and probable protective value of the coating. The effects of changes in crystal structure and surface contour of the basis metal that occur during pressing, drawing, and forming operations upon the quality of the plated coatings are explained by J. D. Jevons.[1]

In general, this effect of the basis metal finish upon the contours of the deposit is more marked with a thin than with a thick deposit. Beyond a certain point, however, the roughness of the deposit may increase with thickness. Deposits from baths with good covering power or from those containing addition agents,

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[1] *J. Electrodepositors' Tech. Soc.,* vol. 20, p. 93, 1945.

e.g., bright-nickel baths, may cover over and smooth up small scratches or defects in the basis metal.[1]

It has generally been assumed that a deposit produced on a rough metal surface will be more porous and hence have less protective value than a deposit on a smooth surface. In a research of the American Electroplaters' Society[2] it was found that, on a good grade of cold-rolled steel, deposits of a given thickness of copper, nickel, and chromium yielded about the same protection in the atmosphere regardless of the finish of the basis metal. The latter ranged from that produced with a 90-grain abrasive to a *superfinish.* The mean values of the finish, measured with a *Profilometer*,[3] varied from 65 to less than 1 *root-mean-square microinches* on these extreme types of finish.

This failure to obtain an effect of basis metal finish upon protective value appears to contradict the previously reported results of W. L. Pinner[4] and of others that roughly polished surfaces lead to more porous deposits. This difference can be explained by the fact that Lux and Blum used cold-rolled steel, which has fewer inclusions than hot-rolled or forged steel. Such inclusions may be revealed by coarser polishing and lead to pores in the coating. Further studies are in progress to check these conclusions with hot-rolled steel and with brass and zinc-base die castings.

In interpreting the above results, it should be borne in mind that the deposits applied to the coarse finishes were not polished or buffed to produce a smooth bright surface. If that were done, there would be a tendency to reduce the thickness on the peaks or even to cut through the deposits there and cause pores.

Another effect of the basis metal is that any nonmetallic or poorly conducting particles in the surface are likely to prevent or retard deposition at those points and hence to cause pores in

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[1] Gardam, G. E., *J. Electrodepositors' Tech. Soc.*, vol. 22, p. 155, 1948, and Willson, K. S., and Du Rose, A. H., *Plating*, vol. 36, p. 246, 1949.

[2] Lux, G. A., and Blum, W., *J. Research Natl. Bur. Standards*, vol. 34, p. 295, 1945, RP 1645.

[3] The Profilometer is a device used to measure and compare surface finishes. The movement of a fine steel stylus across the surface causes the point to fluctuate in accordance with the irregularities of the surface. This movement of the stylus is converted to electrical readings on a scale. The latter values are expressed as the *root mean square*, *i.e.*, the square root of the average of the squares of the values, in *microinches*, *i.e.*, millionths of an inch. A high numerical value represents a rough surface and vice versa. Similar measurements are made with a *Brush surface analyzer.*

[4] *Proc. Am. Electroplaters' Soc.*, vol. 27, p. 137, 1940.

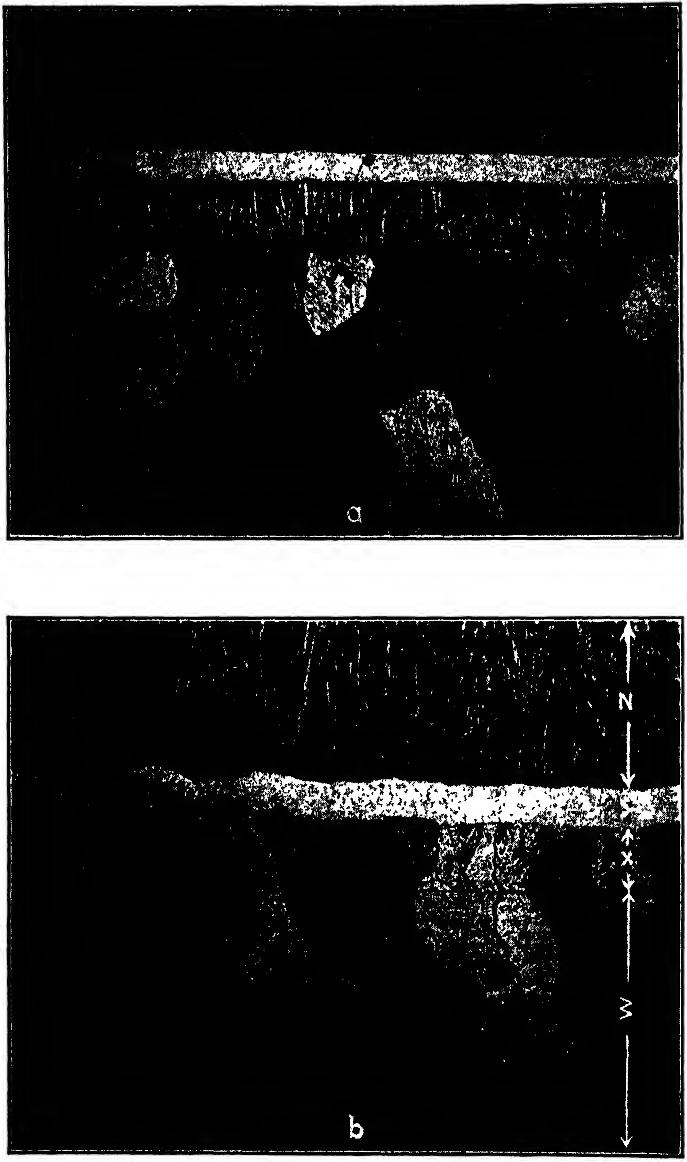

Fig. 18. Section of the chilled side of cast copper, upon which copper was electrodeposited (100 diam.). (*a*) The surface was cleaned but not pickled prior to the electrodeposit. (*b*) The surface was pickled (bright-dipped) after cleaning. The various zones indicated in (*b*) apply also to (*a*), *i.e.*, *W*, base metal; *X*, electrodeposited copper (first layer); *Y*, electrodeposited nickel; and *Z*, electrodeposited copper (second layer).

the deposit. This behavior justifies the use for fine plated finishes of *clean* steel, *e.g.*, a high grade of cold-rolled steel. Unfortunately there are no quantitative standards for the inclusions in steel.

Another less obvious but possibly important effect of the basis metal is related to its actual crystal structure and grain size. In 1916 G. B. Hogaboom[1] predicted this effect of the basis metal. In 1921 he noticed in published photographs of deposits that some of the copper deposit crystals were continuations of the crystals in the copper basis metal. This observation was confirmed by W. Blum and H. S. Rawdon[2] (Fig. 18) and by A. K. Graham.[3] Later, A. W. Hothersall[4] showed that such reproduction of the basis metal structure may occur even with dissimilar metals that may vary appreciably in lattice structure and spacing. The principal significance of these observations is that the structure of deposits cannot be studied apart from the basis metal and that control of the latter may help to obtain a deposit having desired structure and physical properties, including adhesion (page 127).

THROWING POWER AND THE DISTRIBUTION OF DEPOSITS

General Principles. It is not sufficient for an electroplater to produce deposits having the desired appearance and properties. He must be able to apply these coatings in such a way as completely to cover the article with a deposit as nearly uniform in thickness as practicable. The latter goal is especially important in view of the modern requirements for a certain minimum thickness on significant surfaces. Economy demands that this minimum thickness be obtained while depositing as little metal as possible on the rest of the surface. On the many irregularly shaped surfaces that must be plated it is not practicable to obtain an even approximately uniform thickness, but this goal should always be kept in mind.

The term *throwing power* was first applied to plating solutions as a qualitative measure of their ability to deposit metal over the entire surface of an article. This meaning is better expressed by

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[1] *Trans. Am. Electrochem. Soc.*, vol. 29, p. 369, 1916.

[2] *Trans. Am. Electrochem. Soc.*, vol. 44, p. 303, 1923.

[3] *Trans. Am. Electrochem. Soc.*, vol. 44, p. 427, 1923.

[4] *J. Electrodepositors' Tech. Soc.*, vol. 7, p. 115, 1932.

the term *covering power*. In recent years the term throwing power has been used principally as a measure of the distribution of the deposits, *i.e.*, of their relative thickness on different parts of an article. In practice, the two terms are closely related, since solutions with poor throwing power usually have poor covering power and vice versa. As will be seen, it is much easier to attach a quantitative significance to throwing power than to covering power.

The factors that determine the distribution of metal deposits are now well understood even though their combined effects cannot always be predicted. They can be briefly explained as follows:

Primary Current Distribution. On any article of a given shape, placed in a certain position with respect to the anodes, tank walls, and other cathodes, an applied potential will produce a certain distribution of current to which the name *primary current distribution* is applied. This distribution is independent of the resistivity or other properties of the surrounding solution but will be changed if any polarization occurs at either the anode or cathode. This primary current distribution is determined solely by the shape and position of the electrodes.

For certain simple geometric shapes it is possible to compute this primary current distribution, usually on the basis of certain simplifying assumptions. It cannot be calculated exactly for complicated shapes. The most exhaustive studies of this subject from the standpoint of electrodeposition were conducted by C. Kasper and published in a series of papers,[1] which should be consulted for details.

There are three arrangements in which it is possible to obtain a perfectly uniform current distribution, *viz.*, linear, cylindrical, and spherical conductors. These are represented diagrammatically in Figs. 19, 21, and 22. In Fig. 20 the solid lines represent *equipotential* surfaces and the lines perpendicular to them are *lines of current flow*.

The linear conductor (Fig. 19) may be represented by a rectangular box with plane parallel electrodes, such as is used for measuring throwing power. The equipotential surfaces are planes that are parallel to the electrodes and equally spaced. The current density over each electrode is uniform, and the

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[1] *Trans. Electrochem. Soc.*, I, vol. 77, p. 353, 1940; II, vol. 77, p. 365, 1940; III, vol. 78, p. 131, 1940; IV, vol. 78, p. 147, 1940; V, vol. 82, p. 153, 1942.

resistance and hence the *IR* drop are uniform throughout the length of the box.

If, however, as shown in Fig. 20, one electrode (*e.g.*, the cathode) is inclined, the equipotential surfaces are no longer plane and parallel. Because they are closer together near the obtuse angle *B* than near the acute angle *C*, the current density is higher at *B* than at *C*. As we proceed away from the angle, the equipotential surfaces ultimately (at *H*) become plane and parallel. If the anode had been closer to the cathode than this point *H*, moving it as far away as *C* would have made the current density more uniform in the angles, but its movement beyond *H* would have had no such effect. This same relation applies with more complicated shapes and systems.

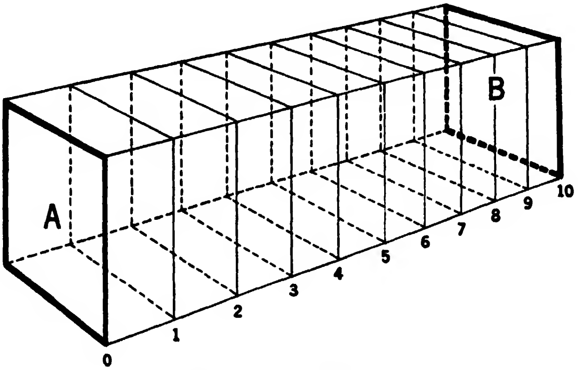


FIG. 19. Diagram representing *linear* conductor.

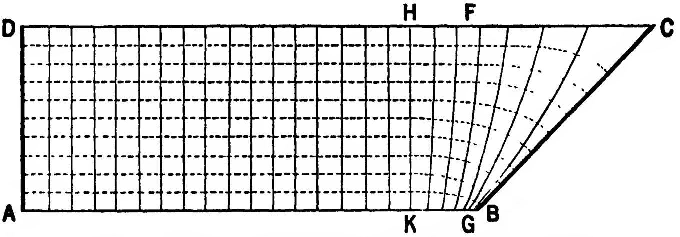
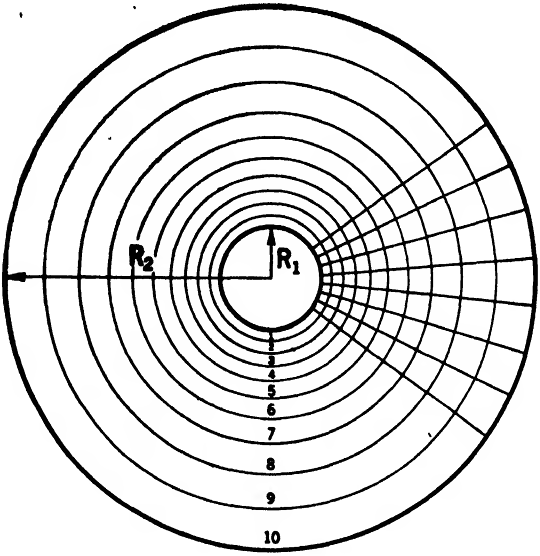


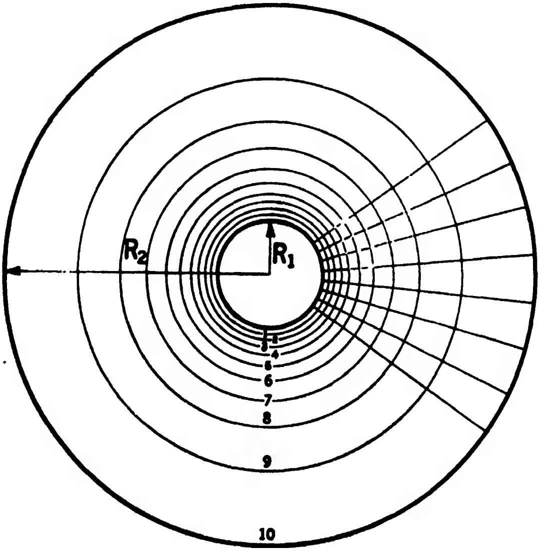
FIG. 20. Effect of inclining one electrode (as in Hull cell).

With two concentric cylinders (Fig. 21) the current density is uniform over each cylinder. As, however, the same current passes from the outer cylinder to the inner cylinder, which has a smaller area, the current density on the inner cylinder is higher. This is



CYLINDERS

FIG. 21. Equipotential surfaces and current lines between concentric cylinders.



SPHERES

FIG. 22. Equipotential surfaces and lines of flow between concentric spheres.

illustrated by the fact that the equipotential surfaces are closer to each other as we approach the inner cylinder. The potential drop (IR) varies as the logarithm of the distance from the center, and the total resistance of the system having a specified length depends solely upon the ratio of the radii of the two cylinders regardless of their actual dimensions.

With concentric cylinders the current lines are radial. Therefore, to plate a section of a cylinder uniformly, the side walls of shields should be placed radially.

With concentric spheres (Fig. 22) the current density on the inner sphere is higher, because the areas of two spheres vary as the squares of their radii. If the outer sphere is relatively large, the resistance of such a system depends almost entirely on the radius of the inner sphere.

These few simple examples illustrate the methods by which the primary current distribution can be computed. In more complex systems, such as a point to a plane, a line to a plane, eccentric cylinders, or angles, the current density is not uniform. It is possible by more involved computations to calculate the distribution of current in many such systems and especially the effects of changes in shape or position of the electrode. It must be emphasized, however, that the current distributions so computed are *primary current distributions*, which exist only when there is no polarization.

Except in the few simple systems discussed, the primary current density is not uniform and may vary on different parts of commercial articles by as much as 5 or 10 to 1. To make it more nearly uniform, we can employ (1) parallel or concentric anodes, (2) nonconducting shields to reduce the current density at certain points, or (3) conducting wires, or *thieves*, to detract the current from such points. Moving the anode farther from the cathode is an advantage only up to a certain distance.

Effect of Polarization. As explained on page 45, polarization, *e.g.*, at a cathode, represents a voltage drop that exists in addition to the IR drop caused by the passage of current through the bath. In general, this polarization increases with an increase in current density. Hence, on any irregularly shaped article the polarization is greatest at the points of highest current density. This fact makes it more difficult for the current to reach those points than if there were no polarization. Consequently, the distribution of current, *e.g.*, the ratio of the current densities at two points, becomes more nearly uniform than corresponds to the primary current distribution. The higher polarization at the points of high current density makes the current distribution more nearly uniform, not by making it easier for current to pass to the far points, but by making it more difficult to pass to the near points. Whenever the cathode polarization increases rapidly with current density the resultant current distribution, *i.e.*, the *secondary current distribution*, is more uniform than the primary current distribution.

This simple principle is illustrated by the well-known difference in throwing power of acid and cyanide copper baths. As shown in Fig. 6 the cathode polarization in an acid copper bath is relatively small and the curve soon becomes nearly vertical. In the cyanide copper bath, however, the polarization curve is more inclined from vertical and continues to increase up to fairly high current densities. The marked difference in throwing power of these two types of copper baths is principally the result of this difference in polarization.

Effect of Conductivity. As stated above, the primary current distribution in a given system is not influenced by the conductivity of the bath. If there were no polarization, the conductivity would not affect the distribution of current or of metal. If, however, there is appreciable polarization (as is true in all plating baths at the customary current densities), an improvement in conductivity magnifies the effect of this polarization. An increase in conductivity reduces the *IR* drop in the bath. Hence, if a certain total bath voltage is applied, a given polarization, *e.g.*, 1 volt, represents a larger part of the total voltage and has a greater effect upon the secondary current distribution. In general an increase in conductivity improves the throwing power.

Effect of Cathode Efficiency. The above discussion refers merely to the distribution of current. If in a given bath the cathode efficiencies are equal at all current densities, the resulting *metal distribution* will be the same as the current distribution. If, however, especially as in low pH nickel and chromium plating, the cathode efficiency increases with the current density, the metal distribution will be less uniform than the current distribution and may more than counteract any benefit of polarization. If, as occurs in some baths, the cathode efficiency decreases with current density, the metal distribution is thereby made more uniform and the throwing power is increased.

Methods of Measuring and Expressing Throwing Power. Because the throwing power of a given bath is the result of a number of factors that cannot be conveniently evaluated and correlated, many efforts have been made to measure the throwing power directly. Consideration of the above principles shows that the main value of such measurements, however made, is to detect and compare large effects produced by a change in bath composition or in operating conditions. The throwing power of a solution is not a single, measurable property of that bath, even under specified operating conditions. It will depend upon the shape of the article and its position with respect to anodes or other cathodes, cell walls, and solution surface. Since no single geometric device can reproduce all these factors for all possible shapes and conditions, the most that any such test can show is whether the throwing power of one bath is decidedly different from that of another. Small measured differences are usually insignificant and may be misleading, because the extent to which one factor will compensate for another will vary with such conditions as the distance from the anode to the cathode, and their relative areas.

Measurements of throwing power are chiefly of pedagogical value and serve to show the direction and magnitude of significant changes, *e.g.*, those over 5 per cent on the conventional scales. Because of these inherent limitations, detailed discussion of methods of measurement and expression is unwarranted. They will therefore be summarized briefly.

Conventional Shapes. Two devices used to measure throwing power (or, more strictly, covering power) are the bent cathode and the cavity scale.

BENT CATHODE. In the bent cathode method[1] the cathode consists of a rectangular metal strip, bent to an angle of 90 deg, and placed at a specified distance from a flat anode (Fig. 23). This method has been used principally to study chromium baths by observing the extent to which chromium is deposited within the angle. The results are approximately parallel to the throwing powers obtained in a Haring cell. In a modification of this device[2] the bent cathode is cut into strips that can be weighed

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[1] SIZELOVE, O. J., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 16, p. 15, 1929. PINNER, W. L., and BAKER, E. M., *Trans. Am. Electrochem. Soc.*, vol. 55, p. 315, 1929. FARBER, H. L., and BLUM, W., *J. Research Natl. Bur. Standards*, vol. 4, p. 27, 1930, RP 131.

[2] ONITSCHENKO, A., *Z. Elektrochem.*, vol. 39, p. 815, 1933. PORTEVIN, A., and CYMBOLISTE, M., 14'*eme Congr. chim. Ind.*, vol. 2, 1934.

before and after plating and thereby yield data on the distribution of thickness.

Cavity Scale. In the cavity scale[1] a number of cylindrical holes with the same diameter and varying depths are drilled into a metal bar (Fig. 24). The deepest hole that is completely plated defines the covering power, *e.g.*, in terms of the ratio of depth to diameter. A single tube closed at one end can also be used, and the depth to which the deposit penetrates is used as a measure of the covering power.

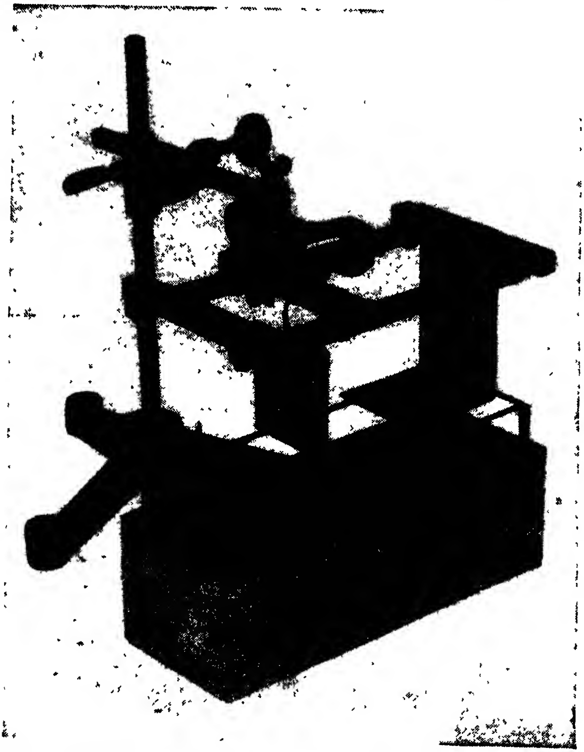

Fig. 23. Bent cathode, used to measure the *covering power* in chromium plating.

Schematic Devices. Most quantitative measurements of throwing power have been made in boxes in which the electrodes represent but do not imitate parts of articles that may be plated. Most of these methods involve the weighing and comparison of deposits on two or more plates, which is by far the most accurate method of measuring the average thickness of deposits.

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[1] Pan, L. C., *Metal Ind.* (*N.Y.*), vol. 28, p. 271, 1930.

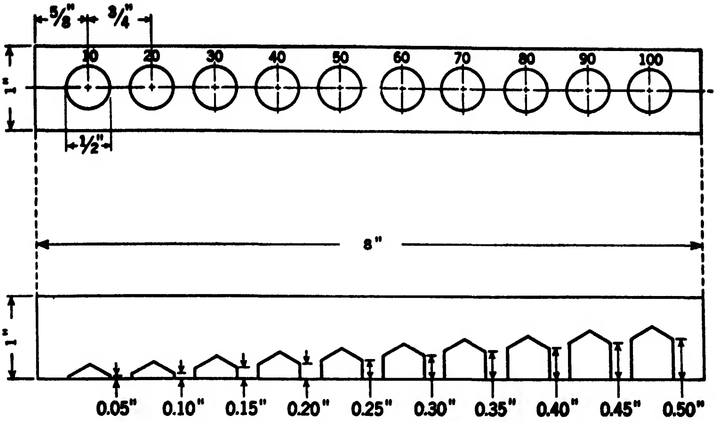

FIG. 24. Cavity-scale used to measure throwing power. (*Pan.*)

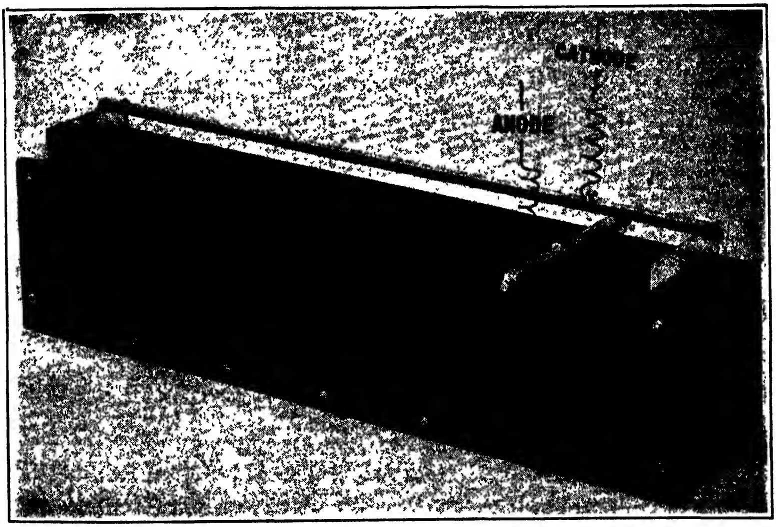

FIG. 25. Throwing-power box. (*Haring and Blum.*)

PLANE, PARALLEL ELECTRODES (Fig. 25). In this method[1] two parts of a hypothetical cathode are represented by means of a linear conductor. Two plane parallel cathodes are connected by a good conductor. Each cathode completely fills the cross section

[1] HARING, H. E., and BLUM, W., *Trans. Am. Electrochem. Soc.*, vol. 44, p. 313, 1923.

of a rectangular box at such distances from a plane gauze anode that a certain primary current distribution on the two plates is obtained, *e.g.*, 5 to 1. On each cathode the current density is uniform. A gauze or other perforated anode is used in order to reduce the polarization on the two sides of the anode, on which different anode current densities prevail. The vessel is filled with the solution to a specified depth, and a measured current is passed through the solution to give a desired average current density. The two cathode plates are weighed before and after the test to determine the weights of the deposit.

As measured in such a box, the throwing power is expressed as the percentage improvement of the metal ratio M above the primary ratio P. If the far plate is five times as far from the anode as the near plate, the primary ratio is 5. If in a given experiment the weight of deposit on the near plate is four times that on the far plate, the metal ratio is 4; hence the metal distribution is more uniform than would be expected from the positions of the two plates.

$$T \text{ (throwing power)} = \frac{P - M}{P}$$

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

If in another experiment, the metal ratio is 6,

$$T = \frac{5 - 6}{5} = \frac{-1}{5} = -20 \text{ per cent}$$

It must be emphasized that a numerical value for throwing power is meaningless unless all factors are defined, including the size of the box and electrodes, the distance of each cathode from the anode (hence the primary ratio), the solution composition and temperature, and the average current density. For economy and convenience a box with a solution cross section of 5 by 5 cm (2 by 2 in.) and a total length of 15 cm (6 in.) is recommended. The values are directly comparable only when measured in the same size box.

Owing to the fact that more current passes through the portion of solution between the anode and the near cathode than through the other compartment, the former solution tends to become warmer. If the resistivity of the solution and the current density are both high, this difference in temperature will be sufficient to change the ratio of the resistances in the two paths. B. K. Braund[1] suggests a correction based on the temperatures of the two compartments. In many cases it will be more convenient to transfer part of the solution from one compartment to the other at intervals to equalize the temperature. It is also possible, but difficult, to hold the temperature of the whole cell nearly constant by placing it in a well-circulated oil bath.

S. Field[2] has suggested a modification in which the two parts of the cathode are on the same side of the anode, made of sheet metal. Ammeters are used to measure the currents to each cathode, which express the secondary current distribution but not the throwing power unless the cathode efficiencies are equal.

Several authors[3] have suggested modification of the equation for throwing power so that, when the latter (also called by them the *throwing efficiency*) is 100 per cent, the metal distribution is perfectly uniform. Their equation is

$$T \text{ efficiency} = \frac{P - M}{P - 1}$$

If in a hypothetical case the primary ratio is 5 and the metal ratio is 1 (*i.e.*, the deposit is entirely uniform)

$$T \text{ efficiency} = \frac{5 - 1}{5 - 1} = 100 \text{ per cent}$$

instead of (as on page 98)

$$T \text{ (throwing power)} = \frac{5 - 1}{5} = 80 \text{ per cent}$$

The advantage sought is illusory, because in no known plating solution is it possible to approach a uniform distribution of deposit on a cathode having a primary ratio of 5 or more, *i.e.*, when throwing power becomes important. It was first assumed that the throwing efficiency for a given bath would be more nearly uniform with a change in current density. However Pan showed that this is true only if the throwing power is positive. If it is negative, the throwing efficiency is less uniform than the throwing power.

INCLINED-PLANE ELECTRODES. A large number of ingenious methods for measuring throwing power have been devised, but not extensively used. W. Pfanhauser and G. Elsner, O. Busse,

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[1] *J. Electrodepositors' Tech. Soc.*, vol. 7, p. 19, 1931.

[2] *J. Electrodepositors' Tech. Soc.*, vol. 7, p. 83, 1932.

[3] Including L. C. PAN, *Trans. Am. Electrochem. Soc.*, vol. 58, p. 423. 1930.

and E. Mantzell all use a box with an inclined cathode on which the metal distribution is measured. The arrangement is similar to that in a Hull[1] cell, in which the properties of the deposit at different parts of the inclined cathode are used to define the effective current density range of the solution under those conditions. Such observations can be used to estimate the content of some constituent, such as of a brightener in a plating bath.

TANDEM-PLANE ELECTRODES. W. G. Horsch and T. Fuwa[2] measured the weights of deposit received by three or more cathodes in tandem in a plane perpendicular to the anode.

PERPENDICULAR-WIRE CATHODE.[3] The same idea was used by A. J. Krombholz and by R. Harr in the form of a wire placed perpendicular to a plane cathode. In each case the ratio of the thickness of deposit at different distances from the anode was used as a measure of throwing power.

PERFORATED CATHODE. K. Arnt and O. Clemens[4] determined the amount of metal deposited on a plane cathode that was placed back of another cathode having a circular hole in it.

CONCENTRIC ELECTRODES. A. Portevin and M. Cymboliste[5] used a cathode consisting of two concentric spirals and determined the ratio of the weights of metal on the inner and outer spirals.

Available evidence indicates that each of these devices yields qualitatively similar results for major differences in throwing power but that none can be relied upon to predict the exact performance of a given bath with a cathode of irregular shape. Such results can be obtained only by trials with the actual articles. Preliminary measurements of throwing power may serve, however, to indicate the most promising directions for trial.

[1] HULL, R. O., *Proc. Am. Electroplaters' Soc.*, p. 52, 1939.

[2] *Trans. Electrochem. Soc.*, vol. 41, p. 363, 1922.

[3] *Trans. Electrochem. Soc.*, vol. 68, p. 425, 1935.

[4] *Chem. Ztg.*, vol. 46, p. 925, 1922.

[5] *Compt. rend.*, vol. 201, p. 819, 1935.

CHAPTER V

THE SELECTION, SPECIFICATION, AND INSPECTION OF ELECTRODEPOSITS

During the past fifteen years there have probably been more research and more progress in the methods of testing plated coatings than in any other phase of the plating industry. The extension of plating to new applications, including many military devices, and especially its use on a very large scale, for example, in the automobile industry, have created demands for coatings of consistently high quality. Early attempts to specify such coatings showed the lack of reliable data regarding the properties required for a given purpose and suitable methods for measuring those properties. To meet this need, investigations have been conducted in several countries by industrial laboratories and technical organizations. Many of the problems require and are receiving further study; hence any summary such as the following is necessarily incomplete, and the conclusions are subject to change in the light of investigations now in progress.

PROPERTIES AND TESTS

Before attempting to discuss the basis and content of specifications to meet particular needs, it may be desirable to consider the significance and measurement of those properties upon which the choice is likely to rest. In the last analysis an electrodeposited coating is used because of some desirable properties and usually in spite of some undesirable properties or limitations.

The principal properties that determine the value of a metallic coating for a given purpose are its thickness and adhesion and the protection it provides against corrosion and abrasion. Color and luster are minor but sometimes important properties. As protection is almost always required, it might seem that its consideration should take precedence. Practically, however, it has been found that the thickness is more important than any other single factor and is therefore almost invariably included in specifications.

Thickness. *Significance.* The importance of the thickness of coatings of the *sacrificial* metals, such as of zinc and cadmium, is obvious, because the value of such coatings rests upon their tendency to corrode more readily than the basis metal and to thus protect the latter. A thick coating of a metal that is dissolving (under the conditions present) at a given rate will naturally last longer than a thinner coating. Numerous exposure tests[1] have shown that, especially in an industrial atmosphere, the protection furnished by zinc and cadmium coatings is practically proportional to their thickness. This behavior is illustrated by Curve *A* in Fig. 26.

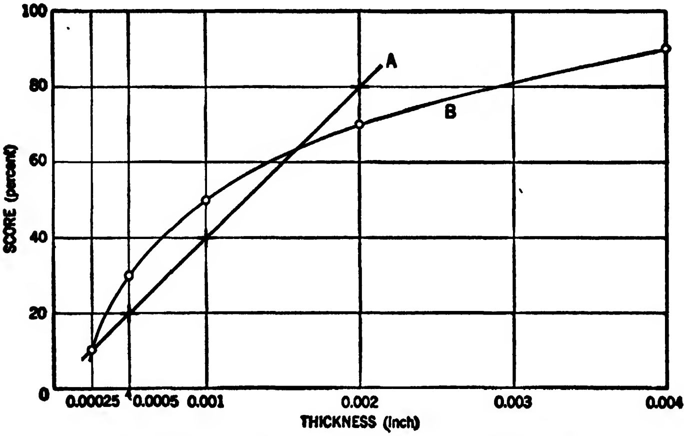

FIG. 26. Typical curves for failure of various plated coatings, in, for example, one year's exposure. Curve *A*: Zinc and cadmium coatings on steel. Curve *B*: Copper, nickel, chromium coatings on steel.

Any similar relation with coatings of noble metals such as those of copper and nickel is not obvious, since their protection depends primarily upon their porosity. While the latter undoubtedly varies to some extent with the conditions of preparation and deposition, experience shows[2] that the most practical method

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[1] HIPPENSTEEL, C. L., BORGMAN, C. W., and FARNSWORTH, F. F., *Proc. ASTM*, vol. 30 (II), p. 456, 1930. HIPPENSTEEL, C. L., and BORGMAN, C. W., *Trans. Am. Electrochem. Soc.*, vol. 58, p. 23, 1930. PASSANO, R. F., *ASTM Symposium*, vol. 49, 1934. Report of Subcommittee VII on field tests of metallic coatings, *Proc. ASTM*, vol. 33 (I), p. 149, 1933. BLUM, W., STRAUSSER, P. W. C., and BRENNER, A., *J. Research Natl. Bur. Standards*, vol. 16, p. 185, 1936, RP 867.

[2] BLUM, W., STRAUSSER, P. W. C., and BRENNER, A., *J. Research, Natl. Bur. Standards*, vol. 13, p. 331, 1934, RP 712. BAKER, E. M., *J. Soc. Auto-*

of reducing the porosity and increasing the protective value is to increase the thickness. In general, this improvement in quality is not, as with zinc and cadmium, proportional to the thickness, but as shown in Curve *B* of Fig. 26, a given increase (*e.g.*, 0.0002 in.) in the thickness of a thin coating has a more pronounced benefit than a similar increase in the thickness of a thick coating. Very roughly, the same actual increase in protection is obtained by a given *proportional* increase in thickness. Purely as an example, in Curve *B* each doubling of the thickness improves the quality (for a given scale and period of exposure) by 20 per cent. Therefore, to obtain a nearly perfect coating (100 per cent) for the period considered it will require a much greater increase in the thickness of nickel than of zinc above those thicknesses which yielded scores of 80 per cent.

In any discussion of coating thickness it is necessary to distinguish clearly between the *average* thickness over the entire plated surface and the *local* thickness, *i.e.*, the thickness at a particular point, and especially at the thinnest spot. The above considerations show that the protective value of a coating usually depends more upon the minimum than upon the average thickness; *i.e.*, a coating is only as good as its thinnest part. Consequently, most plating specifications are now based on the minimum thickness *on significant surfaces.* The latter term excludes those parts of the surface which are concealed or unimportant or on which it is not economically practicable to apply the designated thickness. (The designation of significant surfaces upon a particular article is usually decided by the parties concerned and may conveniently be indicated on the specification drawings.)

Although the measurement of local thickness is assuming increasing importance, some specifications are still based on the average thickness. One reason for the latter usage is that it is easier for the plater to estimate the time required at a given current density to produce a given average thickness than a specified minimum thickness on any part of the article. Even when the average thickness is specified, particularly on small articles or on articles made of numerous small parts, it is necessary to allow a considerable margin to ensure that the required aver-

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motive Engrs., vol. 15, p. 27, 1924. JACQUET, P., *Bull. soc. franc elec.*, 5, vol. 2, p. 631, 1932. BLUM, W., and STRAUSSER, P. W. C., *J. Research Natl. Bur. Standards*, vol. 24, p. 443, 1940, RP 1293.

age thickness will be present on each piece that is plated. Careful study of the racking and spacing and of methods of plating will reduce this margin, but even under the best conditions it is probable that the average thickness of all the pieces must be at least 25 per cent above the average thickness required on each piece.

When a certain minimum thickness on any part of the surface is specified, it is still more difficult to predetermine the time of plating required at a given average current density. This time depends upon the shape and the position of the article, according to which the average thickness may be from two to five times the minimum thickness[1] on a given piece. In addition, the average (and therefore the minimum) current density may vary widely on similar pieces plated on a given rack. It must be clearly recognized that the present trend toward the requirement of a minimum thickness represents in most cases a tightening of the specifications, which is justified because it usually results in a corresponding increase in the useful life of the coatings.

Thickness Measurement. AVERAGE THICKNESS. The most satisfactory method for measuring the average thickness of a coating is to dissolve off and determine the weight of the coating from a specimen of known or measured area. The thickness is then computed from the weight and area and the density (or specific gravity) of the coating, using the formula

$$T \text{ (thickness)} = C \frac{W \text{ (weight)}}{A \text{ (area)} \times D \text{ (density)}} \tag{1}$$

where C is a constant that depends simply upon the units employed.

In metric units the equation becomes

$$T \text{ (mm)} = 10 \frac{W \text{ (gr)}}{A \text{ (cm}^2\text{)} \times D} \tag{2}$$

In English units

$$T \text{ (in.)} = 1.73 \frac{W \text{ (avoir oz)}}{A \text{ (in.}^2\text{)} \times D} \tag{3}$$

As the weighings are almost invariably made in grams, it is more direct and logical to measure the area in square centimeters and first to compute the thickness in millimeters. Dividing this value by 25.4 (or multiplying by 0.0394) gives the thickness in

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[1] BRENNER, A., *J. Research Natl. Bur. Standards*, vol. 18, p. 565, 1937, RP 994.

inches. These two steps may be expressed in a single formula

$$T\ (\text{in.}) = \frac{0.394W\ (\text{gr})}{A\ (\text{cm}^2) \times D} \tag{4}$$

For each metal having a specified density, a single factor for the thickness in inches can be derived by dividing 0.394 by the density. Thus, for nickel, 0.394/8.9 = 0.0442; hence, for nickel

$$\text{T (in.)} = 0.0442\ \text{g/cm}^2 \tag{5}$$

A list of these convenient factors is included in Table 15 in the Appendix.

Example. If on a fixture having a total area of 60 cm² (9.3 in.²) the nickel coating (which has a density of 8.9) weighs 2.35 gr, what is the average thickness?

$$T\ (\text{mm}) = \frac{10 \times 2.35}{60 \times 8.9} = 0.044\ \text{mm} \tag{2}$$

$$\frac{0.044}{25.4} = 0.00173\ \text{in.}$$

$$\text{T (in.)} = \frac{0.394 \times 2.35}{60 \times 8.9} = 0.00173\ \text{in.} \tag{4}$$

$$T\ (\text{in.}) = 0.0442 \times \frac{2.35}{60} = 0.00173\ \text{in.} \tag{5}$$

The process of dissolving a coating from a basis metal is known as *stripping*. If this operation can be carried out so as to dissolve the coating completely and cause no appreciable attack of the basis metal, the weight of the coating is equal to the loss in weight produced by stripping. This procedure is commonly used for zinc, cadmium, and chromium coatings. If, however, as in electrolytic stripping of nickel coatings from brass, the basis metal is slightly attacked, it is necessary to determine analytically the amount of nickel in the resultant solution, *e.g.*, by the dimethylglyoxime precipitation. For many metals it is most satistactory to dissolve the coating electrolytically with *reverse current*, *i.e.*, by making the article the anode in a suitable solution.

In general, during the stripping of the coating by either procedure there is some, however slight, attack of the basis metal, or intermediate coating. Consequently the results by any stripping method tend to be slightly high. The conditions that will yield an accuracy of about 10 per cent in stripping typical commercial coatings from specified basis metals are summarized in Table 14.

The same methods can be employed for stripping defective coatings prior to replating. For this purpose slight attack of the basis metal is not usually objectionable, and hence the cheapest of these solutions and methods are generally employed.

The following notes will assist in the quantitative application of the methods listed in Table 14, which are based largely upon the studies conducted by A. Brenner[1] and P. W. C. Strausser.[2] Recently a review of methods of stripping copper was published.[3]

The following comments are numbered according to the methods listed in Table 14.

Method 6. It is very difficult to strip nickel from steel with sulfuric acid at a reasonable rate without some attack of the steel. The addition of a small amount of glycerin reduces but does not entirely prevent attack. Some pitting is likely to occur, which is especially objectionable on replating.

Method 7. When stripping nickel in sodium nitrate, the solution tends to become alkaline and should be neutralized, when necessary, to a pH of about 5 by the addition of nitric acid. This method is not quantitatively applicable to high-carbon steel or to articles of very irregular shape, on which attack may occur at recesses with low current densities.

Method 8. There is usually sufficient attack of the brass when stripping nickel in hydrochloric acid to prevent quantitative results, although the articles are suitable for replating. It is therefore customary to determine the nickel in the resultant solution by precipitation with dimethylglyoxime. If cobalt is present, it can be determined with nitrosobeta naphthol.

Method 9. At the conclusion of stripping nickel in thiocyanate there is a very thin dark film, which should be removed by light scrubbing before drying and weighing. The solution should be kept slightly acid by occasional small additions of sodium bisulfite.

Method 15. The vessel containing sulfuric and nitric acid should be kept covered to prevent absorption of water. Nitric acid should be added to replace that consumed by solution of the silver.

Method 16. The results are usually almost quantitative with only concentrated hydrochloric acid, but the antimony chloride

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[1] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 20, November, 1933.

[2] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 24, p. 822, 1937.

[3] MATHERS, F. C., LANDERWERTEN, C. E., and MARTIN, E. L., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 32, pp. 268 and 672, 1945. (*Am. Electroplaters' Soc. Research Report*, Serial No. 4.)

(or oxide) acts as an inhibitor and reduces attack of the exposed steel.[1]

The chief source of error in determining the average thickness is the uncertainty in the area of irregularly shaped articles. The best method for estimating such areas is to make a series of measurements and approximate computations, on the assumption that each part of the surface may be considered as a portion of a figure such as a cylinder, a cone, or a sphere. In making such measurements it is frequently possible to set upper and lower limits, *e.g.*, by means of an inscribed and a circumscribed cone. If these differ by, say, 20 per cent, their average almost certainly represents the true area within 10 per cent. In some cases the areas can be estimated by cutting cross-section paper to cover the surface exactly and counting the number of squares. Except on very simple shapes, it is very difficult to estimate the areas within 10 per cent, which introduces a corresponding uncertainty in the computed average thickness. When articles are stamped out of sheet metal, their area can be estimated from the thickness of the sheet metal and the weight of the piece. In this method it is assumed that the change in area produced by stretching the metal during the forming operations is negligible; otherwise a corresponding error is introduced.

Indirect methods for estimating areas, such as measuring the amount of liquid retained on immersion and withdrawal, the amount of liquid condensed on the surface, or the current produced by a specified voltage, do not appear promising. It has been suggested that the application of monomolecular layers might permit measurements of the surface area.

Sometimes the average thickness is computed from a number of measurements of local thickness. While this procedure does not involve exact measurements of area, it requires a large number of local measurements, which should be nearly uniformly distributed. Otherwise it is necessary to *weight* the individual values according to the areas they represent. If, for example, the thickness of nickel at one point on a faucet handle with an area of 1 in.^{2} is found to be 0.0005 in. and on the body of the faucet with an area of 10 in.^{2} the thickness is 0.0001 in., it is obviously incorrect to take the average of these two, *i.e.*, 0.0003 in., as the average thickness. If the two points measured are representative of their respective areas, ten times as much weight should be given to the

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[1] Clarke, S. G., *Trans. Electrochem. Soc.*, vol. 69, p. 131, 1936.

value on the body, as to that on the handle; *i.e.*, the average thickness is equal to

$$\frac{0.0005 + 10\,(0.0001)}{11} = \frac{0.0015}{11} = 0.00014 \text{ in.}$$

If the specific gravity of the coating is very different from that of the basis metal, *e.g.*, silver (10.5) on steel (about 8.0), it is possible to compute the weight of coating and hence its average thickness from the average specific gravity of the article.[1] This method suffers from the limitations that (1) the coating must be relatively thick, (2) the specific gravities of the coatings and basis metal must be accurately known, and (3) the weighings must be made with high accuracy, since small errors are multiplied in the final calculations. The method is most likely to be useful in routine production checking of similar articles.

LOCAL THICKNESS. The numerous methods that have been proposed or used for measuring the thickness of a coating at a specified point may be classified according to the three types of measurement involved.

1. Length measurements
   - *a.* Direct microscopical measurement of a section
   - *b.* The chord method, which measures a geometric function of the thickness
2. Rate of chemical action
   - *a.* Immersion methods
   - *b.* Spot tests, in which a single drop of reagent is applied
   - *c.* Dropping tests, in which discontinuous drops of the reagent act upon the coating
   - *d.* Jet tests, in which a continuous stream of liquid is applied
   - *e.* Electrochemical methods
3. Magnetic methods
   - *a.* Measurement of the magnetic attraction of a magnetic coating on a nonmagnetic base metal
   - *b.* Measurement of the reduction in attraction of a magnetic base metal caused by the presence of a nonmagnetic coating

In certain cases the local thickness can be determined by cutting out a small specimen having an accurately known area and determining the weight of coating on it by a stripping and

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[1] LARKIN, L. S., *J. Electrodepositors' Tech. Soc.*, vol. 18, p. 48, 1943.

chemical method. Recently W. S. Claybaugh[1] has described a method for measuring the thickness of very thin gold coatings, in which an area of 1 mm^2 is punched out and the gold is dissolved and determined colorimetrically, using o-tolidine to produce a characteristic color. Almost any of the stripping methods described above for various metals could be adapted to this procedure, but for most metals and coatings other methods are more convenient.

For a given purpose the choice of method depends upon its accuracy, convenience, and expense for the particular coating and basis metal to be tested. In some cases, especially in testing large or expensive articles, the cost of the samples destroyed may be so great as to limit the number or proportion of specimens tested. For such purposes the nondestructive magnetic methods are preferable. In general, the chemical methods and the chord method destroy only the coatings, so that, if desired, the tested specimens can be salvaged by replating. The microscopical method is necessarily destructive of the piece tested. On the other hand, it is the most direct and is dependent only on length standards, which are usually of high accuracy and can be readily calibrated. With care and experience the results of the microscopical measurement for coatings more than 0.0001 in. thick are usually accurate to within about 5 per cent, while with most of the other methods errors of 10 to 15 per cent may enter. The microscopical method is therefore usually considered as the standard, or umpire, method. However, for control purposes other methods with an accuracy of only 15 per cent may be adequate, especially if by testing more specimens the reliability of the sampling is thereby improved.

One difficulty in all such testing is the securing of representative samples. No general rule can be given, but the unavoidable variations in plating are so great that usually at least 1 piece of each 100 should be tested even to approach the goal of determining whether either the average or local thickness on every piece probably meets the requirements. However, for many items in large production the testing of only 1 out of each 1,000 might be relatively expensive, especially if the articles were thereby destroyed. It is obvious, therefore, that the customary testing of plated articles by destructive methods cannot ensure compliance

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[1] *J. Research Natl. Bur. Standards*, vol. 36, p. 119, 1946, RP 1694.

of every piece with the specification, although it will usually exclude decidedly inferior products.

The selection of the point on an article at which the local thickness is measured is important. These points must be on *significant surfaces* (page 103). Moreover they should be located where the minimum thickness is most likely to be found. Experience in testing similar articles may so define these points that the required number of tests is reduced. In particular cases, such as the *overlay* on silver-plated spoons, the points to be tested are designated in the specification.

The principles and procedures used in each of the above methods may be summarized as follows:

1. Length measurements.

a. Microscopical.[1] One or more suitable sections are cut through perpendicular to the surface at the points to be measured. Two or more flat pieces may be clamped together by small bolts. Curved pieces should be first plated with a relatively thick coating of copper to prevent rounding of the coating during polishing. The specimens are then placed in a suitable metallic ring and are mounted in a low-melting alloy, or in a thermoplastic material such as bakelite or transparent lucite. The section to be measured must be perpendicular to the surface that is being tested. (A deviation of 10 deg from normal produces an error of 2 per cent in thickness.)

The surface is ground and polished with successively finer abrasives and is then treated with a suitable etching reagent, which will produce the greatest contrast between the coating and base metal.

Typical etching reagents are as follows:

For nickel on steel or zinc (to etch the steel or zinc):

	VOLUMES
Nitric acid, conc.	5
Alcohol, 95 per cent	95

For nickel over copper on steel or nickel on brass (to etch the copper or brass):

	VOLUMES
Ammonium hydroxide, conc.	1
Hydrogen peroxide, 3 per cent	1

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[1] CARL, FRED, *Monthly Rev. Am. Electroplaters' Soc.*, vol. 20, October, 1933, and *Metals & Alloys*, vol. 5, p. 39, 1934. HEUSSNER, C. E., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 23, p. 5, 1936.

For zinc or cadmium coatings on steel (to etch the zinc or cadmium):

	g/l
Chromic acid, CrO_3	200
Sodium sulfate, Na_2SO_4	15

The thickness of the coating at any desired point is measured either by means of a filar micrometer that has been accurately calibrated or by projecting the image at a known magnification on the ground-glass focusing plane of the camera of a metallographic microscope. The width of the projected line of deposit is measured with a linear scale, the reading of which is divided by the magnification (*e.g.*, 500) to obtain the thickness of the coating.

b. Chord method.[1] This method, devised by F. C. Mesle for testing plated spoons, is based upon the fact, illustrated in Fig. 27 that, when a coating on a spherical surface is just cut through by a plane *C*, *e.g.*, a flat file, the width of the cut depends upon *R*, the radius of curvature, and *T*, the thickness of the coating. If the curvature is known, the thickness may be computed by the formula

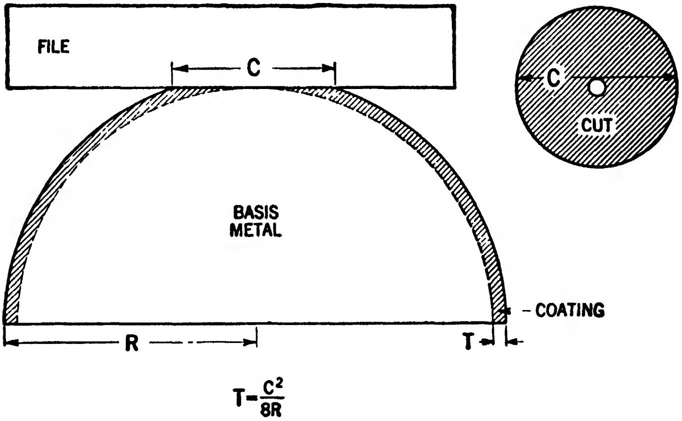

Fig. 27. Chord method—use of file on a curved surface.

$$T = \frac{C^2}{8R} \qquad (1)$$

Exactly the same principle and formula apply if, as shown in

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[1] Mesle, F. C., *Metal Ind.* (*N.Y.*), vol. 33, p. 263, 1935. Blum, W., and Brenner, A., *J. Research, Natl. Bur. Standards*, vol. 16, p. 171, 1936, RP 866.

Fig. 28, a coating on a plane surface is just cut through with a grinding wheel with a radius R.

Example. Suppose that when the coating on a tube with a radius of 2 in. is just cut through with a flat file, a cut 0.2 in. wide is produced. Then

$$T = \frac{C^2}{8R} = \frac{(0.2)^2}{8 \times 2} = 0.0025 \text{ in.}$$

As the file may "rock" and give too wide a cut, it may be preferable to employ a precision grinder, even on curved surfaces. If the width of cut is measured in the direction of the flat edge of the wheel, the above formula is still used, with R equal to the curvature of the article. If the cut is measured in the direction of the wheel circumference, the formula is

$$T = \frac{C^2}{8} \times \frac{R_1 + R_2}{R_1 \times R_2} \qquad (2)$$

where R_1 is the radius of the object and R_2 the radius of the wheel.

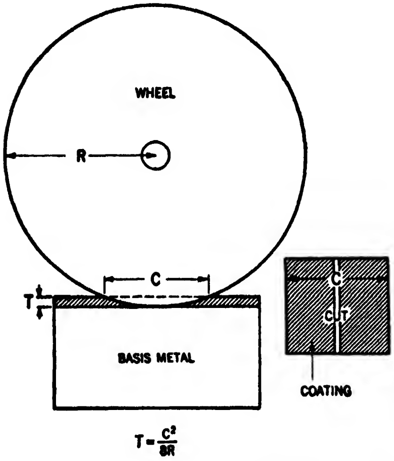

FIG. 28. Chord method—use of a grinding wheel on a flat surface.

As a precision grinder is relatively expensive, its use would not be justified unless a large amount of testing is required. In the effort to simplify the apparatus, F. C. Mesle[1] has suggested a device in which a curved file of known and relatively large radius, *e.g.*, 10 in., is moved around its axis in such a way as just to cut through the coating on a plane surface.

If a precision grinder is used on a plane surface, it is preferable to tilt the specimen very slightly, so that, as it passes under the wheel, a cut such as that in Fig. 29 is obtained. The thickness of each layer is then computed by Eq. (1) from the width of cut measured at the point where the next lower layer, or the basis metal, is just exposed. A grinding wheel with a radius of 4 to 6 in. is usually satisfactory. For hard metals such as nickel and chro-

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[1] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 24, p. 754, 1937, and *Metal Finishing*, vol. 47, p. 15, 1949.

mium, a fine wheel is employed (*e.g.*, 120 grain or finer), and for soft metals such as zinc and copper, a coarser wheel, such as 90 grain. The width of cut can be measured with sufficient accuracy with a pocket lens and attached scale.

Measurements made on a variety of coatings and basis metals showed that this method is simple and quick and usually yields an accuracy of at least 10 per cent on coatings 0.0002 in. or more in thickness. It is not suitable for thinner coatings unless a larger radius wheel is used with special precautions.

2. Rate of chemical action. Each of these methods depends upon the use of some reagent that will dissolve the coating at a uniform rate and will indicate when the basis metal is exposed. The thickness is measured in terms of time, *i.e.*, in minutes or seconds. In all cases the temperature must be noted and controlled within certain limits, as the rate of most chemical reactions increases rapidly with a rise in temperature.

FIG. 29. Chord method—typical cut on a flat surface slightly inclined with respect to the grinding wheel. The successive layers, starting at the center, are steel, nickel, copper, nickel.

a. Preparation of thickness standards. These methods all require standardization against similar deposits of known uniform thickness. The preparation of such deposits is not easy. It is well known that, when a flat specimen is plated in a tank having a cross section larger than the specimen, there are a higher current density and hence a thicker deposit on the edges and corners than toward the center. Even in the central portion the thickness may vary considerably, especially if the anodes are not continuous and uniform. Under such conditions the thickness near the edges may be 100 per cent greater than the average, and near the center variations of as much as 20 per cent may exist.[1]

This difficulty can be almost completely overcome if both the anodes and cathodes fill the cross section of the tank or if smaller cathodes are held in an uncoated metal rack that completes the cross section, with just a small space between the specimens and the rack or each other. A typical cross section of the resultant

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[1] CLARKE, S. G., *J. Electrodepositors' Tech. Soc.*, vol. 12, p. 1, 1936–1937.

deposit is shown diagramatically in Fig. 30. By merely cutting off a strip, in this case about 0.5 in. wide, from each edge, a specimen is obtained on which the maximum variation from the average is less than 5 per cent. The weight and average thickness of the coating on this portion is determined by subtracting from the total weight of deposit the amount present on the cut-off edges as determined by stripping or analysis. It is preferable to plate such standards on one side only (with the back insulated), as the thickness on two sides may vary, especially if one side of the basis metal has a brighter surface than the other.

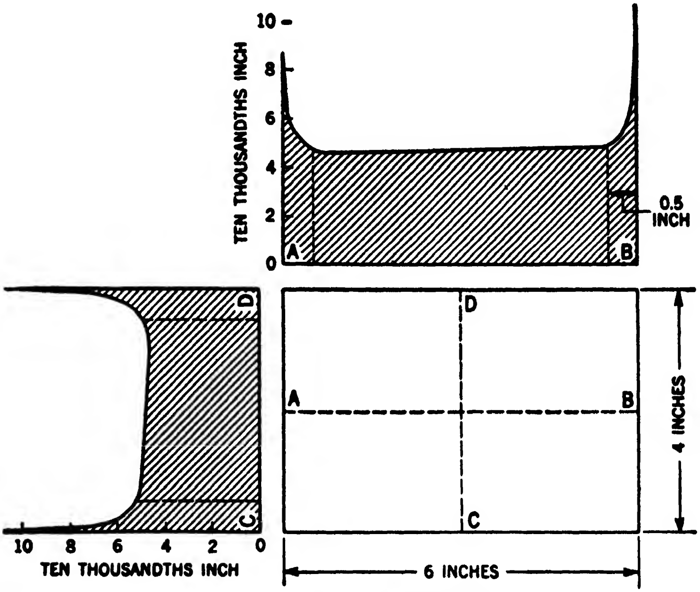

Fig. 30. Distribution of thickness of coating plated on a flat sheet under favorable conditions.

b. Immersion methods. The best known of these methods is the Preece test for measuring the uniformity of thickness of zinc coatings. This method depends upon dipping the cleaned specimen into a neutral solution of copper sulfate (sp gr 1.186) at 18°C (64°F) for successive periods of 1 min each. After each immersion the article is rinsed and the loosely adherent copper is rubbed off. The end point is the presence of an adherent bright deposit of copper after this cleaning. Very small areas of copper or those within 1 in. of a cut edge are usually disregarded. If, for example, adherent copper appears at the end of the fourth dip, the specimen is reported as having withstood three dips.

This method has been most extensively used for hot-dipped zinc coatings, but it is sometimes specified for plated zinc. Numerous investigations[1] have shown that this method yields different results with zinc coatings produced by hot dipping, sherardizing, and electroplating. In general, the plated zinc coatings dissolve more rapidly than the hot-dipped. Groesbeck and Walkup found that on wires the plated coatings dissolve at the rate of approximately 0.00037 in. per 1-min dip while hot-dipped zinc coatings dissolve at the rate of approximately 0.00027 in. per dip. It is obvious, therefore, that a given number of dips, *e.g.*, four, corresponds to a 40 per cent thicker coating of plated than of hot-dipped zinc. This is no evidence, however, that in atmospheric exposure electroplated coatings dissolve more rapidly than hot-dipped coatings. Actually, numerous exposure tests have shown that plated zinc coatings furnish at least as much protection as hot-dipped coatings of the same thickness.

Another objection to this and other immersion methods, is that the rate of solution is influenced by stirring and even by the shape and position of the article, which may cause different convection currents in the solution. Still another objection to this method is the use of relatively few long periods, *e.g.*, four 1-min dips, which automatically reduces the precision to about 25 per cent.

A somewhat similar method[2] has been occasionally used for detecting and estimating thinly plated areas during the stripping of silver from tableware (page 106) by the change in color when the basis metal is exposed. This method is hard to standardize accurately owing to the difficulty of keeping the stripping solution at a constant concentration and temperature. B. Egeberg and N. E. Promisel[3] report that in this test (as specified in Table 14) 0.001 in. of silver dissolves in from 6 to 8 min but that the rate of solution is changed by stirring. Such methods are therefore more useful for measuring the relative distribution of the coatings than their minimum thickness.

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[1] Summarized by Groesbeck, E. C., and Walkup, H. H., *J. Research, Natl. Bur. Standards*, vol. 12, p. 785, 1934.

[2] Mesle, F. C., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 24, p. 754, 1937.

[3] *Metal Cleaning Finishing*, vol. 9, p. 25, 1937.

c. Spot tests. These depend upon the application of a single drop of the reagent to the surface and the measurement of the time required to expose the basis metal. One early example is the testing of copper deposits on steel with a drop of nitric acid.[1] The best known example is the testing of chromium coatings with one drop of concentrated hydrochloric acid.[2] W. L. Pinner and L. B. Sperry[3] emphasized the importance of temperature control in making this test. More recently it was shown[4] that the concentration of the hydrochloric acid must be closely controlled, *e.g.*, to a specific gravity of 1.180 at $\frac{60°\text{F}}{60°\text{F}}$.

P. W. C. Strausser suggested the use of a small wax ring, within which the drop of hydrochloric acid (sp gr 1.180) is placed in order to prevent its gradual spread and consequent uncertainty in the end point, which is the cessation of bubbling in the drop. If, as sometimes happens, the chromium is passive and does not instantly start to dissolve, the surface may be touched with a fine nickel wire, which causes immediate action. The time is recorded with a stop watch from the beginning to the end of bubbling, and the temperature of the test is noted. The thickness can be then derived from a curve such as in Fig. 31. This method is extensively used in specifications for the minimum thickness of chromium. It is not directly applicable to coatings more than about 0.00005 in. thick. S. G. Clarke[5] suggested the use of hydrochloric acid containing antimony chloride for this spot test.

For several years a spot test for nickel coatings has been used by the French railways. In a study of this method[6] M. Ballay used the following reagent:

	Milliliters
Nitric acid, conc.	80
Sulfuric acid, conc.	20
Water	40

One drop of this reagent is applied to the cleaned nickel surface for exactly 1 min. It is then wiped off, and the surface is examined

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[1] Maeder, R. E., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 9, No. 11, p. 5, 1922.

[2] Stocker, O. A., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 16, p. 11, November, 1929.

[3] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 25, p. 340, 1938.

[4] Blum, W., and Olson, W. A., *Proc. Am. Electroplaters' Soc.*, p. 25, 1940.

[5] *J. Electrodepositors' Tech. Soc.*, vol. 14, p. 25, 1938.

[6] *J. Electrodepositors' Tech. Soc.*, vol. 14, p. 1, 1937–1938.

to see if the basis metal is exposed. If not, another drop is similarly applied. The thickness is expressed in terms of the number of 1-min treatments the coating must withstand. Ballay found that different nickel deposits dissolve at about the same rate, except that very porous coatings dissolve more rapidly. A variation of only 5 per cent in concentration produces a change of about 30 per cent in the rate. The effect of temperature is very marked.

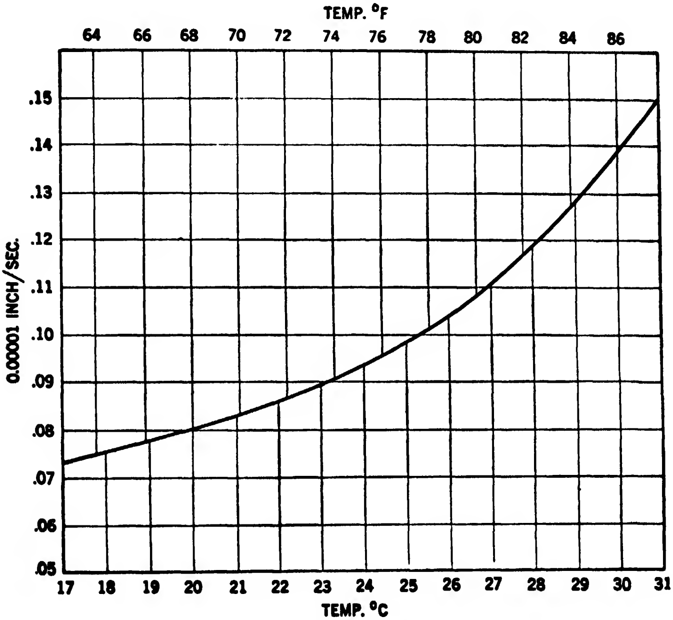

FIG. 31. Rate of solution of electrodeposited chromium in hydrochloric acid (sp gr 1.180).

The tests should be made at a recorded temperature between 15 and 25°C (60 and 77°F), and the corresponding factor used. At 65°F, 0.000066 in. (1.64 microns[1]) of nickel is dissolved in 1 min, and at 73°F, 0.000078 in. or 1.94 microns per minute.

d. Dropping tests. These methods depend upon the application of a reagent in successive drops until the basis metal is exposed. As first suggested by S. G. Clarke,[2] the number of drops was counted and used as a measure of thickness. If, however, the rate of dropping is rapid and is kept fairly constant, *e.g.*, 100 ± 10

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[1] One micron is 0.001 mm.

[2] *J. Electrodepositors' Tech. Soc.*, vol. 8, No. 11, 1933.

drops per minute, the rate of solution is practically independent of the exact rate of dropping, and hence the elapsed time, as measured with a stop watch, is a measure of the thickness. This method has been applied chiefly to zinc and cadmium coatings on steel.

Clarke recommended for cadmium a solution containing 100 g/l of iodine and 200 g/l of potassium iodide, with which 18 drops (at 60 drops per minute) were required for each 0.0001 in. of cadmium. R. O. Hull and P. W. C. Strausser[1] employed the following acidified solutions of ammonium nitrate, each of such strength that at 20 to 30°C (70 to 90°F) it dissolved the specified coatings at the rate of 0.00001 in./sec, with the solution dropping at 100 drops per minute.

For zinc:

Plated coatings, including those which contain up to 2 per cent of mercury:

Ammonium nitrate, NH_4NO_3......	100 g/l
Nitric acid, HNO_3 (sp gr 1.42)....	55 ml/l

Hot-dipped coatings:

Ammonium nitrate.............	100 g/l
Hydrochloric acid (sp gr 1.180)....	75 ml/l

For cadmium:

Ammonium nitrate..............	110 g/l
Hydrochloric acid (sp gr 1.180)....	10 ml/l

A. Brenner[2] recommended the use of a single solution containing 200 g/l of chromic acid, CrO_3, and 50 g/l (27 ml/l) of sulfuric acid, H_2SO_4, for testing all types of zinc and cadmium coatings. The factors for a given temperature in Fig. 32 apply to electroplated cadmium coatings and to electroplated, hot-dipped, and sherardized zinc coatings.

For tin coatings a solution containing 100 g/l of trichloroacetic acid is used in the same apparatus. At 75°F (24°C) this solution dissolves tin at the rate of 0.00001 in./sec.

For testing copper coatings on steel or zinc the solution contains 450 g/l of ferric chloride, $FeCl_3 \cdot 6H_2O$; 20 g/l of antimony trioxide, Sb_2O_3; 200 ml/l of concentrated hydrochloric acid; and 250 ml/l of glacial acetic acid, $HC_2H_3O_2$. This solution dissolves copper at the rate of 0.000,005 in./sec at room temperature.

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[1] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 22, March, 1935.

[2] *J. Research Natl. Bur. Standards*, vol. 23, p. 387, 1939, RP 1240.

The surface to be tested is cleaned and is supported under the outlet tip so that the solution hits the spot to be tested and runs off quickly. The solution is contained in a separatory funnel. In the earlier forms two stopcocks were used between the outlet and a small glass tip. The upper cock was used to turn the flow on or off, and the lower cock to adjust the rate of flow, after which this cock was not moved. A small capillary tube now replaces the lower stopcock. W. B. Stoddard[1] proposes to calibrate the tip of a burette and to use the volume of solution consumed as a measure of the thickness. The time is measured from the beginning of the dropping until the basis metal is exposed.

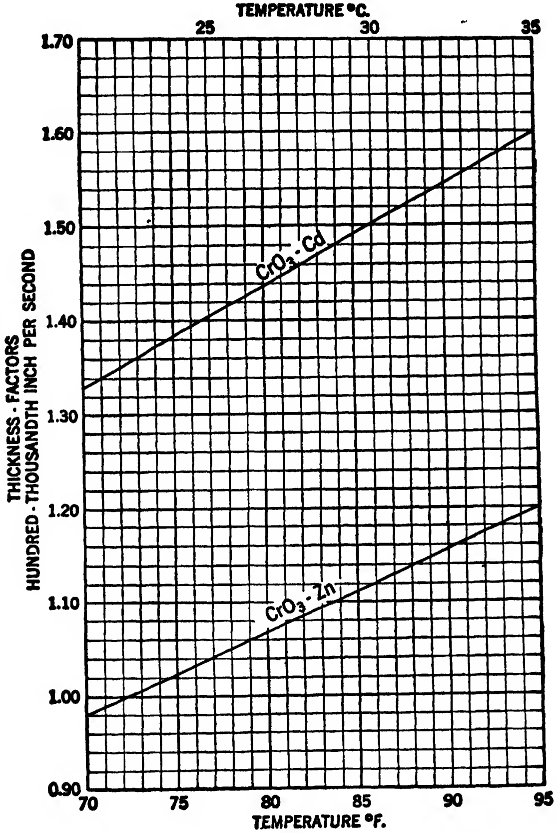

FIG. 32. Dropping test. Rates of solution of zinc and cadmium in chromic acid solution.

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[1] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 30, May, 1943.

Published data indicate that for most zinc and cadmium coatings the results by this method are reliable within about ±15 per cent. Uncertainty in the end point is sometimes noted with the ammonium nitrate solution, especially when the deposit is dark as a result of a poor surface on the basis metal. To reduce this uncertainty, R. O. Hull[1] suggested the addition of 3 g/l of potassium ferricyanide to the test solution. This produces a blue spot when the steel is exposed. This modification makes no appreciable change in the rate of solution and in some cases makes the end point more distinct.

e. Jet tests. It is difficult to dissolve the less active metals such as nickel at a rapid and uniform rate, especially in a dropping test. S. G. Clarke[2] devised the *BNF jet test,* in which a suitable reagent is applied to the metal in a continuous fine stream. Under these conditions it is necessary to stop the flow in order to observe whether or not the basis metal is exposed. In order to measure the total period during which the jet is applied, a *stop-and-go* watch is used instead of the ordinary stop watch. This method is likely to prove especially useful for nickel coatings. It is also applicable to but possesses no unique value for zinc and cadmium coatings.

In order to control the rate of flow, the solution is kept in a reservoir bottle, with a constant head of 10 in. (25 cm). To provide a jet with a uniform cross section, the glass tip should have a gradual taper of about 1 part in 20 to 30. If a capillary tube with 1.2-mm bore and an orifice of 0.6 mm is used, the length of the tip should be between 15 and 23 mm. The exact size of the orifice is not important, but it should deliver about 20 ml/min of water. A small glass tube surrounding and attached to the tip serves to protect it and also to define the distance (about 0.25 in. or 6 mm) of the orifice from the surface tested.

Solution F.C., recommended by Clarke[3] for testing nickel coatings on most basis metals, has the following composition:

	g/l
Ferric chloride, $FeCl_3 \cdot 6H_2O$...........	300
Copper sulfate, $CuSO_4 \cdot 5H_2O$..........	100

In this reagent the ferric chloride is the principal solvent for the nickel, and the copper sulfate sharpens the end point, especially

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[1] Private communication to the authors.

[2] *J. Electrodepositors' Tech. Soc.,* vol. 12, pp. 1 and 157, 1936.

[3] *Proc. Am. Electroplaters' Soc.,* p. 24, 1939.

when testing nickel coatings on steel, aluminum, or zinc, which precipitate copper as a red or black spot.

As the rate of solution of the nickel is markedly influenced by the temperature, it is necessary to employ a curve to determine the thickness. Curves were published by Clarke for various solutions and coatings. It is necessary first to remove chromium from the nickel, *e.g.*, by solution in dilute hydrochloric acid, and to have the nickel surface clean before applying the reagent.

Two possible sources of error in this method are (1) changes in the composition and rate of reaction of the reagent and (2) variations in the rate of dissolving nickel coatings that were deposited from different baths or under different conditions.[1] Clarke found that most ordinary nickel deposits dissolve at the same rate, within about ±15 per cent. A *bright-nickel* deposit from a bath containing aromatic sulfonates dissolved 1.8 times as fast as normal nickel, but a bright deposit of a nickel-cobalt alloy dissolved at the normal rate.

For silver coatings[2] the jet solution contains 250 g/l of potassium iodide and 7.44 g/l of iodine. At 77°F (25°C) a silver coating is penetrated at the rate of 0.0001 in. in 5.6 sec and at 64°F (18°C) in 6.6 sec.

f. Electrochemical tests. These methods depend upon the rate at which a metal dissolves when it is made anodic in a suitable solution. A good example is the electrolytic test for the thickness of chromium developed by S. Anderson and R. W. Manuel.[3] A definite small area of the chromium is defined by pressing against the surface a sheet of rubber in which a circular hole, 3/16 in. (0.47 mm) for a flat surface or 3/32 in. (0.24 mm) for a curved surface, has been cut. A brass tube, which serves as a cathode, is pressed against the rubber disk, and a solution that is *N* in trisodium phosphate (127 g/l of $Na_3PO_4 \cdot 12H_2O$) and *N* in sodium sulfate (71 g/l of Na_2SO_4) is introduced. A definite current, *e.g.*, 35 ma for the larger hole or 9 ma for the smaller hole, is then passed through the cell until there is a sudden decrease in the current. The stripping period, noted with a stop watch, is a measure of the thickness. For a current of 35 ma and a 3/16-in. hole, the factor in millionths of an inch of chromium per second is 0.98, or practically 1.

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[1] READ, H. J., and THOMPSON, J. H., *Proc. Am. Electroplaters' Soc.*, p. 79, 1948.

[2] HAMMOND, R. A. F., *J. Electrodepositors' Tech. Soc.*, vol. 16, p. 69, 1940.

[3] *Trans. Electrochem. Soc.*, vol. 78, p. 373, 1940. FRANCIS, H. T., *Trans. Electrochem. Soc.*, vol. 93, p. 79, 1948.

It is evident that in this and all methods depending on the rate of chemical or electrochemical reaction some variations are to be expected with different types of deposit of a given metal. These variations do not prevent the useful application of that method for plant control, with appropriate standardization against similar coatings, but they may restrict its application in the testing of miscellaneous coatings, *e.g.*, by purchasers. More critical study of all such methods will be required before they can be accepted as fully satisfactory standards for formal specifications.

1. Magnetic methods. Any method that depends upon the relation of thickness to some readily measurable physical property would have the advantage of being nondestructive and therefore applicable to a larger proportion or, if warranted, to all the plated products of a given plant. To some extent the magnetic methods meet this need. They depend directly or indirectly upon (*a*) the attraction of a magnetic coating, which may consist of nickel, cobalt, or iron, deposited upon a nonmagnetic basis metal such as copper, brass, or zinc; (*b*) the reduction in the attraction of a magnetic basis metal, such as steel, caused by the presence of a nonmagnetic coating, which may be metallic (*e.g.*, copper, zinc, or cadmium) or nonmetallic (lacquer, paint, or enamel); or (*c*) the change in the *reluctance* of a magnetic circuit as a result of the coating.

a. Magnetic coatings. A method of this type was developed by A. Brenner[1] for nickel coatings on copper, brass, and zinc. This method depends upon the fact that the attraction of a small permanent magnet to a nickel coating is practically proportional to the thickness of the nickel at that point for the usual range of thickness, *i.e.*, between 0.0001 and 0.001 in. This attraction is measured by means of a simple spring balance, illustrated in Fig. 33. By having the magnet rigid, with a similar magnet at the other end of the beam to balance it magnetically, the instrument can be used in any position. For ordinary testing, it is preferable to use a freely suspended magnet on one end of the beam and any suitable pointer attached to the beam, as this arrangement is more sensitive.

Nickel coatings deposited over a fairly wide range of conditions from a given bath have almost identical magnetic properties, but deposits from different baths, including those containing organic brighteners, differ magnetically. When various nickel coatings

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[1] *J. Research Natl. Bur. Standards*, vol. 18, p. 565, 1937, RP 994.

are annealed at 400°C (750°F) for 15 min, they become more magnetic and all acquire the same magnetic properties. The method is applicable for works control by calibrating and occasionally checking the instrument against the type of nickel there used, without annealing, but for purchase testing of deposits of variable or unknown origin, annealing should always be applied.

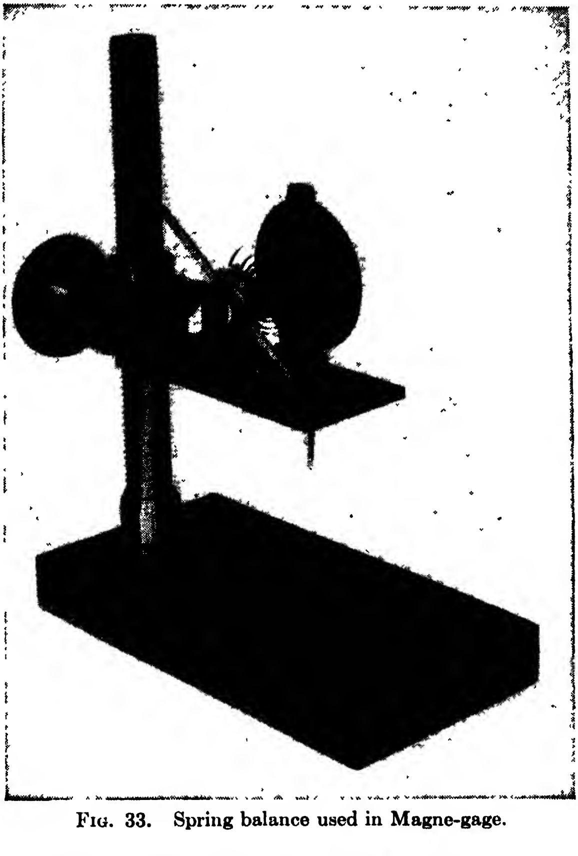

Fig. 33. Spring balance used in Magne-gage.

The calibration of the instrument can be conveniently expressed by a graph (Fig. 34). If, as is usual, this is practically a straight line, its slope may be expressed by a constant C for the type of deposit used, *e.g.*, in hundred-thousandths of an inch per scale division. Thus, if a nickel deposit known to be 0.00030 in. thick gives a reading of 20 divisions, each division is equal to $0.00030/20 = 0.000015$, or the constant $C = 1.5$. If then a similar deposit of unknown thickness is tested and yields a reading of 30 divisions, its thickness is equal to 30 × 1.5 = 45/100,000, or 0.00045 in.

With this instrument reliable readings are obtained on even a small flat surface if its diameter is at least four times the diameter of the magnet. The magnet should not be used within about twice its diameter from an edge or corner. The readings are not affected by curvature if the radius of a spherical surface is at least five times the magnet diameter or if the radius of a cylinder is at least twice the magnet diameter. Each per cent of iron in a nickel deposit increases the attraction by about 4 per cent, and each per cent of cobalt by about 2 per cent. Such effects are usually negligible unless these metals are intentionally added in appreciable amounts. The method is applicable to alloy deposits only if their composition is known and uniform. With proper precautions, this magnetic method is usually accurate within about 10 per cent.

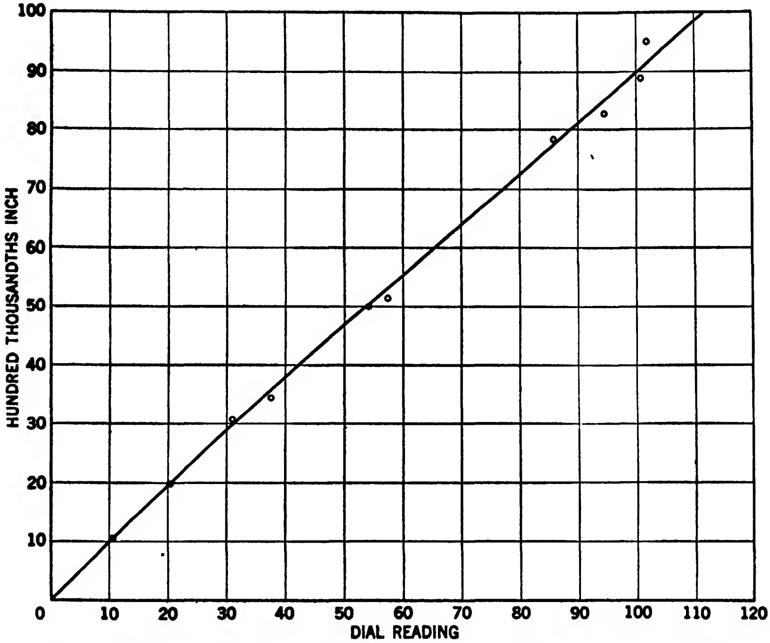

FIG. 34. Typical curve for thickness of nickel on brass vs. dial reading of Magne-gage.

b. Nonmagnetic coatings on magnetic basis metals. These methods depend upon either (1) measuring the decrease in the attraction of a magnet as the result of interposing a layer of nonmagnetic material between the magnet and the steel or (2) measuring the increase in magnetic reluctance (which corresponds to electrical resistance) in a circuit that includes the coated iron and an electromagnet. The latter principle is used in an apparatus made by the General Electric Company for measuring the thickness of coatings on iron or steel. It requires special calibration for curved surfaces and for different nonmagnetic coatings such as copper, silver, and zinc. Similar devices have been described by W. H. Tait,[1] by W. B. Elwood,[2] and by Branson Instruments as the "Coatingage."

The methods of the first group differ principally in the mechanism for measuring the force required to detach the magnet. In one method[3] the magnet is attached to the needle of a galvanometer, through which a current is passed to detach the magnet from the coated steel. In another method[4] the magnet is attached to one arm of a lever balance and water is introduced into a graduated tube supported on the other arm until the magnet is detached.

The same principle is used in an instrument described by S. Lipson[5] except that the detaching force is applied by a solenoid that surrounds the magnet. This solenoid is moved upward until the magnet is detached from the surface, and the position of the solenoid on a scale is used to define the attraction of the magnet and hence the thickness of the coating.

In another method[6] the magnet is detached by moving a weight along a beam and noting the position of the weight when the magnet is separated from the surface.

A. Brenner[7] employs a spring balance with a freely suspended magnet, in an instrument known as a *Magne-gage*. The calibration curves for these measurements are not straight lines but, as shown in Fig. 35, are roughly hyperbolic curves. Hence they yield about the same proportional accuracy for all thicknesses that can be reliably measured. With a 1-mm magnet, the attraction is not greatly affected by differences in the composition of the basis metal

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[1] *J. Electrodepositors' Tech. Soc.*, vol. 14, p. 108, 1938.

[2] *Bell Lab. Record*, vol. 19, p. 37, September, 1940.

[3] RADTCHENKO, I. V., and SHESTAKOVSKY, S. K., *J. Tech. Phys.* (*U.S.S.R.*), vol. 5, p. 1372, 1935.

[4] HOARE, W. E., and CHALMERS, B., *J. Sci. Instruments*, vol. 14, p. 248, 1937, and *J. Electrodepositors' Tech. Soc.*, vol. 14, p. 113, 1938.

[5] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 32, September, 1945.

[6] SPENCER-TIMMS, E. S., *J. Electrodepositors Tech. Soc.*, vol. 20, p. 139, 1945.

[7] *J. Research, Natl. Bur. Standards*, vol. 20, p. 357, 1938, RP 1081.

(high- or low-carbon steel or cast iron) or by its thickness if this is at least 0.01 in. The results are not affected by the diameter of the specimen or the radius of curvature provided that these are a few times the diameter of the magnet.

With a suitable curve (Fig. 36) it is possible to measure nickel coatings on steel because the nickel is less magnetic than iron. If a layer of copper and one of nickel are present, the magnetic reading is not a direct measure of thickness unless the proportion of copper and nickel is known. It is possible to determine the thickness of each of the two coatings by using two magnets of different strength, previously calibrated against composite coatings. By reference to these calibration curves the thickness and composition of the coating are defined by the readings of the two magnets.[1]

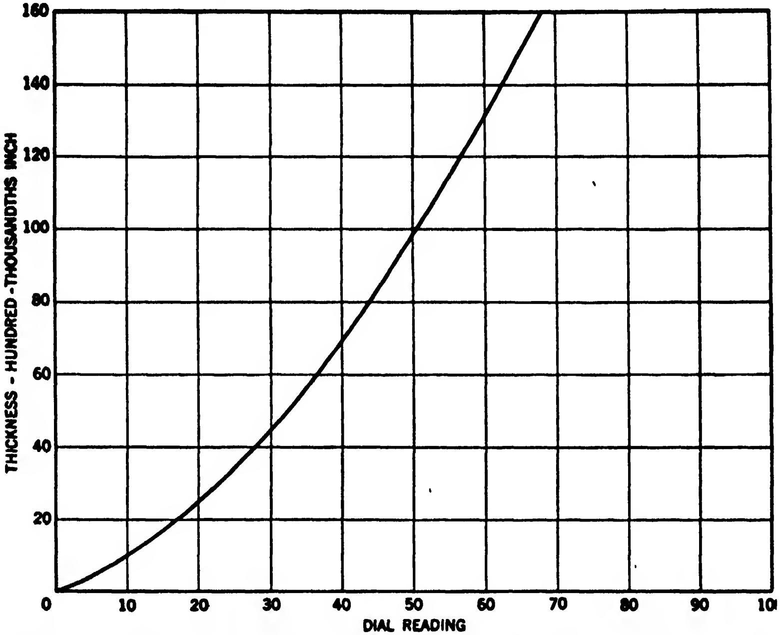

FIG. 35. Typical curve for thickness of copper vs. dial readings of Magne-gage.

For most coatings over 0.0002 in. (0.005 mm) thick, the Magne-gage yields results that are accurate to within about 10 per cent. For thin alloyed coatings, such as of hot-dipped tin or zinc, the

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[1] BRENNER, A., and KELLOGG, E., *Plating*, vol. 35, p. 242, 1948.

direct results are less accurate, although for a given type of coating a special calibration curve will yield satisfactory accuracy.

4. Miscellaneous thickness methods. Other physical methods for measuring the thickness of coatings have been suggested but have not yet been developed for general application. Among these may be mentioned the following:

a. Interference fringes. W. E. Hoare and B. Chalmers[1] measured the depth of small perforating pits present in or produced in thin tin coatings by counting the fringes when observed under a microscope.

b. X-ray measurement. R. C. Woods[2] measured the thickness of coatings by comparing the intensity of an X-ray photograph with that of a coating of known thickness.

c. Spectroscopic measurement. It has been proposed to use the intensity of appropriate lines in a spark spectrum as a measure of the thickness of the coating. This method resembles the spectroscopic method of analyzing metals for minor constituents.

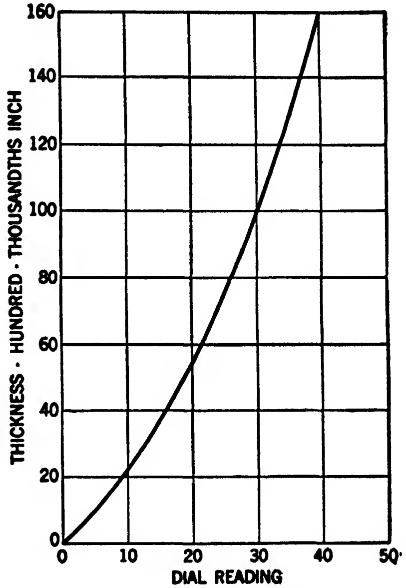

Fig. 36. Typical curve for thickness of nickel on steel vs. dial readings of Magne-gage.

Adhesion. *Significance.* The importance of good adhesion of plated coatings arises from the fact that without it the coatings may detach when any stress is applied as a result of mechanical deformation, changes in temperature, evolution of occluded gases, or incipient corrosion through fine pores. The principal causes of apparent poor adhesion are (1) the presence of a foreign material between the coating and basis metal, (2) the presence of a weak layer of metal either upon the surface plated or in the initial deposit, and (3) the presence of stresses in the deposited metal.

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[1] *J. Iron Steel Inst.*, vol. 132, No. 11, p. 135, 1935.

[2] *Metal Finishing*, vol. 39, p. 365, 1941.

In case (2), part of the basis metal may adhere to the coating when the latter is detached or vice versa. Strictly speaking, this is not evidence of poor but of good adhesion, since the bond is evidently stronger than one of the members. As it is impracticable to measure a force of adhesion that is stronger than one of the constituents, adhesion equal to the strength of one or both members must be considered for most purposes as *perfect* adhesion. In such cases any direct improvement in the observed adhesion must be sought in the avoidance of those steps that will produce a surface layer of structurally weak metal or in the inclusion of steps that will remove such a layer. In general, buffing or fine polishing of a metal surface tends to break up the crystals into a fine-grained though probably not amorphous layer, which may be weaker than the original surface layer. Abrasion of metal surfaces with coarse particles that produce relatively large scratches may also weaken the surface layer and reduce the apparent adhesion, even though the surface is rough.

Etching the metal before plating usually increases the adhesion, because it removes any weakened surface layer and also oxides or other foreign materials and hence in certain cases produces a clean and strong but rougher surface. The roughening effect is involved in the methods formerly used prior to plating on aluminum (page 378), because it is difficult to obtain or retain a chemically clean surface on that metal. One objection to etching the surface appreciably before plating is that the resultant roughening causes the deposited metal to be coarser and to require more polishing or buffing. For such purposes electrolytic polishing (page 215) might be desirable, as it apparently leaves the surface clean. Anodic pickling of steel (page 212) and other metals is extensively used to ensure good adhesion. From an extensive investigation of the adhesion of nickel to brass A. W. Hothersall[1] concluded that light anodic etching in solutions of cyanide or ammonium citrate yielded good adherence most consistently.

It has been frequently reported that it is difficult to secure good adhesion of deposited nickel to nickel owing to the presence of a passive film, probably oxide, on the old nickel surface. Hothersall[2] has confirmed the presence of the oxide film and has shown that good adhesion can be obtained by anodically etching the nickel in dilute sulfuric acid (25 to 30 per cent by weight) at room tem-

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[1] *J. Electrodepositors' Tech. Soc.*, vol. 7, p. 115, 1932.

[2] *J. Electrodepositors' Tech. Soc.*, vol. 13, No. 12, 1937.

perature. A current density of 20 amp/ft^2 (2 amp/dm^2) is used for 10 min, followed by 200 amp/ft^2 (20 amp/dm^2) for 3 min. The current is then reversed for about 1 sec, and the article is rinsed and introduced directly into the nickel bath. A *nickel strike* (see below) is also effective.

The presence of an oxide film also accounts for the difficulty in obtaining adherent deposits, *e.g.*, of nickel, on chromium-plated surfaces or on chromium alloys such as stainless steel. G. E. Gardam[1] has obtained good adhesion by cathodically treating the steel in a solution containing 240 g/l (32 oz/gal) of nickel sulfate and 50 g/l (7 oz/gal) of sulfuric acid. A current density of 150 amp/ft^2 (16 amp/dm^2) is used for 5 min at 35°C (95°F). D. Wood[2] recommends an initial strike in a solution containing 240 g/l (32 oz/gal) of nickel chloride and 125 ml/l (16 fl oz/gal) of concentrated hydrochloric acid.

It has frequently been suggested that the maximum adhesion of a coating should be obtained when the crystal structure of the basis metal is continued in the deposits (page 89). This condition may exist not only when the same metal constitutes the basis and the deposit[3] but also when the two consist of different metals.[4] As shown by A. Phillips and W. R. Meyer,[5] the continued growth of the basis metal crystals is confined to relatively low current densities, which should therefore be advantageous for good adhesion, especially as internal stresses are then also low.

The suggestion is often made that if a deposit *alloys* with the basis metal, its adhesion will be increased. That such alloying does sometimes occur is quite certain. It was early shown by W. G. Traub[6] and later by F. Carl[7] and by W. Castell[8] that, when copper is deposited on zinc, diffusion occurs, especially at elevated temperatures. This frequently produces brittle layers, which may foster subsequent detachment or blistering of the composite coat-

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[1] *J. Electrodepositors' Tech. Soc.*, vol. 13, No. 13, 1937.

[2] *Metal Ind.* (*N.Y.*), vol. 36, p. 330, 1938.

[3] BLUM, W., and RAWDON, H. S., *Trans. Am. Electrochem. Soc.*, vol. 44, p. 305, 1923. GRAHAM, A. K., *Trans. Am. Electrochem. Soc.*, vol. 44, p. 427, 1923.

[4] HOTHERSALL, A. W., *Trans. Faraday Soc.*, vol. 31, p. 1242, 1935.

[5] *J. Electrodepositors' Tech. Soc.*, vol. 13, No. 17, 1937.

[6] *Trans. Am. Electrochem. Soc.*, vol. 42, p. 55, 1922.

[7] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 20, October, 1933.

[8] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 21, October, 1934, and *Trans. Electrochem. Soc.*, vol. 66, p. 427, 1934.

ings. In this case diffusion has reduced the effective adhesion, even though there must certainly be very intimate contact to permit diffusion. Whether or not alloying occurs is therefore not so important as are the properties of the resultant alloy.

Measurement of Adhesion. A very complete bibliography and review of the methods of measuring adhesion was recently published.[1] The importance of good adhesion is such that it would be very desirable to include a quantitative specification that could be applied to a certain proportion, say 1 per cent of the finished products. No such method is at present available, and hence the adhesion tests commonly applied to finished products are largely qualitative. Such tests involve the ability of the coating to adhere during deformation of the article, caused by repeated bending, sometimes to fracture; by sudden stretching in a tensile test machine or in an Erichsen extrusion tester or *cup test;* or by shot blasting, hammering, penetration with a Brinell ball, chiseling a section, or rapidly vibrating a hammer.[2] Such tests indicate merely whether or not a coating adheres under the particular conditions used in the test but do not give quantitative data. The net result is roughly to characterize the adhesion of a particular coating as poor, fair, or good, depending upon the extent of detachment in the test. As shown by F. P. Romanoff[3] and others, the results of deformation tests depend upon the ductility of the coating and basis metal as well as the adhesion of the coatings and are therefore significant only under strictly comparable conditions.

The so-called "black-light test" depends upon the exposure of a clean cross section of the coating and basis metal, treating the surface with oil and wiping off the excess. The presence of oil in any minute crack between the coating and basis metal is then detected by exposure to ultraviolet light, which causes fluorescence. This test has been used to detect poor adhesion of silver coatings on bearings but has no quantitative value.

The two principal methods that have been proposed for quantitative tests of adhesion both require the preparation of special

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[1] Ferguson, A. L., and Stephan, L. F., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 32, pp. 168, 894, 1006, 1116, 1237, 1945; pp. 45, 166, 279, 620, 1946. Also *Am. Electroplaters' Soc. Research Repts.*, Serial Nos. 1 and 2, 1946, and 8, 1948.

[2] Hothersall, A. W., and Leadbetter, C. J., *J. Electrodepositors' Tech. Soc.*, vol. 19, p. 49, 1944.

[3] *Trans. Electrochem. Soc.*, vol. 65, p. 385, 1934.

specimens and are therefore not suitable for testing plated products. They are chiefly valuable for research, *e.g.*, the effect of each step upon the adherence of a particular coating to a given metal.

Ollard Method. In the method of E. A. Ollard,[1] illustrated in Fig. 37, a very thick coating, such as of nickel (which requires a long time to deposit), is applied to one end of a cylinder, *e.g.*, of brass. It is next machined down on the sides, so as to leave a shoulder of nickel. A hole is then drilled in the center. The resultant specimen is placed on a steel ring and is subjected to a load in a suitable compression machine. The load required to separate the coating is then divided by the area of the annular surface involved to obtain the adhesion, *e.g.*, in pounds per square inch.

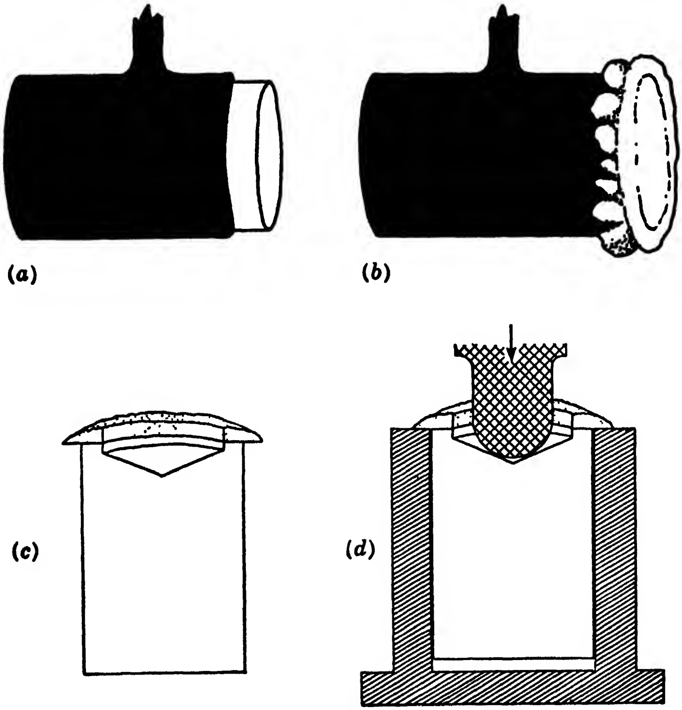

Fig. 37. Diagram of specimens used in Ollard test for measuring adhesion of plated coatings.

The results obtained by this method show that, with proper preparation of the steel surface, adhesion of nickel with a force as

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[1] *Trans. Faraday Soc.*, vol. 21, p. 81, 1926.

great as 50,000 lb/in.^{2} (3,500 kg cm^2) may be obtained. If this load is greater than the strength of the surface layer of the basis metal, the latter adheres to the detached nickel. This method has the advantage of measuring the perpendicular force required to detach the coating. The results are not, however, very reproducible and hence do not serve to measure small differences in the adhesion.

In a critical study of Ollard's method, E. J. Roehl[1] showed that, in order to obtain reproducible and significant results, the fracture must occur in tension and not in shear. To make the shear strength at least 1.3 times the tensile strength, it is necessary to define all dimensions accurately. With nickel on steel the best results were obtained with a cylinder 1.00 in. in diameter, supported in a die 1.02 in. in diameter. The inside hole was 0.938 in., and the plunger was 0.375 in. With a nickel coating at least 0.09 in. thick the adhesion to steel was 85,000 lb/in.^{2} (6,000 kg cm^2), which was slightly above the measured tensile strength of this nickel.

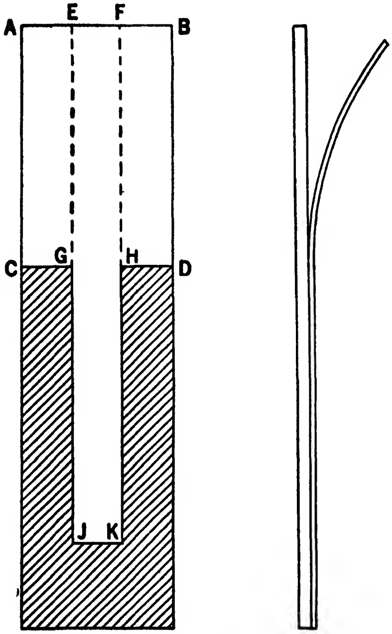

Fig. 38. Diagram of Jacquet test for measuring adhesion of plated coatings.

J. S. Hart and C. E. Heussner[2] employed a *micro-Ollard* test in which coatings of silver 0.02 in. thick were tested on a 0.25-in. cylinder with walls 0.010 in. thick.

Jacquet Method. The method of P. A. Jacquet[3] (Fig. 38) depends upon pulling off a strip of the coating, one end of which has been intentionally deposited with poor adhesion in order to provide a means for attaching the load to it. In this case the degree of adhesion is expressed in terms of the load per unit *width* of the

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[1] *Iron Age*, vol. 146, p. 17, September, 1940, and p. 30, October, 1940.

[2] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 33, p. 142, 1946.

[3] *Trans. Electrochem. Soc.*, vol. 66, p. 393, 1934.

strip, *e.g.*, in pounds per inch. In this test also portions of the basis metal frequently adhere to the coating if the adhesion is good. A few unpublished tests by A. Brenner indicate that in this test the apparent adhesion obtained with given preparation and conditions of deposition varies with the thickness of the deposit. This probably arises from the fact that the load is not continuously applied normal to the surface at the point of detachment but at an angle that depends upon the curvature assumed by the coating, which is partly a function of its thickness. At best, therefore, the method is useful only for strictly comparable deposits. A modification of this method was used by F. C. Mesle[1] to study the effects of numerous variables upon adhesion. In a qualitative test of the adhesion of nickel to aluminum[2] a narrow strip is twisted around a small rod.

It is evident that much more research is required to develop even a semiquantitative method for measuring the adhesion of plated coatings for purposes of inspection, if, indeed, this goal can ever be reached. In the meantime the qualitative tests may serve to detect decidedly poor coatings.

Protection against Tarnish and Corrosion. Electroplated coatings are used chiefly in order to obtain, on the surface, properties that are different from those of the metal to which the coatings are applied. One of the most important purposes is to improve the appearance and particularly to maintain for a longer period a desirable appearance, free from stains or tarnish. Ultimately, the basis metal may corrode sufficiently to weaken it structurally, but usually the plating must be considered as having failed long before that time.

The property that determines the behavior of a plated coating is its susceptibility to chemical action, especially in the atmosphere, which always contains as corroding agents oxygen, moisture, and carbon dioxide; in industrial locations also sulfur compounds, chiefly sulfur dioxide; and in marine locations sodium chloride. Strictly speaking, it is not so much the properties of the coating as their relation to the properties of the basis metal that determines the behavior of the plated article. With respect to a given basis metal, coatings are classified according to whether (1) they corrode more readily than the basis metal, in which case they protect small exposed areas of the latter, or (2) they corrode less readily

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[1] *Proc. Am. Electroplaters' Soc.*, p. 152, 1939.

[2] BROOK, G. B., and STOTT, G. H., *J. Inst. Metals*, vol. 61, p. 73, 1929.

than the basis metal, in which case they do not prevent and may accelerate corrosion of the basis metal exposed through any pores in the coating. This behavior is usually explained by the electrolytic theory of corrosion, according to which two metals in contact with any conducting solution (such as condensed moisture) form a small primary cell, in which the more active metal becomes the anode, *i.e.*, dissolves, and the less active becomes the cathode, *i.e.*, is prevented from dissolving. This *galvanic* action led to the early use of the term *galvanized* for zinc-coated iron. This theory has led to the use in England of the terms *anodic* and *cathodic coatings* for these two classes. One practical objection to this usage is that it may cause confusion with the coatings produced on aluminum and magnesium by anodic treatment or *anodic oxidation* in suitable electrolytes.

The two classes of coatings are best illustrated by deposits on iron and steel, which metals corrode in any natural atmosphere. On other metals it is more difficult to make a simple classification, because the behavior of the basis metal is more variable with changes in the atmosphere. On iron, protection against corrosion through pores is generally furnished only by zinc and cadmium coatings, while practically all other commercial coatings, including copper, nickel, tin, gold, silver, and even chromium, accelerate the corrosion of exposed iron. Under some conditions lead protects exposed steel.

Reference to the electromotive series of standard potentials (Table 10) shows that this classification does not exactly correspond to that table. For example, while zinc is more negative than iron and therefore would be expected to protect it, cadmium, which also protects iron, is slightly less negative than iron. On the other hand, chromium, which accelerates the corrosion of iron, is more negative, *i.e.*, stands above iron in this series. These anomalies illustrate the fact that the electromotive series is of value in predicting the relative behavior of metals only when they are *active*, *i.e.*, readily reach an equilibrium condition, and when they are in similar *environment*, *i.e.*, in equilibrium with similarly ionized compounds. In the atmosphere chromium acts as a noble metal because it is *passive* (page 50), probably as a result of a thin oxide film, which keeps it bright and at the same time prevents it from dissolving and thereby protecting the adjacent iron. Cadmium certainly protects iron against corrosion. Possibly the values of the potential of cadmium in Table 10 may be in error and subject to correction through further research. Moreover, cadmium tends to form, even in chloride solutions, compounds that are only slightly ionized and in which the cadmium has a more negative potential than the iron. The electromotive series is therefore only a rough guide to the protective value of metals.

Outdoor Exposure Tests. These general principles have been fully confirmed in extensive atmospheric exposure tests of plated coatings that have been conducted in different countries.[1] Tests of this kind are useful for observing the actual behaviors of typical coatings of known composition, thickness, and history under marine, industrial, urban, and rural conditions. Atmospheric exposure tests have only a limited value, however, (1) because it is impossible to represent all types of climate in any reasonable number of locations and (2) because in actual service, *e.g.*, on automobiles, plumbing fixtures, and hardware, factors other than continuous atmospheric exposure often have a strong influence. Another possible source of uncertainty is the system of inspection and rating employed. In order to permit correlation of results by different observers in separate locations and to facilitate quantitative comparisons, some impersonal numerical system of rating is necessary. Such a system was used in the joint exposure tests recently conducted in the United States. A numerical, but not linear, scale from 0 to 5 was applied, depending upon the extent of rust, stains, blisters, peeling, or other defects on the surface. One objection to such a system is that it gives equal weight to different defects, the relative importance of which may vary according to the service required or to the purely personal preference of the user. Therefore the results of atmospheric tests must be considered only as a guide in the selection or specification of coatings.

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[1] JACQUET, P. A., *Bull. soc. franc. élec.*, 5, vol. 2, p. 631, 1932.

FIGOUR, H., and JACQUET, P. A., *Compt. rend.*, vol. 194, p. 1493, 1932.

HIPPENSTEEL, C. L., BORGMAN, C. W., and FARNSWORTH, F. F., *Proc. ASTM*, vol. 30 (II), p. 456, 1930.

Report of Subcommittee VIII on field tests of metallic coatings, *Proc. ASTM*, vol. 33 (I), p. 149, 1933.

BLUM, W., STRAUSSER, P. W. C., and BRENNER, A., *J. Research Natl. Bur. Standards*, vol. 13, p. 331, 1934, RP 712.

BLUM, W., STRAUSSER, P. W. C., and BRENNER, A., *J. Research Natl. Bur. Standards*, vol. 16, p. 185, 1936, RP 867.

BLUM, W., and STRAUSSER, P. W. C., *J. Research Natl. Bur. Standards*, vol. 24, p. 446, 1940, RP 1293.

The principal results obtained in atmospheric exposure tests *on steel* may be summarized as follows:

1. The protective value of nickel coatings depends principally upon their thickness. An average thickness of at least 0.0005 in. (0.013 mm) is required for good protection under mild conditions and at least 0.001 in. (0.025 mm) under severe conditions.
2. The conditions of nickel deposition and of the cleaning and pickling have no marked effects on the protective value, provided adherent coatings are obtained.
3. The presence of a layer of copper either next to the steel or between two nickel layers reduces the protective value, especially of thin nickel deposits, under severe conditions. If chromium is subsequently applied to the final nickel layer, the presence of a copper layer has very little harmful effect in thick deposits. Buffing of the copper layer increases its protective value.
4. A very thin coating of chromium, *e.g.*, less than 0.00001 in. over nickel, may reduce the protective value, especially of thin nickel coatings. Chromium coatings about 0.00002 in. thick add very little to the protective value, but they increase the resistance to surface tarnish.
5. The use of zinc or cadmium coatings under nickel produces blisters and white stains and reduces the protective value.
6. In marine or rural atmospheres, thin coatings of zinc or cadmium furnish better protection against corrosion than do equally thin coatings of nickel or chromium.
7. In industrial locations both zinc and cadmium coatings fail rather rapidly, the cadmium in about 70 per cent of the time required for zinc of the same thickness.
8. In industrial locations the protective value of either zinc or cadmium coatings is practically proportional to their thickness.
9. Neither the methods of preparation nor of plating zinc or cadmium coatings that were used had any marked effect on the protective value, but they may affect the mechanical properties, *e.g.*, in forming operations.
10. Plated zinc coatings furnish about the same protection as hot-dipped coatings of the same thickness.

The exposure tests of plated coatings on *copper and brass* led to the following conclusions; based on the solutions and methods used in the above investigation.

1. A given degree of protection is furnished by somewhat thinner nickel coatings on brass than on steel or zinc. This is probably

caused by the greater resistance of any exposed brass to corrosion and not because of any decidedly lower porosity of the coatings.

2. The methods of preparation and plating, including the use of *bright nickel,* do not have much effect on the protective value, provided adherent coatings are obtained.

3 Coatings of chromium more than 0.00003 in. thick applied over 0.0002 in. of nickel on brass show a marked tendency toward cracking, with ultimate corrosion of the brass.

4. The results are not greatly affected by the composition of the brass. In fact, nickel-brass (nickel-silver) with 18 per cent of nickel requires about as much nickel and chromium for its complete protection as does yellow brass.

On *zinc and zinc-base die castings,* the coatings behave much like those on steel, except that the corrosion products are white instead of red.

1. It requires at least 0.0003 in. of nickel to furnish any appreciable protection to zinc.

2. About the same protection is obtained with a given thickness of nickel (*a*) deposited from the high-sulfate bath or (*b*) as duplex nickel coatings, consisting of a high-sulfate layer plus a *standard* nickel layer. However, high-sulfate deposits more than 0.0005 in. thick tend to crack and are therefore not practicable for general plating.

3. When an initial layer of copper from the cyanide or Rochelle salt bath is applied to zinc followed by regular nickel or bright nickel, the copper adds little to the protective value unless the copper is at least 0.0003 in. thick and the total thickness of copper plus nickel is at least 0.001 in. The practical advantages of applying an initial copper layer more than offset its limited protective value.

In Fig. 39 the results of all these exposure tests are graphically summarized. These curves show that to obtain a given degree of protection, *e.g.*, 60 per cent for one year in all locations, it requires about 0.0002 in. of nickel on brass, 0.0007 in. of copper plus nickel on zinc, and 0.00085 in. of copper plus nickel on steel.

Accelerated Tests. The long time and large expense required for atmospheric tests emphasize the desirability of accelerated tests in the hope of obtaining in a short period, preferably less than 24 hr, results that will be at least in the same order as will be found in the actual conditions to be met. Such acceleration can be obtained only by using more severe conditions, *e.g.*, more corrosive solutions or higher temperatures, or more rapid replenishment than would exist naturally. The results thus obtained are not usually parallel to those in service. If the corrosion is of the same type as in service, the method may be useful in comparing the quality of different coatings of the same metal or of closely similar metals in a corresponding atmosphere but not of widely different coatings or in an entirely different exposure. For example, the accepted greater resistance of cadmium than of zinc in the salt-spray tests is only roughly parallel to the relative behavior of these two metals in a purely marine atmosphere but has no bearing on the fact that in an industrial atmosphere cadmium coatings fail in about two-thirds of the time required for zinc coatings of the same thickness.

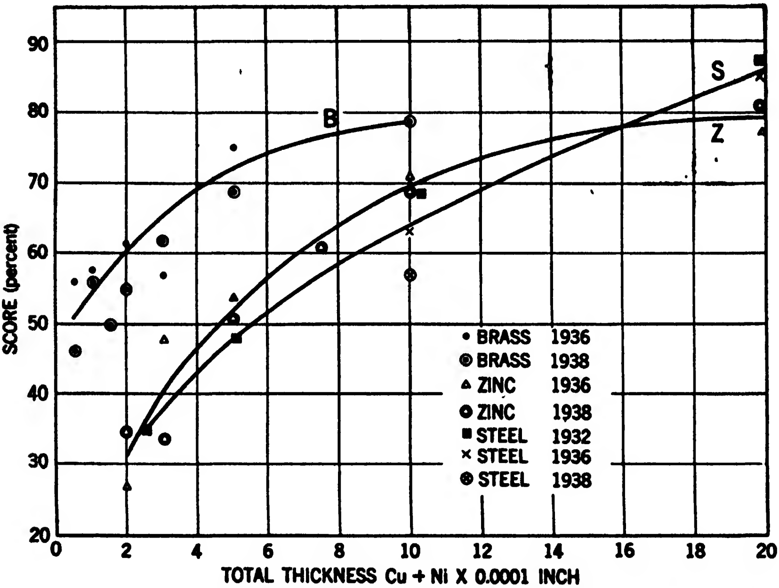

FIG. 39. Summary of exposure tests of nickel and chromium coatings on steel, zinc, and brass.

Salt-spray test (*salt-fog test*). The principal accelerated tests that have been applied to plated coatings are the salt-spray test and the intermittent immersion test, both usually conducted with sodium chloride (common salt). Occasionally other salts, such as calcium chloride,[1] or ammonium chloride,[2] sodium chloride plus

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[1] MOUGEY, H. F., *Trans. Am. Electrochem. Soc.*, vol. 58, p. 93, 1930.

[2] FARNSWORTH, F. F., and HOCKER, C. D., *Trans. Am. Electrochem. Soc.*, vol. 45, p. 281, 1924.

acetic acid,[1] are substituted for sodium chloride, but without any apparent advantages unless specific resistance to that chemical is desired or a definite correlation with service has been established. No obvious advantages have been reported for the intermittent immersion, and hence the salt spray is most frequently used.

The salt-spray test depends upon the application of a very fine mist to the cleaned articles and their inspection for evidence of corrosion after definite intervals. This test is included in many specifications for various metals and coatings. It is therefore very important to standardize it so as to secure reproducible results.

Intensive studies of the salt-spray test have shown that the corrosion is usually a direct result of the settling of very fine fog particles upon the metal surfaces. In fact, the test has been recently referred to as the *salt-fog test.* Realization of this mechanism has led to better definition of the factors that should be controlled to obtain reproducible results. These may be summarized as follows:[2]

1. The apparatus consists of (*a*) a fog chamber made of materials that will not affect the test in which the specimens are suitably supported, (*b*) a salt-solution reservoir, (*c*) a supply of suitably conditioned compressed air, (*d*) one or more atomizing nozzles, and (*e*) provision for controlling the temperature.

2. No drops of solution that accumulate on the top or cover of the box will be allowed to drop on the specimens, and the solution that condenses on the specimens shall not be returned to the reservoir.

3. The specimens shall be suitably cleaned, *e.g.*, with magnesium oxide and water, so as to be free from water break.

4. The specimens shall not be hung vertically (unless so specified) but at an angle of about 15 deg from vertical. Because very little condensation occurs on vertical surfaces, their corrosion is less rapid. Specimens shall be so placed as not to touch or shield each other or to allow solution to drop from one to another.

5. The salt solution shall contain 20 ± 2 per cent of pure sodium chloride in distilled water or in water containing not over 200 parts per million of dissolved solids. (Concentrations from 3 to 10 per cent are often specified, but the 20 per cent solution is most commonly used.) The salt shall be at least 99.8 per cent sodium

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[1] NIXON, C. F., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 32, p. 1105, 1944.

[2] ASTM Tentative Method B117-44T, *Tentative*, Part I-B, p. 773, 1946.

chloride and shall contain not more than 0.1 per cent of sodium iodide. The solution shall be free from suspended solids and shall have a pH between 6.5 and 7.5.

6. The temperature in the test zone of the chamber shall be between 92 and 97°F (33.3 to 36.1°C).

7. In collectors placed within the exposure zone, the amount of salt solution condensed shall be equivalent to 0.5 to 3.0 ml/hr on an area of 80 cm^2. This area corresponds to the horizontal area of a funnel or crystallizing dish 10 cm (4 in.) in diameter used to collect the condensed fog.

8. The solution condensed in the receiver shall contain 20 ± 2 per cent of sodium chloride. This limitation ensures that the air used for producing the fog does not have too low a humidity (in which case the condensed solution will be more concentrated) or too high a humidity (which will produce a more dilute condensate).

9. The nozzles shall be so baffled as to prevent direct impingement of spray on the specimens.

10. At the conclusion of the test the specimens shall be gently washed in water at not above 100°F and then immediately dried, after which the nature and extent of corrosion shall be observed and recorded.

Operation of this test with no temperature control, *e.g.*, in an unheated room, may yield inconsistent results in winter and summer, with temperatures that may range from 40 to 95°F (5 to 35°C). Some temperature control is therefore highly desirable. If thermostatic control is installed, it is preferable to operate at a relatively high temperature such as 95°F (35°C), as then no artificial cooling is required in summer. Another advantage is that the test is further accelerated by the high temperature. No exact formulas have been derived upon the effect of changes in temperature of the salt spray, but roughly it may be assumed that failure will occur about twice as rapidly at 95°F (35°C) as at 70°F (21°C).

The results of the salt-spray test are sometimes defined in terms of the period required to produce corrosion of the basis metal, without, however, defining the extent of rust that constitutes failure. Experience has shown that more consistent results are obtained by expressing the extent of the rust at the end of a definite period, such as 24 or 100 hr. Of two specimens, one may show a single rust spot after 24 hr and no more up to 100 hr, while the other may show no rust until 50 hr but then develop a large number of spots. In general, the latter coating is inferior, although by the older system it would have been reported as the better of the two. To some extent this source of error is removed by defining[1] *appreciable corrosion* as "the presence of more than six rust spots per square foot that are visible to the unaided eye or of any rust spots larger than 1/16 in. in diameter."

Various observations[2] have shown that the results of the salt-spray test are not closely parallel to the behavior in a marine atmosphere of coatings of copper, nickel, or chromium on steel or on zinc. They are of less value for testing coatings on copper or brass[3] and of little value for coatings of zinc or cadmium on steel.[4]

As a result of the more extensive use of the salt-spray test, equipment has been designed that will function reliably and neatly for extended periods. This includes durable compressors, efficient air filters and humidifiers (to prevent clogging of the atomizer), water seals on the box that will not permit leakage of liquid or spray, and means of completely removing the exhaust spray from the box without contaminating the room, the general ventilation system, or surrounding buildings.

Porosity Tests. In coatings of zinc or cadmium on steel slight porosity of the coatings has no significant effect on their protective value unless the coatings are less than about 0.0002 in. thick.[5] In that case the coating is likely to dissolve more rapidly because of the accelerating action of the iron exposed at pores and thus finally to expose larger areas of iron than can be protected by the surrounding zinc or cadmium. There is, however, little justification for considering this or any other value as a *critical thickness*,[6] since the porosity varies with many conditions, including the character of the steel and the condition of the bath. For practical purposes porosity of the usual coatings of zinc or cadmium can be disregarded.

Pores in cadmium coatings can be readily detected by immersing the cleaned article in 1 per cent hydrochloric acid (by volume) at

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[1] Tentative specifications for electrodeposited nickel and chromium on steel (A166-45T), *ASTM Tentative Standards*, Part I-B, p. 743, 1946.

[2] Strausser, P. W. C., Brenner, A., and Blum, W., *J. Research Natl. Bur. Standards*, vol. 13, p. 519, 1934, RP 724.

[3] Strausser, P. W. C., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 24, p. 822, 1937.

[4] Blum, W., Strausser, P. W. C., and Brenner, A., *J. Research Natl. Bur. Standards*, vol. 16, p. 185, 1936, RP 867.

[5] Clarke, S. G., *J. Electrodepositors' Tech. Soc.*, vol. 8, No. 12, 1933.

[6] Patterson, W. S., *J. Electroplaters' Depositors' Tech. Soc.*, vol. 5, p. 96, 1930. Wernick, S., *J. Electroplaters' Depositors' Tech. Soc.*, vol. 6, p. 129, 1931.

room temperature for about 10 min. Bubbles of hydrogen appear at the pores. There is almost no attack of the cadmium coating in that period.[1]

With coatings of the noble metals, such as of nickel, copper, and chromium on iron, the porosity largely determines the protective value. If, therefore, a simple, reliable, quantitative test for porosity were available, it would replace most other tests. In principle, all that is required is to apply to the surface a reagent that will not attack the coating but will attack any exposed basis metal and give visual evidence of such attack. An extensive bibliography of porosity tests was recently published.[2]

FERROXYL TEST. The best known and most used porosity test is the *ferroxyl* test, in which the corroding agent is usually sodium chloride and the indicator is sodium or potassium ferricyanide, which produces a blue color where iron is exposed. In a preliminary report of an extensive American Electroplaters' Society research[3] on porosity of electrodeposits, N. Thon has shown that the ferroxyl test as previously conducted may yield very erroneous results for porosity. He recommends the use of a reagent with a relatively high concentration of ferricyanide, 50 g/l of $K_3Fe(CN)_6$, and a low concentration, 0.2 g/l of NaCl, or with 10 g/l of Na_2SO_4 and no chloride. These reagents do not dissolve nickel at any appreciable rate, but they may not reveal all the fine pores that exist and that may be exhibited in long-time exposure. More study is required to define a satisfactory ferroxyl reagent.

To prevent spread of the blue spots, a gelatinous substance such as agar (about 10 g/l) may be added. To facilitate the reading and recording of spots, the reagent may be absorbed in paper,[4] which is stored dry and moistened before application to the surface to be tested.

In order to preclude any solvent action of the reagent upon the nickel, it has been suggested that the paper contain only sodium chloride and agar, and after the moistened paper is applied to the plated steel and removed, it is dipped into a ferricyanide solution

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[1] CLARKE, S. G., *J. Electrodepositors' Tech. Soc.*, vol. 8, No. 12, 1933.

[2] THON, N., and ADDISON, E. T., JR., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 34, pp. 445, 568, 722, and 831, 1947, and *Am. Electroplaters' Soc., Research Rept.*, Serial No. 5, 1947. THON, N., and KELEMEN, D. K., *Proc. Am. Electroplaters' Soc.*, p. 105, 1949.

[3] *Proc. Am. Electroplaters' Soc.*, p. 128, 1947.

[4] PITSCHNER, K., *Proc. ASTM*, vol. 27, pt. II, p. 304, 1927.

to develop the blue spots.[1] Another method of applying the reagent, especially to large objects, is by spraying.

It is difficult to express quantitatively the result of porosity tests. Counting the spots per unit area does not take into account their relative size or determine if a coating with five relatively large spots per square foot is inferior to one with one hundred very fine spots per square foot. The observed size of the spots is not very reproducible, as it depends on the concentration of the reagent, which, with ferroxyl paper, depends in turn on the amount of water applied to the paper and the amount that evaporates during the test. In consequence, this and most porosity tests are only qualitative and serve merely to distinguish relatively good and poor coatings.

For detecting pores in coatings on copper or brass, the ferroxyl test is also used, as it gives red spots of copper ferrocyanide where copper is exposed through nickel or chromium. For this purpose ferrocyanide is probably preferable to ferricyanide. Tests[2] show that the ferroxyl test serves only to distinguish between very porous and relatively impervious coatings on copper or brass and is not sufficiently sensitive to serve in specifications.

Hot Water Test. This test, which was originally devised for detecting porosity in tin coatings on steel,[3] has also been applied to nickel coatings on steel.[4] It depends upon immersion of the cleaned specimen in pure distilled water having a pH between 4.5 and 7.0 at a temperature of 95 to 100°C (203 to 212°F) for 6 hr. Rust spots then appear at any points where the steel is exposed. About the same results are obtained if the specimen is kept in the hot water for 3 hr and then allowed to stand in the water while it cools for 18 hr. In his 1939 report Strausser found that the hot-water test yielded fewer pores than did the ferroxyl test, even when the paper was developed in ferricyanide, as above.

Another type of porosity test, *e.g.*, for nickel on brass, depends on immersion in a solution of ammonium trichloroacetate or of

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[1] Strausser, P. W. C., *Proc. Am. Electroplaters' Soc.*, p. 194, 1939.

[2] Strausser, P. W. C., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 24, p. 822, 1937.

[3] Macnaughtan, D. J., Clarke, S. G., and Prytherch, J. C., The determination of the porosity of tin coatings on steel, *J. Iron Steel Inst.*, vol. 125, No. 1, p. 159, 1932.

[4] Hothersall, A. W., and Hammond, R. A. F., *Trans. Electrochem. Soc.*, vol. 73, p. 449, 1938.

ammonium persulfate,[1] which will slowly dissolve any exposed brass. The extent of the attack in a given period and hence the degree of porosity of the nickel can be estimated by the intensity of the blue color produced in the solution by the dissolved copper. This is determined by comparison of the color with that of similar solutions containing known amounts of copper. The results are of value only in detecting very porous coatings.

CHROMIUM COATINGS. Pores or cracks are very prevalent in most chromium coatings.[2] They can be detected and roughly estimated by an electrolytic test[3] that depends upon the fact that, with a low voltage, copper will not deposit upon chromium. If the plated article is made the cathode in a bath containing 200 g/l of copper sulfate and 75 g/l of sulfuric acid and a potential of 0.2 volt is applied between the cathode and a copper anode, copper deposits only at pores or cracks in the chromium. The relative extent of the porosity can be judged by the weight of copper deposited or by the current that passes.

COATINGS ON ZINC. Porosity of nickel or chromium coatings on zinc or zinc-base die castings can be detected by treating the surface with a solution containing 100 g/l of copper sulfate, $CuSO_4 \cdot 5H_2O$, and 10 ml/l of concentrated sulfuric acid. Copper is then deposited at any pores in the coating.

Another test[4] involves immersion of the plated die castings in a solution containing 300 g/l of sodium hydroxide and sufficient cane sugar to make a viscous solution when hot. A little glycerin is added to prevent crystallization of the sugar. When this solution reacts with any zinc at pores, bubbles of hydrogen are evolved. By allowing the solution to cool with the article immersed in it, these bubbles are fixed in place and can be recorded.

P. W. C. Strausser[5] found that the last two methods readily detect large or numerous pores that exist in very thin coatings but do not serve to differentiate somewhat thicker and less porous

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[1] STRAUSSER, P. W. C., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 24, p. 822, 1937.

[2] BLUM, W., BARROWS, W. P., and BRENNER, A., *J. Research Natl. Bur. Standards*, vol. 7, p. 697, 1931, RP 368.

[3] BAKER, E. M., and RENTE, A. M., *Trans. Electrochem. Soc.*, vol. 54, p. 337, 1938.

[4] BAUER, ARNDT, and KRAUSE, "Chromium Plating," translated from the German by E. W. Parker, Edward Arnold & Co., London, 1935.

[5] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 24, p. 822, 1937.

deposits on zinc die castings. For this purpose the salt-spray test is more satisfactory.

Wear Resistance. All plated coatings must exhibit some resistance to wear or abrasion in service, and for special purposes, *e.g.*, on printing plates and bearing surfaces, increased resistance to wear may be the determining factor in the choice of a plated coating. It is therefore highly desirable to measure and control those properties which affect the wearing quality of the surface.

Practically, wear is so variable and so complicated that it is not possible to devise any single simple test from which the performance of a coating might be predicted. In a broad sense, *wear* may be the result of (1) deformation, (2) abrasion, or (3) erosion or any combination of these three factors. These may be simply illustrated by the behavior of printing plates, for which these three effects can be more readily distinguished than for more involved mechanisms.

Deformation. If a printing plate is *soft* and is subjected to an excessive pressure, it simply flattens out, with a corresponding alteration in the design. It is largely for this reason that for *plate printing*, where considerable pressure is applied, steel or copper is used while for surface, or *letterpress*, printing, where, in good practice, there is almost no pressure between the paper and the plate, relatively soft type metal is most commonly used. The application of a hard surface, such as chromium, to an article subjected to deformation is seldom advantageous. In fact, the yielding of the soft basis metal is likely to foster cracking and flaking of the hard coating.

Abrasion. Abrasion is the result of the scratching and the tearing out of fragments from the surface. This is most likely to occur when hard particles, such as the pigments in printing inks, are rubbed against the surface. Even in the absence of foreign particles any fragments of the surface that are initially detached, *e.g.*, by high local pressures, are likely to cause further abrasion. It is evident that, in order to prevent abrasion, the surface must resist both the penetration of particles into it and the rending or tearing of portions of the surface material. Speaking crudely, it must be both *hard* and *tough*. For such purposes plated coatings, especially of chromium, are frequently advantageous, even though the usual brittleness of chromium may limit its usefulness, especially if any sudden impacts, or *pounding*, are involved.

Erosion. Erosion is usually defined as the result of both abrasion and corrosion. The latter facilitates the detachment of particles, especially if it causes selective or intercrystalline attack. On printing plates such action is illustrated by the effects of certain colored inks that attack copper or lead but not nickel or chromium. Nickel is therefore often applied to printing plates when the actual extent of abrasion would not warrant its use. Other examples of erosion are the effect of steam in turbines and the effect of tide and sand on marine structures.

Hardness. It is customary to say that in order for a surface to resist wear it must be *hard.* But the above examples show that different types of hardness are required to withstand different kinds of service. These types are illustrated by the various methods used to measure hardness.[1]

BRINELL. In the Brinell (and also the Rockwell) method a hard steel ball is pressed into the surface with a prescribed load and the diameter or depth of the resulting indentation is measured. The result is expressed in terms of the Brinell number. A high number corresponds to a small indentation and therefore a greater hardness. This method measures essentially the resistance to deformation.

VICKERS. In the Vickers method the ball is replaced by a diamond point with a specified angle and the size of the impression is measured. The result is expressed in numbers that usually agree closely with corresponding Brinell numbers. This method is principally a measure of resistance to deformation, with possibly some *cutting* effect of the diamond edges.

KNOOP INDENTER. A new type of indenter[2] for hardness measurements consists of a diamond that has been cut with a pyramidal face, which produces a diamond-shaped indentation seven times as long as it is wide and thirty times as long as it is deep. The length of the indentation produced by a given load and measured with a microscope is a measure of the hardness of the material. Because the impressions are very shallow, relatively thin coatings can be tested. Tests with chromium coatings on steel[3] showed that if the thickness of coatings is fourteen times the depth of

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[1] A summary of methods of hardness testing will be found in *Proc. ASTM*, vol. 43, p. 803, 1943.

[2] KNOOP, F., PETERS, C. G., and EMERSON, W. B., *J. Research Natl. Bur. Standards*, vol. 23, p. 39, 1939, RP 1220.

[3] PETERS, C. G., and KNOOP, F., *Metals & Alloys*, vol. 12, p. 292, 1940.

indentation, the measured hardness (in this case equivalent to about 900 Brinell) is independent of the hardness of the underlying steel. Practically, this method is applicable to chromium coatings that are at least 0.001 in. thick. Similar results are obtained on thin coatings by the *micro-Vickers* apparatus, in which a small diamond point is pressed into the surface and the width of the impression is measured with a microscope.

SCLEROSCOPE. The scleroscope, or Shore, method measures the height to which a steel ball rebounds when dropped from a specified height upon the surface. As this operation usually produces a slight indentation, deformation is also involved, but principally the *elasticity* of the metal is tested.

SCRATCH HARDNESS. In various forms of scratch hardness measurements, the point of a hard object, usually a diamond of specified shape, is drawn across the surface under a definite load. The width of scratch thereby produced is measured with a microscope. A narrow scratch corresponds to a high hardness. It is usually assumed that the hardness varies inversely as the square of the width of scratch. In that case a material *A* with a scratch half as wide as that on *B* would be reported as being four times as hard as *B*. At best, such a relation is hardly quantitative, as it is not possible to define just what is meant by *hardness*.

All the methods for measuring the hardness of thin coatings are likely to be influenced by the hardness of the basis metal. For this reason it is customary to make hardness measurements on relatively thick coatings, the properties of which are not necessarily the same as those of the customary thin coatings. Egeberg and Promisel[1] use a micro-Brinell test with a 1-mm ball. However, especially with hard metals, the indentations are then too small to measure accurately.

Indirect indications of hardness and toughness can be obtained from measurements of tensile strength, elastic limit, and elongation. Roughly, an increase in tensile strength of a given metal corresponds to an increase in hardness. It is doubtful, however, if such measurements, which are necessarily made on relatively thick, separated deposits, always represent the properties of the much thinner coatings usually employed.

Measurements of hardness of various plated metals are summarized in Table 16 (Appendix) based largely on the work of

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[1] *Metal Cleaning Finishing*, vol. 9, p. 25, 1937.

Macnaughtan and associates.[1] Much more significant than the variation in hardness of different metals is the great range obtained with the same metal deposited under different conditions. This is important, because it shows that, if an electrodeposited metal approaches the properties desired for a given purpose, the hardness can be considerably increased or decreased in order to meet any given requirements more closely. In general, hardness of deposits is increased by an increase in current density, at least nearly up to the point where visible burning appears. To some extent this increase is caused by a decrease in crystal size, although, as pointed out by Macnaughtan and others, the inclusion of basic materials may also be an important factor.

As indicated above, there is no simple relation between any measurement of hardness and the actual wear resistance, although such measurements may furnish a rough guide. For abrasion resistance, which plated coatings must often possess, the results of scratch hardness tests may be most significant. Unfortunately such measurements are not very reproducible, especially on very hard surfaces.[2]

Accelerated Wear Tests. In the absence of an entirely satisfactory hardness test, accelerated wear tests are sometimes proposed but less often used. These may involve resistance to rolling metal surfaces with or without abrasive, or to abrasive wheels. Other methods depend upon the loss in weight produced by contact with an abrasive powder, which may be dropped upon the surface from a known height. Such methods do not yield very reproducible results, and their results are significant only if the conditions at least approximate those which exist in service. Accelerated wear tests are even less conclusive than are accelerated corrosion tests.

Reflecting Power and Brightness. A large proportion of plated coatings, particularly those of the noble metals, such as gold, silver, and platinum, and of the passive metals, such as nickel and chromium, owe their use largely to the presence and maintenance of a high luster. The recent development of *bright-nickel-plating* solutions has for its object the production of coatings sufficiently bright to permit the subsequent application of chromium with no

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[1] MACNAUGHTAN, D. J., and HOTHERSALL, A. W., *J. Electroplaters' Depositors' Tech. Soc.*, vol. 4, p. 31, 1928, and vol. 5, p. 63, 1930. MACNAUGHTAN, D. J., *J. Iron Steel Inst.*, vol. 109, p. 409, 1924.

[2] GRANT, L. E., and GRANT, L. F., *Trans. Am. Electrochem. Soc.*, vol. 53, p. 509, 1928.

buffing of the nickel. In recent years there has also been a demand for bright coatings of zinc and cadmium, although it is well known that in even mild outdoor service these soon lose their luster. For these metals the initial bright finish is therefore largely for "sales appeal," the importance of which may not, however, be disregarded.

It is comparatively easy for average persons to agree that, of two similar surfaces, one is brighter than another but not whether, for example, a particular gold surface is brighter than a certain chromium surface. It is still more difficult to devise a method or specification to ensure a uniformly high luster of plated articles.

In one of the few researches having this particular purpose, B. Egeberg and N. E. Promisel[1] pointed out the difficulties and suggested a procedure for measuring the brightness. In any such comparison it is necessary to take into account the fact that different metal surfaces, though equally *bright*, reflect light to different extents. In Table 17 (Appendix) are given the percentage reflectivities of the common metals for visible light. (These values are different for other wavelengths, such as infrared and ultraviolet.) From these data it is evident that a chromium-plated surface will reflect only about two-thirds as much light as a silver surface. This is the reason that chromium-plated reflectors are rarely used except in those applications, such as in locomotive headlights, where silver is tarnished so rapidly that its reflectivity soon falls below that of chromium, which resists tarnish. The extensive use of rhodium plating on searchlight and floodlight reflectors is based on the fact that it has a relatively high reflectivity (about 75 per cent) and also resists tarnish. The choice of a metal for a reflecting surface therefore depends upon its initial reflectivity and its ability to retain it under the prevailing conditions of service.

Having selected the metal coating, it is desirable to measure and control its brightness, whether this is required for actual reflectivity or for appearance. In such measurements it is necessary to distinguish between *specular reflection* and *diffuse reflection.* If a beam of light strikes a perfectly plane polished surface at any angle, such as 45 deg, it is reflected in a direction such that the angle of incidence is equal to the angle of reflection, in this case 45 deg. If the surface is perfectly plane and bright, all the

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[1] *J. Electrodepositors' Tech. Soc.*, vol. 13, No. 29, 1937.

light is reflected in this way; in other words the *specular* reflection is 100 per cent.

In a microscopical sense, only a perfectly bright surface is plane; *i.e.*, any departure from brightness is caused by slight irregularities in the surface. Each of these irregularities represents a surface, however small, that the light beam hits at an angle different from the assumed angle (in this case 45 deg) and, of course, is reflected at a different angle. The net result of a large number of such minute irregularities is to scatter, or *diffuse*, the light.

Egeberg and Promisel propose to measure on a plane surface the proportion of light that is reflected specularly, *i.e.*, at the same angle as it struck the plane, and the proportion that is diffused, *i.e.*, reflected at other angles. They express the brightness as the relation of these two quantities. A surface with 100 per cent specular reflection is *perfectly* bright, and one with 90 per cent specular reflection and 10 per cent diffuse reflection is brighter than one with only 80 per cent specular reflection.

The exact measurement of light intensities is difficult and not highly accurate, especially if, as these authors reported, most fairly bright surfaces reflect over 99 per cent of the light specularly. In such a case it is necessary to measure and compare two widely different light intensities. In the above research the measurements were made with a photometer, first at 45 deg (specular reflection) and then at 5-deg intervals from 40 to 0 deg. (The latter angle represents a direction perpendicular to the surface.) The sum of the latter measurements represented the diffuse reflection.

By such measurements six silver coatings were placed in the same order of brightness as through visual examination by several observers. One difficulty with the direct ratio is that, as expressed in terms of the formula used by these authors, the brightness of the best specimen was 100 per cent and those of the next two were about 99.6 and 99.4 per cent. To increase the numerical difference in these ratios, the authors proposed to expand them to the eighth or even the fiftieth power, a very cumbersome process. It would be much simpler and probably more significant to express the results merely in terms of the departure from perfect reflection (as indeed these authors defined brightness). Strictly speaking, it would be better to call this a scale of *dullness*, which is what the eye probably notes. In such a scale the nearly perfect specimens would be given ratings of, for example, 0.4 and 0.6 per cent, and very dull specimens might be rated at 5 or 15 per cent.

E. Raub and M. Wittum[1] used a method similar to that of Egeberg and Promisel for measuring the brightness of nickel deposits.

At best, the above methods or those similar to them will be useful only as research tools, *e.g.*, to study the relative brightness of deposits from specified baths. They require especially prepared specimens on flat plates. These methods are therefore not applicable for inspection of plated articles, except possibly flat mirrors. For general inspection, visual observation by skilled observers with suitable lighting is probably the best procedure, which, however, is hard to fit into specifications.

Stress in Electrodeposits. It has long been known that during the deposition of many metals, especially of iron, cobalt, and nickel, stresses are set up that cause the metal deposit to contract. Early measurements of these stresses were made by V. Kohlschütter and his associates[2] in Switzerland and by E. A. Vuilleumier[3] in America. They used a device known as a *contractometer*, in which a narrow strip of metal was held rigidly at one end and the back was insulated. When metal was deposited on the one side, the strip curved toward the anode. The measured extent of its deflection indicated the magnitude of the stress in the deposit.

This subject assumed increased importance with the application of bright-nickel plating, in which stresses were sometimes produced that caused subsequent cracking and failure of the deposits. In two recent papers on this subject[4] bibliographies and experimental data are included. These authors each employed flat strips, the deformation of which was measured after deposition. From these measurements the stress, *e.g.*, in pounds per square inch, can be computed. Subsequently[5] a spiral contractometer was described, by means of which the effects were magnified and more easily measured.

No simple relation has been found between the stress and other physical properties such as hardness and tensile strength. Certain

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[1] *Z. Elektrochem.*, vol. 46, p. 71, 1940, translation in *Metal Ind.* (*N.Y.*), vol. 38, p. 206, 1940.

[2] *Z. Elektrochem.*, vol. 24, p. 300, 1918.

[3] *Trans. Am. Electrochem. Soc.*, vol. 42, p. 99, 1922.

[4] Soderberg, G. K., and Graham, A. K., *Proc. Am. Electroplaters' Soc.*, p. 74, 1947. Phillips, W. M., and Clifton, F. L., *Proc. Am. Electroplaters' Soc.*, p. 97, 1947.

[5] Brenner, A., and Senderoff, S., *Proc. Am. Electroplaters' Soc.*, p. 53, 1948.

impurities, either metallic or organic, may greatly increase the stress in nickel deposits. On the other hand, certain organic additions, *e.g.*, saccharin, greatly reduce the stress. In a few baths, *e.g.*, zinc baths, a *negative* stress has been observed, *i.e.*, a tendency for the deposit to expand.

No adequate theory of stress has been developed. In most baths the stress is less when impurities are absent and when relatively high temperatures and low current densities are employed. The effects of organic addition agents on stress are highly specific.

PLATING SPECIFICATIONS

Specifications that can be adopted for electroplating fall into two classes, *viz.*, *process* specifications and *product* specifications, which are sometimes confused.

Process Specifications. The purpose of process specifications is to define the work cycles, the limiting conditions for favorable operation, and the methods of control to be used in order consistently to yield coatings of the desired quality. Strictly speaking, such data constitute instructions rather than specifications and are of interest principally to the factory staff and not to the consumer.

Purity of Materials Used. Among the factors that affect the process directly and the product indirectly are the composition and purity of the anodes and chemicals used. Since the consumer of plated articles has no control over and no direct concern with these materials, their regulation is a part of the process specifications, to which too little attention has been paid.

There has been less standardization of the requirements for plating materials in the United States than in England. In the preparation of such specifications a few simple principles may be helpful.

The requirements should be no more severe than experience justifies. The use of moderate requirements not only permits the acceptance of the cheapest material that will serve the purposes but also fosters competition by firms that may not be willing to bid upon more stringent requirements. When similar products are used in other industries, the specifications of the latter should be used if appropriate, in order to reduce confusion and to simplify the manufacturing processes. The requirements should be explicit and include where feasible the minimum acceptable content of the desired constituents and the maximum permissible content of each harmful impurity. Methods of test should be described, or reference should be made to published methods.

Product Specifications. The consumer is concerned with the quality of the products and not with the method by which they were produced. If the quality can be fully measured by appropriate tests, the process need not be mentioned in the product specifications. When such mention is necessary, it is usually because no adequate definitions and tests for quality are available.

A product specification, *e.g.*, for plated articles, should be confined to the minimum number of requirements that will ensure the desired quality and performance. In that case failure to meet any one of the requirements should constitute cause for rejection. Typical features may be illustrated by the tentative specifications[1] for electrodeposited coatings that were adopted by the American Electroplaters' Society and the American Society for Testing Materials in recent years; these are summarized in Table 18 (Appendix).

Scope. The scope of the specification, including types of coating, must be stated. In most of the above specifications, products are defined for three or more types of service. For special purposes other grades may be justified. In general, however, as few grades should be used as possible, in order to reduce confusion and to facilitate the manufacture and testing. At best, any such requirements are merely estimates, because similar articles are not necessarily or usually subjected to just the same service. The consumer must therefore select a grade that will probably meet most of his needs at a reasonable cost.

Manufacture. The process of manufacture should be defined in general but sufficiently definite terms to ensure that the desired article and coating are supplied. In this section it may be necessary to include statements about properties, such as appearance, that are important but are not subject to quantitative tests. Such statements should be as few as possible, since they are apt to lead to controversy and have little legal value.

Properties. Those properties of the coatings, such as average or minimum thickness, freedom from porosity, resistance to corrosion, and hardness, which are believed to be essential and which can be reliably measured should then be stated as concisely as possible for each type or class.

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[1] *ASTM Tentative Standards*, Part I-B, pp. 737–779, 1946.

Tests. Methods to be used for testing the specified properties should be described in sufficient detail to ensure consistent results, or a definite reference should be made to some description of the method, which thereby becomes a part of the specification.

Sampling. The methods of sampling and the basis of rejection should be described. In view of the wide variety in the articles and in the scale of manufacture and sale, it is very difficult to do more than to enumerate principles, which must be adapted to the conditions involved in each particular contract. The ultimate decision depends largely upon (1) the cost of the articles, (2) the cost and nature of the testing, and (3) the type of service. Only if the latter is very critical and if the method of test is cheap and nondestructive can 100 per cent of the product be tested. Otherwise *a few samples* must be taken to represent the quality of the entire lot. The proportion of samples that will represent the average within any desired degree of probability (but never absolutely) depends upon the extent of the variation in properties that previous tests indicate may exist. Calculations made according to the laws of probability are accurate only when large numbers of tests of similar articles are involved. Actually, the number of tests to be made is more likely to be governed (sometimes erroneously) by the cost and convenience of the testing. Such arbitrary ratios as 1 of each 100 or 1,000 are justified only if experience has confirmed them. Actually, too few service data are available to determine with reasonable certainty if plated products of specified quality are always satisfactory and those below the standard are always unsatisfactory. The specified values are therefore merely approximate estimates.

The impossibility of plating large numbers of articles with identical and uniformly distributed coatings makes it necessary to include, explicitly or tacitly, a *tolerance* to cover the variations. In some cases this tolerance is written into the specifications. In effect the specification then represents the lowest quality the purchaser will accept and the highest the producer will guarantee. In any case the producer must allow a considerable margin above the specified thickness of coating to ensure that each piece has at least the required average or minimum thickness. This margin may amount to 50 per cent and is seldom less than 25 per cent. The net result is that the *average* quality of all the articles purchased is always considerably above the specification. This fact should be taken into account in fixing the latter.

Definitions. Any new, ambiguous, or highly technical terms (*e.g.*, *significant surfaces*) should be defined and thus made a part of the specification.

Notes. In most specifications it is desirable to attach notes or advice regarding methods of manufacture and testing. Such information should be clearly marked as *advisory* and not mandatory. It is not legally a part of the specification, and the producer is not required to follow it, nor is he excused from full conformance with the requirements because he followed this advice.

CHAPTER VI

ANALYSIS OF SOLUTIONS

GENERAL PRINCIPLES

Much of the progress made in commercial plating in the last twenty-five years has resulted from control of the bath composition by analysis at regular intervals. Through classes conducted by branches of the American Electroplaters' Society and by other institutions, many platers have learned how to analyze plating baths with sufficient accuracy for their control. These classes are especially valuable in developing the technic of handling the laboratory apparatus used in making such analyses.

With the growth of large electroplating plants, especially in the automobile industry, the need for frequent and rapid tests of plating baths has led to the employment of many chemists. Large-scale plating operations have justified the application of more elaborate equipment and methods than are generally available for small plants. Such procedures do not necessarily furnish more useful or more reliable information than is gained by simpler methods, but they may yield the results more quickly and, when required in large numbers, more economically. For many plating operations simple methods of test are adequate.

In this connection it is important to note that the reason for analyzing a plating bath is not to determine its exact composition but merely to know if it is within certain limits fixed by experience for that bath. If outside those limits, it is desirable to know what additions are required or, in the case of deleterious impurities, what steps will remove them. The required frequency of tests will depend upon the probable rate at which the bath composition changes, which, in turn, depends principally upon the current (amp-hr) passed through a given bath volume in a specified period and the corresponding drag out. Changes in composition may also occur through (1) *drag in* of water or acid, (2) spray losses, and (3) decomposition, *e.g.*, of cyanide solutions at high temperatures. Purely for illustration the control of a nickel bath will be discussed.

Because the pH of a nickel bath may change rather rapidly, it should be determined and, if need be, adjusted at least once a week and with very busy tanks once or more daily. The nickel content need be measured less frequently, *e.g.*, once a week. Especially if the pH changes rapidly or irregularly, the chloride content (which affects the anode corrosion) should be checked. The boric acid seldom needs to be determined but should be replenished about in proportion to the chloride, since both these constituents are removed principally by drag out. If ammonium salts are used, they need not be determined frequently. Additions of hydrogen peroxide or wetting agents are usually based on the appearance of pits and not on analyses. In some baths measurements of surface tension are used to control the addition of wetting agents.

When organic brighteners are used in a nickel bath, especially in large-scale operations, their content must be checked and adjusted more frequently. Just as with other constituents, systematic records of requirements during normal operations may serve as a basis for regular additions at frequent intervals, with analyses made less frequently as a check.

It cannot be too strongly emphasized that, in all production plating, analyses of the baths should be made primarily to maintain satisfactory operation and not to correct difficulties that have arisen. Periodic analyses should serve as the proverbial "ounce of prevention."

The accuracy required in such analyses will depend upon the particular bath and constituent but will practically never exceed 1 per cent of the constituent determined. Owing to unavoidable variations in bath levels as a result of evaporation and drag out, variations up to 5 per cent of the bath concentration are likely to occur and are unimportant. Plating baths should be kept within certain limits, but these limits are usually not narrow.

Qualitative Analysis. The purpose of qualitative analysis is merely to determine if certain substances are present. It may be useful at times in testing plating chemicals or baths for the presence of a certain impurity. For most purposes, however, if the impurity is deleterious, it is necessary to know at least its approximate concentration, for which quantitative tests must be made.

Quantitative Analysis. The purpose of a quantitative analysis is to determine the concentration of one or more constituents of a bath. The results usually represent the content of a specific metal or ion but can be used to compute the equivalent concentrations of the substances actually used in the preparation of the bath. Suppose, for example, that a nickel bath had been prepared from nickel sulfate, nickel chloride, ammonium chloride, and boric acid. From determinations of nickel, ammonium, and chloride ions it is possible to compute the concentrations of the three salts used. The boric acid need be less frequently determined. For calculations of the compounds probably present it is often convenient to express the results in terms of normalities, as in the following example.

RESULTS OF ANALYSIS	g/l
Nickel, Ni	71
Chloride, Cl	19
Ammonium, NH_4	3

To convert these values to normalities, divide the concentration of each constituent by its equivalent weight.

	N
Nickel, 71 ÷ 29.3	2.42
Chloride, 19 ÷ 35.5	0.53
Ammonium, 3 ÷ 18	0.17

The concentrations of each salt can then be calculated as follows. The ammonium chloride, NH_4Cl, will be equivalent to the ammonium, *i.e.*, to $0.17N$. Since the equivalent weight of NH_4Cl is 53.5, its actual concentration is $0.17 \times 53.5 = 9.1$ g/l $= 1.2$ oz/gal. The nickel chloride is equivalent to the remaining chloride, *i.e.*, to $0.53N - 0.17N = 0.36N$. The equivalent weight of the salt $NiCl_2 \cdot 6H_2O = \frac{238}{2} = 119$. Therefore the content of nickel chloride is $0.36 \times 119 = 41.6$ g/l $= 5.7$ oz/gal. The nickel sulfate is equivalent to the remaining nickel, *i.e.*, to $2.42N - 0.36N = 2.06N$. The equivalent weight of the salt $NiSO_4 \cdot 6H_2O = \frac{262.7}{2} = 131.4$. Therefore the content of nickel sulfate is $2.06 \times 131.4 = 270$ g/l $= 36.1$ oz/gal.

Such calculations can be made quickly with a slide rule. When many similar calculations are to be made, they can be simplified by the use of appropriate factors or by a suitable *nomograph*, or a special form of slide rule.

The principal methods used in quantitative analysis fall into the following groups:

Gravimetric. In gravimetric analyses a reagent is added that forms with the constituent to be determined an insoluble compound having a definite composition. This precipitate is filtered out, washed to remove more soluble salts, dried, and weighed. From the weight of the precipitate obtained from a given sample of the bath, the concentration of the particular constituent is computed. Gravimetric analyses require considerable time, experience, and equipment and are not commonly used to test plating baths. Because the determination of sulfate in chromic acid plating baths is usually done gravimetrically, this procedure will be outlined for illustration. More details are given on page 182.

A 10-ml sample of the bath is diluted, reduced with alcohol (to convert the hexavalent to trivalent chromium), and an excess of barium chloride, $BaCl_2$, is added. This combines with any sulfate, SO_4, present to form barium sulfate, $BaSO_4$, which is insoluble.

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

This precipitate is filtered out, washed, ignited in a porcelain or platinum crucible to destroy the filter paper, and then weighed. From the weight of $BaSO_4$, *e.g.*, 0.0632 g from 10 ml of the bath, that of sulfate, SO_4, is computed thus:

Molecular Weights		Actual Weights, g
$BaSO_4 : SO_4$	::	$BaSO_4 : SO_4$
$233 : 96$	::	$0.0632 : X = 0.0260$

Hence the solution contains 0.0260 g of SO_4 in 10 ml. One liter of the bath therefore contains $100 \times 0.0260 = 2.60$ g/l of SO_4. If this is present as or was added as sulfuric acid, H_2SO_4, the content of the latter will be $\frac{H_2SO_4}{SO_4} = \frac{98}{96} \times 2.6 = 2.66$ g/l of H_2SO_4 or an equivalent amount of any other sulfate that was used. Because the equivalent weight of the sulfate ion, SO_4, is $96/2 = 48$, this solution is $2.60 \div 48 = 0.054N$ in sulfate.

Volumetric. In this type of analysis a *standard* solution of exactly known strength is used containing a reagent that will react quantitatively with the constituent to be determined and will yield an indication of when the reaction is complete. From the volume of solution used in this *titration* of a sample of the bath the content of the constituent is calculated.

The equipment used in the actual titrations is simple, *e.g.*, a pipette or a burette to measure the bath sample, a graduated flask to make exact dilutions, and a burette to measure the volume of standard solution required. In addition a few beakers or flasks of convenient size, some stirring rods, a burner, and stand are needed. To prepare or standardize solutions, an analytical balance is required. It is now possible for a plater to purchase standard solutions for volumetric analysis.

In all such analyses the strength of the solution can be determined or adjusted in several ways, such as the following. The strength should preferably be such that from 20 to 40 ml is required for a titration.

1. A solution with an exactly known strength is prepared by dissolving a definite weight of a pure substance.
2. A solution of approximately the desired strength is prepared, and its exact strength is determined by titration of a standard material.

In either method the solution can be prepared or adjusted so as (1) to have an exact normality; (2) to have 1-ml equivalent in a given titration to a specified concentration of the constituent, *e.g.*, to 1 g/l or to 0.1 oz/gal; or (3) the value found by standardization may be used directly. Procedure (1) is usually most convenient for research, and (2) for works control. However, when a slide rule is available, (3) is equally convenient. Method (3) must be used if the titrating solution is unstable and requires frequent standardization.

Several types of reactions are employed in volumetric analysis. An example of each will be outlined, and further details will be given later for specific determinations.

ACIDIMETRIC. In acidimetry or alkalimetry the amount of acid present is determined by titrating with a standard alkali and vice versa. In general, an indicator is used to show by its change in color when the solution is exactly neutralized. The change in potential of an electrode can also be used as the end point. This is designated as an *electrometric* titration. A simple illustration of acidimetry is the titration of hydrochloric acid with standard sodium hydroxide, according to the equation

$$HCl + NaOH = NaCl + H_2O$$

An indicator such as methyl orange or methyl red is used to detect the end point.

Oxidation and Reduction. A reducing agent such as ferrous sulfate is titrated with an oxidizing agent such as permanganate. The pink color produced by an excess of one drop of the permanganate serves to detect the end point. The equation may be written

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

Considering only the change in valence, the equation is

$$5Fe^{+II} + Mn^{+VII} = 5Fe^{+III} + Mn^{+II}$$

Especially when an oxidizing agent such as dichromate is employed or involved, the end point can be determined by electrometric methods, *i.e.*, by the change in potential of a platinum wire with respect to a standard calomel half cell.

Precipitation. When a solution of silver nitrate, $AgNO_3$, is added to a solution containing a soluble chloride, such as nickel chloride, $NiCl_2$, the following reaction takes place:

$$NiCl_2 + 2\,AgNO_3 = 2\,AgCl + Ni(NO_3)_2$$

nickel chloride + silver nitrate = silver chloride + nickel nitrate

The silver chloride is insoluble and forms a white precipitate. If a small amount of sodium chromate, Na_2CrO_4, is added to the sample before titration, a red precipitate of silver chromate, Ag_2CrO_4, is formed as soon as all the chloride has been precipitated as silver chloride. The appearance of a red color hence serves as the end point of the titration.

Cyanometric Methods. Because many cyanide baths are used in plating, their analysis is of special interest. The principal reaction is the titration of *free cyanide* with silver nitrate, according to the equation

$$2NaCN + AgNO_3 = NaAg(CN)_2 + NaNO_3$$

The double cyanide, $NaAg(CN)_2$, is soluble. However, as soon as any further addition of silver nitrate is made, it reacts as follows:

$$NaAg(CN)_2 + AgNO_3 = 2AgCN + NaNO_3$$

Silver cyanide, AgCN, is insoluble and therefore forms a precipitate or turbidity, which serves to mark the end point. Because silver iodide, AgI, is somewhat less soluble than silver cyanide, AgCN, a small amount of potassium iodide is usually added to the cyanide solution before titration to sharpen the end point.

Colorimetric and Spectrophotometric Methods. The fact that certain salts of metals present in plating solutions have characteristic colors immediately suggests the use of colorimetric methods for measuring the concentration of the metal. In principle, all that is necessary is to have a series of tubes of equal diameters in which solutions of known concentration are placed. By then filling a similar tube with the plating bath and comparing its color with that of the standards, the concentration of the bath can be estimated. In certain cases, *e.g.*, acid copper baths, it is often possible by this very simple and rapid method to estimate the content of copper sulfate within about ±10 per cent, which may be adequate for control.

There are, however, certain difficulties in these direct methods, which may lead to large errors. The average eye is less sensitive to changes in the intensity of a green color than of most other colors; hence this direct method is not very reliable for nickel baths. To some extent this difficulty can be overcome by viewing the nickel solutions through a pink solution or screen, which optically *neutralizes* the green to produce a gray color.

Another objection is that the color of the bath may be so changed by additions or impurities as to prevent satisfactory matching with the standards. Sodium citrate changes the color of a nickel solution from green toward blue. The presence of iron or organic matter in an acid copper bath changes its color toward green. Both trivalent chromium and iron in a chromic acid bath change the color from orange to red or brown.

For these reasons direct colorimetric methods cannot be counted on to yield an accuracy better than 10 per cent and may have larger errors. If used for approximate measurements they should be checked at intervals by more exact methods.

In recent years an instrument known as a *spectrophotometer* has been improved and simplified to adapt it to very convenient laboratory measurements of color. This device depends upon the fact that a colored solution absorbs light of a given wavelength to an extent that is characteristic of the specific substance present. In general, a solution will absorb most strongly the "complement" of the rays that it transmits. For example, a blue solution, *i.e.*, one that transmits blue light, will strongly absorb red and yellow light.

The *color* of any light rays is defined by their wavelength. Light rays that are visible to the unaided eye have wavelengths between 400 and 650 millimicrons (millionths of a millimeter), ranging from violet at about 400 to red at 650. Below 400 are the ultraviolet rays, and above 650 are the infrared rays.

With light of a given wavelength, *e.g.*, that at which the maximum absorption occurs for a solution of a given substance, the extent of absorption will depend upon the concentration of that substance. In principle, therefore, only two steps are required before using the spectrophotometer to measure the concentration of a colored constituent of a solution. (1) A spectral transmittance curve is prepared, in which the percentage of transmittance of light of each wavelength by the colored substance is measured. From this curve the wavelength that yields the minimum transmittance (or maximum absorption) by that substance is selected. (2) Light of that wavelength is used to measure the relation between the concentration of the substance and the percentage transmittance. The resultant curve is used to determine the content of the colored substance in a sample that is tested.

Many substances that produce in themselves very little color will react with appropriate compounds to yield more highly colored solutions. These are often used in determining the concentration of impurities in plating baths, or even of major constituents. In the latter case it may be necessary greatly to dilute the plating sample, *e.g.*, by successive quantitative dilutions.

These principles may be illustrated by the method recently developed[1] for determining very small amounts of gold on specimens of plated gold articles but which may also be used to determine the gold content of a bath. This method depends upon the fact that gold in the auric condition, *e.g.*, $AuCl_3$, reacts with ortho-tolidine to produce a bright yellow color. The maximum absorption (or minimum transmittance) occurs with light having a wavelength of 437 millimicrons. With that wavelength the percentage transmissions for different small amounts of gold are determined. From this curve the amount of gold present in the sample can be determined, and in the case of a gold coating its thickness can be computed.

While the spectrophotometric method involves fairly expensive equipment and careful technic, its use warrants consideration whenever a fairly large number of determinations are to be made and saving of time is important.

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[1] CLAYBAUGH, W. S., *J. Research Natl. Bur. Standards*, vol. 36, p. 119, 1946. RP 1694.

Spectrographic Analysis. This method depends upon the fact that most metals or their compounds when heated to the temperature of an arc or a spark emit light of certain wavelengths and thereby produce characteristic lines in a spectrum. The intensity of each important line for a given element depends upon the amount of that element in the flame or arc. By comparing the intensity of the lines produced in a photographic plate with the lines yielded by known amounts of that metal, the concentration of the metal can be estimated.

This method is especially valuable for detecting and determining impurities that may be present in plating baths, anodes, or deposits. It requires expensive equipment and considerable experience, but when available it may prove very useful, especially in research.

Polarographic Methods. In recent years a method of analysis has been developed that depends upon the potential of a *dropping mercury electrode.* This method has been employed for the determination of copper and zinc in brass-plating baths and deposits.[1] It involves the measurement of the relation between current and potential when an emf is applied to a cell in which one electrode, usually the anode, consists of a layer of liquid mercury. The other electrode consists of drops of mercury formed at the end of a fine capillary and continuously dropping through the solution to the layer of liquid mercury. Under these conditions the potential at which a metal ion is discharged serves to identify the element, and the current that passes during the discharge of the element is a measure of its concentration. The discharge of each metal is indicated by its *half-wave potential,* and its concentration by the current at the nearly horizontal portion of the current-potential curve. Details of this procedure will be found in a review.[2]

The method is especially useful for determining very small amounts of metals or compounds, but with appropriate precautions it can be applied for routine control of plating baths.

ANALYSIS OF SOLUTIONS

In this section methods for analyzing the important solutions used in plating will be outlined. Because similar methods are used for many different baths, their assembly in one chapter may lead to clarity and brevity.

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[1] Gordon, H. E. Z., and Roberts, E. R., *Trans. Electrochem. Soc.*, vol. 90, p. 27, 1946.

[2] Kolthoff, I. M., and Lingane, J. J., *Chem. Rev.*, vol. 24, p. 1, 1939.

Sampling. The accuracy and significance of an analysis depends directly upon the care used in selecting a sample of the solution. Unless this is representative of the bath, its analysis may be meaningless or misleading. The simplest way to obtain a typical bath sample is first to mix the bath thoroughly, *e.g.*, till samples from different parts show the same density with a hydrometer. This is necessary because in operation, unless good agitation is used, there is a tendency for stratification to occur. In general, the more concentrated metal solution that flows down from the anodes is heavier and tends to settle to the bottom of the tank. If water is added at intervals to bring up the bath level, it tends to make the top of the solution less concentrated.

One objection to mixing plating baths that are not regularly filtered is that sludge is thereby stirred up and may cause rough or porous deposits. Continuously filtered baths are likely to be uniformly mixed by the circulation. By mixing a bath and allowing it to stand overnight or over a week end before taking the sample, satisfactory results are obtained. If this is not feasible, it is possible to obtain a fair sample by inserting a long glass tube, at least 0.5 in. in diameter, slowly into the solution, closing the upper end with a finger, and withdrawing the sample into a container. This can be done in several parts of the tank.

The sample container, *e.g.*, an 8-oz (250-ml) bottle, should be clean and dry or should be rinsed out with some of the solution. If a precipitate is present, especially in a solution that is agitated in use, it should be retained in the specimen for possible identification. Before an analysis is made, the solution should be filtered if it is not clear. The sample should be carefully labeled to identify the tank and the time of sampling.

Alkaline Cleaning Solutions. Alkaline cleaning solutions are usually not analyzed so regularly or frequently as are many plating baths, largely because they are difficult to analyze and are relatively cheap and when contaminated or ineffective they can be quickly replaced or replenished. However, a few simple analyses will prove very helpful by ensuring more uniform operation during their useful life.

In a report by Committee D 12 of the ASTM,[1] detailed methods are described for the analysis of industrial metal cleaning compositions, such as may be used in the electroplating industry. The possible complexity of such mixtures is indicated by the fact

[1] *ASTM Standards*, Pt. III, p. 128, 1945.

that methods are described for at least 16 determinations. Such complete analyses would be required only in the identification or control of the solid mixtures. The electroplater is much more interested in the determination of those constituents or properties of the cleaning solution which will indicate its cleaning efficiency or the need for replenishment. For a given type of cleaner the following methods will probably be adequate for control, *viz.*, specific gravity, total alkali, free alkali, and in some cases the pH. The specific gravity will indicate any large changes in concentration caused by evaporation or dilution. The total alkali will serve as a measure of the total strength of the solution. The free alkali will indicate the content of sodium hydroxide, which may be reduced in operation because it is converted to carbonate. The pH may be significant in mildly alkaline cleaners, *e.g.*, with a pH below 12, that do not contain appreciable free caustic.

Total Alkalinity as Na_2O. A 20-ml sample of the solution (corresponding to about 1 g of the dry cleaner) is placed in a 250-ml Erlenmeyer flask and diluted to 50 ml. A few drops of methyl orange are added, followed by a measured excess of $0.5N$ hydrochloric acid. The solution is then boiled to expel carbon dioxide and cooled. If soap or rosin is believed to be present, 25 ml of ethyl ether is added to extract the liberated fatty and rosin acids, which would otherwise make a turbid solution. The excess of hydrochloric acid is then titrated with $0.5N$ sodium hydroxide, using methyl orange as indicator. The resultant value for total alkalinity calculated as Na_2O includes that present as (1) sodium hydroxide, $NaOH$; (2) sodium carbonate, Na_2CO_3; (3) sodium silicate, *e.g.*, Na_2SiO_3; (4) two-thirds of the sodium present in trisodium phosphate, Na_3PO_4; or one-half that present in sodium pyrophosphate, $Na_4P_2O_7$; and (5) that combined in any soap present. The total alkali, computed as grams per liter of Na_2O is

$$(\text{ml } 0.5N \text{ HCl} - \text{ml } 0.5N \text{ NaOH}) \times 0.0155 \times 50$$

Suppose that 50 ml of $0.5N$ HCl was added to a 20-ml sample of cleaner and 16 ml of $0.5N$ NaOH was required for the back titration. Then the total alkali is

$$(50 - 16)\ 0.0155 \times 50 = 26.4 \text{ g/l or } 3.52 \text{ oz/gal of } Na_2O$$

$$\frac{26.4}{31} = 0.85N \text{ total alkali}$$

Free Alkali. Evaporate a 20-ml sample to dryness quickly, using an electric hot plate to avoid absorption of carbon dioxide from the air. Dry the residue at 105°C, cool, and add 200 ml of freshly boiled neutral 95 per cent ethyl alcohol (or denatured alcohol). Warm on a steam bath, and filter through paper or asbestos to remove the compounds insoluble in alcohol. Heat the filtrate nearly to boiling, add 0.5 ml of a 1 per cent alcoholic solution of phenolphthalein, and titrate with $0.5N$ hydrochloric acid.

Owing to the high tax on alcohol, this method is relatively expensive. Less accurate but possibly adequate results for free alkali can be obtained by titrating first to the end point of phenolphthalein and then to methyl orange. In order to compute the free alkali, it is necessary to know the other principal constituents and their relative concentrations. For example, in a mixture of Na_2CO_3 and NaOH, titration against phenolphthalein yields the free NaOH plus one-half the Na_2CO_3. Similarly, in a mixture of Na_3PO_4 and NaOH this titration yields the free NaOH plus one-third the Na_3PO_4.

The free alkali, calculated as grams per liter of NaOH = ml $0.5N$ HCl × 0.020 × 50. If in the above titration of a 20-ml sample, 12 ml of $0.5N$ HCl is required, the free alkali is

$$12 \times 0.020 \times 50 = 12 \text{ g/l}$$

$$\frac{12}{40} = 0.30N \text{ NaOH}$$

Example. Suppose that the above cleaner was prepared originally with the following composition.

	N	g/l	oz/gal
Sodium hydroxide, NaOH	0.38	15	2
Sodium carbonate, Na_2CO_3	0.28	15	2
Trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$	0.12	15	2
Sodium metasilicate, Na_2SiO_3	0.25	15	2

This solution, as prepared, would contain 15 g/l or 2 oz/gal of free caustic NaOH. The total alkali, as titrated above, would be equivalent to $0.38N$ NaOH + $0.28N$ Na_2CO_3 + $2/3 \times 0.12 = 0.08N$ Na_3PO_4 + $0.25N$ Na_2SiO_3 or a total of $0.99N$ alkali. This is equivalent to 31 g/l or 4.1 oz/gal of total titratable alkali, calculated as Na_2O.

Suppose that, after a certain period of use, the solution showed the results given above, *i.e.*, 26.4 g/l of total alkali, Na_2O, and 12 g/l of free alkali, NaOH. It is evident that the total alkali has decreased from 31 to 26.4 g/l = 4.6 g/l; *i.e.*, 4.6/31 = 14.8 per cent. That of free caustic has decreased from 15 to 12 g/l = 3 g/l = 3/15 = 20 per cent. If for simplicity we assume that the principal loss has occurred through drag out of the cleaner, it requires an addition of about 15 per cent of the original ingredients, plus about 5 per cent additional free caustic, to restore the solution to approximately its original strength. If for any reason one of the alkaline salts, *e.g.*, the metasilicate, were consumed more rapidly than the others, the above analyses would throw no light on such changes.

Acid Pickles and Dips. *Pickles.* The principal determination made on pickles consisting of sulfuric or hydrochloric acid is that of the free acid. It is seldom necessary or warranted to determine the content of iron salts, but a measurement of the acidity and specific gravity will indicate the approximate content of dissolved iron. Any methods for estimating the content of inhibitors or wetting agents must be specific for the substances used. In most cases the behavior of the pickle and previous experience and records will serve to control these additions.

In order to avoid interference by ferrous or ferric salts in the pickle, the end point of the titration should be at a pH not greater than about 3. This is about the turning point of methyl orange. If electrometric equipment is available, it may serve to measure the end point at, for example, a pH of 2.5. If much ferric salt is present, some ferric hydroxide may precipitate before the end point with methyl orange. In that case the appearance of a permanent brown precipitate may serve as an approximate end point.

A 5-ml sample is diluted to 50 ml, and a few drops of methyl orange are added. Titration is then conducted with $0.5N$ sodium hydroxide. The normality of the free acid = (ml NaOH $\times$ 0.5)/5. If 50 ml of NaOH was required for a 5-ml sample, the free acid in the pickle is $(50 \times 0.5)/5 = 5.0N$. This is equivalent to $5 \times 36.5 = 183$ g/l or 24.4 oz/gal of pure HCl; or to $5 \times 49 = 245$ g/l or 33 oz/gal of pure H_2SO_4.

Bright Dips. In the usual bright dips for brass it is desirable to determine the content of free sulfuric and free nitric acid. This is accomplished by titrating the total acidity in one sample and in a separate portion the nitric acid. (The usual small content of hydrochloric acid can be neglected in these titrations.) The specific gravity is only a rough indication of the total acidity.

A 5-ml sample is diluted to 150 ml, a few drops of methyl orange are added, and the solution is titrated with $2N$ sodium hydroxide until the color changes from red to yellow. This titration yields the sum of the sulfuric and nitric acids.

To another 5-ml sample, 15 ml of concentrated sulfuric acid is added, the mixture is cooled and titrated with a standardized ferrous sulfate solution to the appearance of a faint red or brown color. The ferrous sulfate solution is prepared by dissolving 280 g of pure ferrous sulfate, $FeSO_4 \cdot 7H_2O$, in water, adding 250 ml of concentrated sulfuric acid, and diluting to 1 l. This is standardized at frequent intervals against N nitric acid, as follows:

Five milliliters of N HNO_3 is treated with 15 ml of concentrated sulfuric acid and titrated with the ferrous sulfate to the appearance of a faint pink or brown color. The normality of the ferrous sulfate is computed with respect to the reaction

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

The NO combines with any excess of ferrous sulfate to produce the brown end point.

Example. When 10 ml of the sodium hydroxide was standardized against $0.5N$ HCl, it required 39.4 ml of HCl. The NaOH was therefore $\frac{39.4}{10} \times 0.5 = 1.97N$. If 25 ml of the standard nitric acid was checked against the sodium hydroxide and required 13.2 ml of NaOH, the HNO_3 was $\frac{13.2}{25} \times 1.97 = 1.04N$. If 5 ml of the HNO_3 required 13.6 ml of $FeSO_4$, the $FeSO_4$ was (with respect to this reaction) $5/13.6 \times 1.04 = 0.38N$. When a 5-ml sample of the bright dip was titrated with the sodium hydroxide, it required 61 ml of NaOH. The total acidity of the dip was hence $\frac{61}{5} \times 1.97 = 24.1N$. A 5-ml sample of the dip when titrated with the ferrous sulfate required 45.2 ml of $FeSO_4$. The nitric acid in the dip was equivalent to $\frac{45.2}{5} \times 0.38 = 3.4N$.

$$3.4 \times 63 = 214 \text{ g/l or } 28.5 \text{ oz/gal of } HNO_3$$

The content of sulfuric was $24.1 - 3.4 = 20.7N$.

$$20.7 \times 49 = 1{,}014 \text{ g/l or } 76 \text{ oz/gal of } H_2SO_4$$

Acid or Neutral Plating Baths. *General Principles.* In acid baths the principal determinations required are the metal content and the acidity. The concentrations of salts added to control the acidity or conductivity are not usually critical, and hence they do not require frequent checking. The determination of brighteners and wetting agents must be specific for each substance. To a large extent their additions to the baths are controlled by the bath performance and by previous experience, expressed, for example, in terms of the normal consumption for each 1,000 amp-hr. In some cases definite analytical methods are used.

Acidity and pH. As previously explained, the acidity as determined by a titration is a measure of the amount of acid present, while the pH is an expression of the effective strength of the acid. If no buffers are present, these two methods of expression are roughly equivalent; *e.g.*, a solution that is 0.1N in free HCl or H_2SO_4 has a pH of about 1. If, however, as is customary in plating baths that are operated at pH values between 2 and 7, some weak acid (or its salt) is present to act as a buffer, there is no simple relation between acidity and pH. For any given bath the actual relation can be expressed by a pH titration curve (Fig. 40), which is very useful in indicating the amount of acid or alkali required to change the pH of that bath to any desired value. Suppose that the pH of the bath represented in Fig. 40 was found to be 5.3 and it was desired to lower the pH to 5.0. From Fig. 40 it can be seen that, in the change from pH 5.3 to 5.0, 10 ml of this bath would require approximately 2.5 ml of 0.1N acid, *e.g.*, H_2SO_4. This is equivalent to 100 × 2.5 = 250 ml of 0.1N acid, or 25 ml of N acid for each liter of solution, or 25 × 3.8 = 98, or practically 100 ml of acid for each gallon of the bath; hence 100 × 100 = 10,000 ml or 10 l of N acid for each 100 gal of the bath. As 1 l of N sulfuric acid contains 49 g of H_2SO_4, 10 l will contain 10 × 49 = 490 g of H_2SO_4 or 490/454 = 1.1 lb of H_2SO_4 required for each 100 gal in the bath for this change in pH.

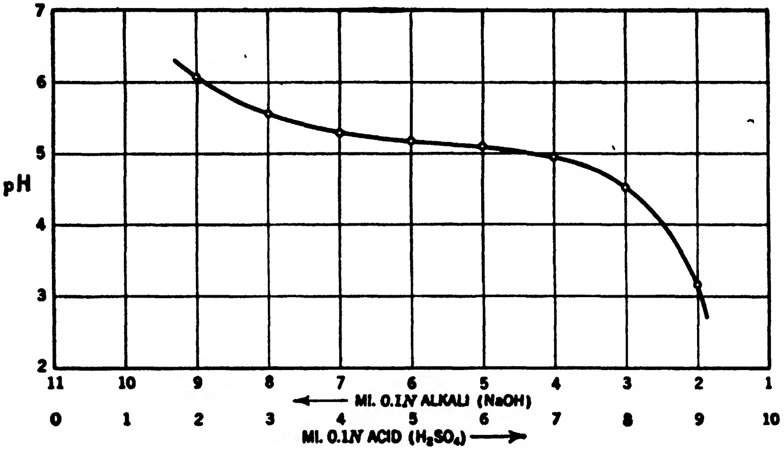

FIG. 40. Typical titration curve of 10 ml of a nickel-plating bath.

Without a sharp distinction, it may be concluded that, below a pH of 2, titrations are more useful and, above 2, pH determinations are employed. A pH measurement in an acid copper bath containing at least $1N$ free sulfuric acid is as meaningless as is a titration of the *free acid* in a nickel bath having a pH of 5. In certain strongly acid baths such as those containing chromic acid, pH measurements as low as 1 or 0 may be useful in research on the constitution of the baths.

DETERMINATION OF ACIDITY. The acidity of an acid bath such as acid copper or zinc can be determined by direct titration with a standard alkali, *e.g.*, $0.5N$ NaOH. The end point should be at a sufficiently low pH, *e.g.*, 3, that the metal salt does not yield a precipitate of the hydroxide. For most such baths, methyl orange is a satisfactory indicator. Even when, as in a copper bath, the color of the solution obscures that of the indicator, there is still sufficient change in color to detect the end point. In a copper bath methyl orange produces a purple color that changes to green at the end point. In such cases slightly more indicator is required than normally.

If many such titrations are to be made, an electrometric end point may be used. This may consist of a platinum wire and a calomel electrode, which both dip into the solution being titrated. The potential of this couple, as read on a simple potentiometer or high-resistance voltmeter, will change sharply at the point of neutralization. With a quinhydrone or glass electrode a specific pH value known to represent the end point of the titration can be selected.

The calculation of the acidity is conveniently made in terms of normality, which can then be converted to other desired units.

Example. Suppose that when a 10-ml sample of an acid copper bath is diluted to 25 ml, a few drops of methyl orange added and titrated with $0.5N$ NaOH, 28 ml of NaOH is required.

$$\frac{28 \times 0.5}{10} = 1.4N\ \text{H}_2\text{SO}_4$$

$$1.4 \times 49 = 68.6\ \text{g/l of H}_2\text{SO}_4$$

$$\frac{68.6}{7.5} = 9.1\ \text{oz/gal of H}_2\text{SO}_4$$

MEASUREMENT OF pH. The determination of pH can be made by any convenient method (page 76). The electrometric method with a glass electrode is now almost universally employed in all large works laboratories for both acid and alkaline baths, because it is practically free from errors from salts or oxidizing agents and gives very reproducible results. It has therefore almost completely displaced the quinhydrone method. For smaller plants colorimetric methods are cheaper and generally adequate.

Content of Metal and Other Constituents in Acid and Neutral Baths. The metal contents of most plating baths are determined by volumetric methods, although for specific metals colorimetric methods may be applicable. In the following outlines the principles and the essential steps are described. A little experience will enable an operator to work out appropriate details for each bath.

COPPER. The content of copper in an acid sulfate bath can be readily determined by three methods, depending respectively on (1) the specific gravity of the bath, (2) electrodeposition of the copper, and (3) titration with sodium thiosulfate.

1. From specific gravity. If a bath contains only two dissolved substances and it is feasible to determine the content of one, that of the other can be derived from the specific gravity of the bath. The specific gravity of a bath containing copper sulfate and sulfuric acid depends only on the sum of the two concentrations. For example, as shown in Table 19 (Appendix), in such a bath a specific gravity of 1.18 corresponds to 303 g/l (or 40.6 oz/gal) of copper sulfate plus sulfuric acid. If then the acid content, determined as on page 171, is found to be 70 g/l (or 9.4 oz/gal), the copper sulfate, $CuSO_4 \cdot 5H_2O$, must be equal to

$$303 - 70 = 233 \text{ g/l or } 31.2 \text{ oz/gal}$$

This method involves the following steps.

a. Measure the specific gravity.

b. From Table 19 determine the total content of copper sulfate plus sulfuric acid corresponding to this specific gravity.

c. Titrate the free sulfuric acid.

d. Subtract the content of sulfuric acid from the total concentration found in *b* to obtain that of copper sulfate, $CuSO_4 \cdot 5H_2O$.

This method is adequate for control of baths that do not contain more than a few grams per liter of intentional additions or of impurities such as iron salts.

2. Electrolytic method. Dilute a 10-ml sample to 100 ml in a 150-ml beaker, add a few drops of nitric acid, and electrolyze with platinum gauze electrodes or with a copper cathode and a lead or platinum anode. A simple arrangement is shown in Fig. 41. A current density of about 0.25 amp/dm^2 can be used in a still

solution or 1.0 amp/dm^2 if the solution is agitated with air or a stirrer. When the blue color of the solution has disappeared, a drop is placed on a spot plate and a drop of potassium ferrocyanide solution added. If any brown color appears, electrolysis is continued until no test for copper is obtained. The cathode is then removed, rinsed quickly with water and then with 95 per cent ethyl alcohol, dried in a warm place, cooled in a desiccator, and weighed. The increase in weight represents the copper content of the sample taken.

If much iron is present in the bath, it should be removed. After the addition of the nitric acid, the solution is heated nearly to boiling, an excess of ammonium hydroxide is added, and the precipitate of ferric hydroxide is filtered out and washed. The filtrate is then acidified with sulfuric acid, of which a slight excess is added. Electrolysis is then conducted as above.

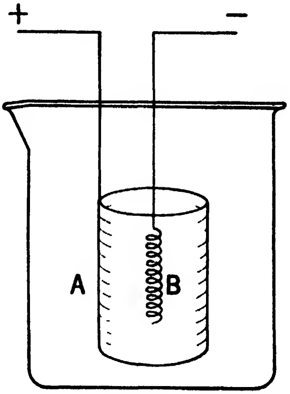

FIG. 41. Diagram of apparatus for electrolytic determination of copper. *A*, platinum gauze cathode. *B*, platinum spiral anode.

Example. If 10 ml of the copper bath yields 0.513 g of copper, the solution contains 100 × 0.513 = 51.3 g/l of copper. As crystallized copper sulfate, $CuSO_4 \cdot 5H_2O$, contains 25.4 per cent of copper, this is equivalent to

$$\frac{100}{25.4} \times 51.3 = 202 \text{ g/l (27 oz/gal) of copper sulfate}$$

3. Thiosulfate titration. This method depends upon the fact that a *cupric* salt, such as cupric sulfate or acetate (in which the copper has a valence of II), is reduced by potassium iodide, KI, to form a white precipitate of cuprous iodide, Cu_2I_2, and free iodine, I_2, according to the equation

$2Cu(C_2H_3O_2)_2$	$+ 4KI$	$= Cu_2I_2$	$+ I_2$	$+ 4KC_2H_3O_2$
cupric acetate	potassium iodide	cuprous iodide	iodine	potassium acetate

The iodine that is liberated is titrated with sodium thiosulfate, $Na_2S_2O_3$, thus:

$Na_2S_2O_3$	$+ I_2$	$= Na_2S_4O_6$	$+ 2NaI$
sodium thiosulfate	iodine	sodium tetrathionate	sodium iodide

The end point of the titration is determined by adding starch and noting when the blue color formed by starch and iodine disappears.

The analysis is conducted as follows: A 5-ml sample is diluted to 50 ml, and ammonium hydroxide is added just until a clear deep blue color is produced. Acetic acid is then added until the color changes to a light blue or green. The solution is allowed to cool, after which 2 g of potassium iodide, KI, is added. The solution is then titrated with a $0.1N$ solution of sodium thiosulfate, containing 25 g/l of $Na_2S_2O_3 \cdot 5H_2O$, until the brown color nearly disappears. A few drops of a starch solution (made by pouring a paste of 1 g of starch into 100 ml of boiling water) are added. The titration is then continued until the blue color just disappears.

The sodium thiosulfate is standardized by the same procedure against a solution containing a known amount of copper. This can be made by dissolving exactly 10 g of pure metallic copper in nitric acid, adding 10 ml of sulfuric acid, and evaporating to fumes of sulfuric acid. The residue is dissolved in water and diluted to 1 l. Each milliliter of this solution contains 0.01 g of copper.

Example. When 25 ml of the standard copper solution (equivalent to 0.25 g of Cu) was treated and titrated as above, 41 ml of $Na_2S_2O_3$ was required. Hence 1 ml of $Na_2S_2O_3$ is equal to $0.25/41 = 0.0061$ g of Cu. If 5 ml of the plating solution required 47 ml of $Na_2S_2O_3$, the copper content is

$$47 \times 0.0061 \times \frac{1{,}000}{5} = 57.4 \text{ g/l or } 7.7 \text{ oz/gal of copper}$$

or

$$57.4 \times \frac{250}{63.6} = 226 \text{ g/l or } 30.1 \text{ oz/gal of copper sulfate, } CuSO_4 \cdot 5H_2O$$

ZINC. 1. Ferrocyanide titration. The zinc content of zinc-plating baths is most commonly determined by titration with potassium ferrocyanide, $K_4Fe(CN)_6$. This method depends upon the fact that when $K_4Fe(CN)_6$ is added to an acidified solution of a zinc salt, a white precipitate is formed, which consists of a mixture of potassium zinc ferrocyanide, $K_2ZnFe(CN)_6$, and zinc ferrocyanide, $Zn_2Fe(CN)_6$. The end point is detected by testing a drop of the solution on a spot plate with uranium acetate, which produces a brown color if any excess of potassium ferrocyanide is present. Another indicator is diphenylbenzidine, which can be added directly to the solution titrated. It turns from purple to pale green at the end point. One milliliter of a solution prepared by dissolving 22 g of potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$, in water and diluting to 1 l is equivalent to about 0.005 g of zinc. It is standardized against pure granulated zinc (not zinc dust). A standard zinc solution can be prepared by dissolving exactly 10 g of pure zinc in dilute HCl and diluting to 1 l. One milliliter of this zinc chloride solution contains 0.01 g of zinc.

The standardization is carried out as follows: twenty-five milliliters of the standard zinc solution is diluted to 100 ml, and 5 ml of concentrated HCl and 5 g of ammonium chloride are added. The solution is heated nearly to boiling, *e.g.*, to 80°C (176°F), and the ferrocyanide is run in from a burette, while the solution is stirred vigorously. When somewhat less than the estimated volume of ferrocyanide has been added, a drop of the solution is placed on a spot plate with one drop of a 10 per cent solution of uranium acetate. If a brown color appears, the end point has been passed, the titration must be repeated, and the first test made when less ferrocyanide is added. If no brown color appears, 1 ml of ferrocyanide is added, a drop tested, and this is repeated till a brown color appears.

Instead of testing on a spot plate with uranium acetate, a few drops of a diphenylbenzidine solution (1 g/l) are added and the titration is made with ferrocyanide till the color changes from purple to pale green. This end point is inaccurate if appreciable amounts of copper or iron are present.

The titration of an acid zinc bath is made similarly on a 5-ml sample, diluted to 100 ml, and 5 ml of HCl and 5 g of NH_4Cl are added. If much iron is present in the bath, it should be precipitated with ammonia and filtered out, and the filtrate titrated with ferrocyanide.

Example. When 25 ml of the standard zinc solution (equivalent to 0.25 g of zinc) was titrated, it required 48 ml of the ferrocyanide solution. One milliliter of the latter is therefore equivalent to 0.25/48 = 0.0052 g of zinc. When a 5-ml sample of an acid zinc bath was titrated, it required 46 ml of the ferrocyanide. The bath therefore contains

$$46 \times 0.0052 \times \frac{1{,}000}{5} = 48 \text{ g/l or } 6.4 \text{ oz/gal of zinc}$$

This is equivalent to

$$\frac{287.6}{65.4} \times 48 = 211 \text{ g/l or } 28.3 \text{ oz/gal of zinc sulfate, } ZnSO_4 \cdot 7H_2O$$

Tin. In acid tin baths the tin is principally in the stannous condition, Sn^{II}. The stannous tin can therefore be titrated directly with a standard iodine solution. The content of stannic tin is then determined by reducing it and titrating the total tin with iodine.

1. Stannous tin. A 10-ml sample is diluted to 200 ml in a 500-ml flask, and 15 ml of concentrated HCl is added. It is then titrated directly with a $0.1N$ iodine solution, which has been standardized against potassium dichromate by means of a sodium thiosulfate solution. Starch is used as the indicator, which produces a blue color when any free iodine is present. The iodine solution can also be standardized against freshly prepared stannous chloride, made by dissolving a weighed amount of tin foil in hydrochloric acid.

Example. When 10 ml of exactly $0.1N$ $K_2Cr_2O_7$ was treated with an excess of potassium iodide and the liberated iodine was titrated with $Na_2S_2O_3$, it required 13 ml of the $Na_2S_2O_3$. Hence the $Na_2S_2O_3$ is $\frac{10}{13} \times 0.1 = 0.077N$. When 10 ml of the standard iodine solution was similarly titrated with the $Na_2S_2O_3$, it required 11.8 ml of the $Na_2S_2O_3$. Hence the iodine solution is $\frac{11.8}{10} \times 0.077 = 0.091N$.

If, then, 10 ml of the tin sulfate bath required 40 ml of the iodine solution, the concentration of stannous tin is $\frac{40}{10} \times 0.091 = 0.364N$. The content of stannous tin is therefore

$$\frac{118.7}{2} \times 0.364 = 21.6 \text{ g/l or } 2.88 \text{ oz/gal of } Sn^{II}$$

That of stannous sulfate, $SnSO_4$, is

$$\frac{214.7}{2} \times 0.364 = 39.2 \text{ g/l or } 5.21 \text{ oz/gal}$$

2. Stannic tin. A 10-ml sample is placed in a 500-ml flask, and 100 ml of concentrated HCl, 15 ml of concentrated H_2SO_4, 3 g of iron powder reduced by hydrogen are added and sufficient water to make a total volume of 300 ml. The flask is closed with a stopper having an outlet tube, and the contents are boiled for 10 min to reduce the stannic sulfate. While the contents are still boiling, the outlet is immersed in a beaker containing 150 ml of a saturated sodium bicarbonate solution. The flame is turned off, and bicarbonate is drawn into the flask, releasing carbon dioxide, which prevents oxidation of the stannous tin. When cool, the solution is titrated with iodine as before. The volume of iodine solution above that in the first titration corresponds to the stannic tin.

Example. If, after reduction, 10 ml of the above bath required 45 ml of iodine, the stannous tin produced by the reduction of stannic tin is equal to

$$\frac{(45 - 40)}{10} \times 0.091 = 0.046N$$

$\frac{118.7}{2} \times 0.046 = 2.73$ g/l or 0.36 oz/gal of Sn originally present as Sn^{IV}

That of stannic sulfate, $Sn(SO_4)_2$, is equal to

$$\frac{310.7}{2} \times 0.046 = 7.14 \text{ g/l or } 0.95 \text{ oz/gal}$$

LEAD. 1. Sulfate precipitation. The most convenient method for determining lead is the gravimetric sulfate precipitation, which is applicable to the fluoborate, fluosilicate, and sulfamate baths. A 10-ml sample is diluted to 100 ml, heated to boiling, and an excess of 10 per cent sulfuric acid is added. The solution is allowed to cool, filtered through a weighed Gooch crucible, washed first with dilute sulfuric acid and then with alcohol, dried, and weighed. The increase in weight is lead sulfate, $PbSO_4$,

$$\frac{Pb}{PbSO_4} = \frac{207}{303} = 0.68$$

Therefore,

$$\text{g } PbSO_4 \times 0.68 \times 100 = \text{g/l of lead}$$

Example. If, from 10 ml of the lead bath, the precipitate of lead sulfate weighed 1.17 g, then the lead content is

$$1.17 \times 0.68 \times 100 = 79.6 \text{ g/l or } 10.6 \text{ oz/gal of Pb}$$

CHROMIUM BATHS. The principal determinations required in the control of a chromic acid bath are hexavalent chromium, trivalent chromium, iron, and sulfate. The approximate content of chromic acid can be estimated from the specific gravity (Table 22, Appendix).

1. Hexavalent chromium. Several methods may be used, all of which depend upon quantitative reduction of the hexavalent chromium to trivalent chromium. If ferrous sulfate is used as the reducing agent, an electrometric end point can be employed or an excess can be added and titrated with potassium dichromate. In another method potassium iodide is added and the liberated iodine is titrated with sodium thiosulfate.

a. Ferrous sulfate titration. (1) Electrometric. An approximately $0.1N$ ferrous solution is prepared by dissolving 40 g of ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, in water; adding 75 ml of concentrated sulfuric acid, and diluting to 1 l.

An exactly 0.1N solution of potassium dichromate, $K_2Cr_2O_7$, is prepared by dissolving in water 4.90 g of pure $K_2Cr_2O_7$, dried at 130°C, and diluting to 1 l.

The electrometric titration is carried out as follows: The ferrous sulfate is standardized against the dichromate by taking 25 ml of the latter, diluting to 300 ml, and introducing a platinum wire and the tip of a calomel electrode, connected as shown in Fig. 42.

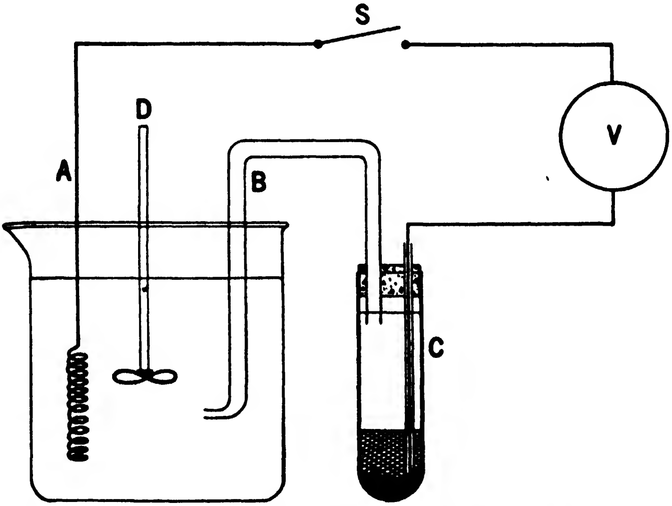

FIG. 42. Diagram of apparatus for electrometric titration. *A*, platinum wire. *B*, tip of calomel half cell. *C*, calomel half cell. *D*, stirrer. *V*, high-resistance voltmeter (or potentiometer). *S*, switch.

The ferrous sulfate is then added from a burette until a sudden marked change occurs in the voltmeter reading. This marks the end point.

To secure a small sample of the plating bath, *e.g.*, 0.5 ml, a 10-ml sample of the bath is diluted to 500 ml and a 25-ml portion of this solution is used, *i.e.*, 0.5 ml of the original. This is diluted to 300 ml and is titrated electrometrically with the ferrous sulfate.

Example. When 25 ml of 0.1N $K_2Cr_2O_7$ was titrated, it required 28 ml of ferrous sulfate. The latter is therefore

$$\frac{25}{28} \times 0.1 = 0.089N$$

If 0.5 ml of the plating bath required 39 ml of the ferrous sulfate, the hexavalent chromium or CrO_3 in the bath is

$$\frac{39}{0.5} \times 0.089 = 6.9N$$

With respect to oxidation, CrO_3 is trivalent; *i.e.*, it loses three valences when reduced from Cr^{VI} to Cr^{III}. Hence this solution is

$$\frac{6.9}{3} = 2.3M \text{ (molar)}$$

As the molecular weight of CrO_3 is 100, the solution contains

$$2.3 \times 100 = 230 \text{ g/l or } 30.7 \text{ oz/gal of } CrO_3$$

(2) Excess method. If an electrometric end point is not available, a measured volume of ferrous sulfate is added, and the excess is titrated with dichromate, using diphenylamine as an inside indicator. The ferrous sulfate is checked against the dichromate with the same indicator.

Example. Suppose that by this titration the ferrous sulfate was found to be $0.089N$ as in the above example. Then 50 ml of the $FeSO_4$ was added to 0.5 ml of the bath, and 12.4 ml of $0.1N$ $K_2Cr_2O_7$ was required to titrate the excess $FeSO_4$. The volume of $FeSO_4$ consumed by the 0.5-ml bath sample was therefore

$$50 - \left(\frac{12.4 \times 0.1}{0.089}\right) = 50 - 13.9 = 36.1 \text{ ml}$$

The remainder of the calculation is the same as in the last example.

b. Iodine-thiosulfate titration. In this procedure it is necessary to add a fluoride to prevent any ferric iron present from liberating iodine. The analysis is conducted as follows:

A 10-ml bath sample is diluted to 500 ml, and 10 ml of this solution (equivalent to 0.2 ml of the original bath) is diluted to 100 ml. Two grams of ammonium bifluoride, NH_4HF_2; 15 ml of concentrated HCl; and 1 g of KI are added. The solution is then titrated with $0.1N$ $Na_2S_2O_3$ until the brown color almost disappears. A few milliliters of a 1 per cent starch solution are added, and the titration is continued till the blue color disappears. The $Na_2S_2O_3$ is standardized against $0.1N$ $K_2Cr_2O_7$ (page 178).

Example. If 10 ml of $0.1N$ $K_2Cr_2O_7$ required 11 ml of $Na_2S_2O_3$, the latter is $0.1 \times \frac{10}{11} = 0.091N$. If 0.2 ml of the chromium bath required 16 ml of $Na_2S_2O_3$, the CrO_3 in the bath is $\frac{16}{0.2} \times 0.091 = 7.3N$ or $\frac{7.3}{3} = 2.43M$ (molar). It therefore contains

$$2.43 \times 100 = 243 \text{ g/l or } 32.4 \text{ oz/gal of } CrO_3$$

2. Trivalent chromium. *a.* Differential titration. The simplest method of determining the content of trivalent chromium involves (1) titration of the hexavalent chromium and (2) titration of the total chromium after the trivalent chromium has been oxidized to

the hexavalent. The difference between the two titrations represents the content of trivalent chromium originally present. One serious objection to this method is that the results depend upon the difference in the titrations of two large concentrations and are hence subject to error. Suppose, for example, that the concentrations of hexavalent chromium before and after oxidation corresponded, respectively, to 247 and 251 g/l of CrO_3. The difference, *i.e.*, 4 g/l, would represent the trivalent chromium that had been oxidized to CrO_3. If an error of only 1 g/l had been made in each titration, so that the values became 248 and 250 g/l, the difference of 2 g/l would represent an error of 50 per cent in the reported value for trivalent chromium. Fortunately, it is usually unnecessary to determine the trivalent chromium unless it is more than about 10 g/l, in which case these errors become relatively small and unimportant. For more accurate determinations of trivalent chromium a direct titration is preferable (see below).

The trivalent chromium can be oxidized under appropriate conditions by means of persulfate or of sodium peroxide. The latter method is simpler. To a diluted sample of the bath (*e.g.*, representing 0.5 ml of the original) about 0.2 g of sodium peroxide, Na_2O_2, is added, and the solution is boiled for about 30 min. It is then cooled and titrated according to one of the methods described above, normally the same one as was used for the first titration of hexavalent chromium.

Example. Suppose another 0.2-ml sample of the same solution as on page 179 was oxidized and titrated with thiosulfate and required 18 ml of the $0.091N$ $Na_2S_2O_3$ solution. Then it is evident that the trivalent chromium is equivalent to 18 − 16 = 2 ml of $Na_2S_2O_3$.

$$\frac{2}{0.2} \times 0.091 = 0.91N\ Cr^{III}$$

$$\frac{0.91}{3} = 0.303M$$

It therefore contains

$$0.303 \times 52 = 15.7 \text{ g/l or } 2.1 \text{ oz/gal of trivalent Cr}$$

While this is probably present as chromium dichromate, $Cr_2(Cr_2O_7)_3$, it is usually most convenient to express the content as metallic chromium in the trivalent state.

b. Direct titration. In this method,[1] the trivalent chromium is oxidized to hexavalent by the addition of an excess of ceric sulfate, $Ce_2(SO_4)_3$. After oxidation is complete, the excess of ceric sulfate

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[1] WILLARD, H. H., and YOUNG, P., *Trans. Electrochem. Soc.*, vol. 67, p. 347, 1935.

is titrated with a standard sodium nitrite solution. The end point is determined electrometrically, *e.g.*, by means of a platinum electrode and a silver-silver chloride electrode.

To a 5-ml sample are added 5 ml of HNO_3 (sp gr 1.42) and water to produce about 150 ml. Exactly 25 ml of a standardized 0.1*N* ceric sulfate solution is added, and the mixture is heated to 55°C and kept there 5 min. The excess of ceric sulfate is then titrated potentiometrically with 0.05*N* sodium nitrite while the solution is kept at 55°C. The tip of the burette should extend under the surface of the liquid. The end point is disclosed by a large change in the potential. The ceric sulfate is standardized against pure As_2O_3, with osmium tetroxide as a catalyst and orthophenanthroline ferrous complex as the indicator, with changes from pink to pale blue at the end point. Unfortunately this indicator is masked by the chromic acid, so that a potentiometric titration must be used for the chromium determination.

3. Trivalent chromium plus iron. *a.* Gravimetric. Because the effects of trivalent chromium and dissolved iron (which is also trivalent) are similar, and because their gravimetric determination involves the precipitation of both, they are conveniently discussed together.

The method depends upon the precipitation of the iron and trivalent chromium as hydroxides, $Fe(OH)_3$ and $Cr(OH)_3$, and their separation by oxidizing the chromium to the soluble chromate. The latter is determined by titration, and the iron is ignited and weighed as ferric oxide, Fe_2O_3. Because the precipitated hydroxides tend to carry down hexavalent chromium, it is necessary to redissolve and reprecipitate them.

A 25-ml sample of the chromium bath is diluted to 200 ml, heated to boiling, and a slight excess of ammonium hydroxide is added. The precipitate of chromic hydroxide, $Cr(OH)_3$, and ferric hydroxide, $Fe(OH)_3$ (which contains some chromate), is filtered out, washed with hot water, and dissolved in dilute sulfuric acid. It is again precipitated with ammonia, filtered, and washed with hot water. The precipitate is dissolved in dilute sulfuric acid, and an excess of sodium hydroxide is added, followed by a few milliliters of hydrogen peroxide or of bromine water. The solution is boiled and filtered; the precipitate is again dissolved in sulfuric acid and boiled with sodium hydroxide and hydrogen peroxide and filtered. The precipitate is ignited and weighed as Fe_2O_3. The combined filtrates containing the chromium oxidized to chromate are acidified, boiled to expel hydrogen peroxide or bromine, and titrated as on page 178.

Example. If 25 ml of the bath yielded 0.0832 g of Fe_2O_3, the solution contained $\frac{1,000}{25} \times 0.0832 \times \frac{2Fe}{Fe_2O_3}$ or $\frac{112}{160}$

$$40 \times 0.0832 \times 0.70 = 2.33 \text{ g/l or } 0.31 \text{ oz/gal of Fe}$$

If the chromate produced from 25 ml of the bath required 35 ml of $0.089N$ ferrous sulfate, the trivalent chromium is equal to

$$\frac{35}{25} \times 0.089 = 0.125N$$

$$\frac{52}{3} \times 0.125 = 2.2 \text{ g/l or } 0.3 \text{ oz/gal of trivalent Cr}$$

b. Indirect methods have been proposed for determining trivalent chromium and iron. For example, if the content of hexavalent chromium in a bath is determined and either the density or the conductivity of the solution is measured, it is possible from appropriate diagrams to estimate approximately the *sum* of the trivalent chromium and iron.

c. Spectrophotometric. In two recent publications[1] methods are described for the colorimetric determination of trivalent chromium and of iron in chromic acid baths, using a spectrophotometer (page 162). The concentration of hexavalent chromium can be similarly determined. In the standardization of the method for trivalent chromium, it is probable that the color (hence the absorption) of the trivalent chromium compound used (which may be green or violet) and its stability must be taken into account.

4. Sulfate. *a.* Gravimetric method. The most common method for determining sulfate is the gravimetric, in which barium sulfate is precipitated, washed, ignited, and weighed as $BaSO_4$. If this method were applied directly to the chromic acid solution, some barium chromate would be precipitated with the sulfate. This difficulty is avoided by first reducing the chromic acid to the trivalent state. It is, however, difficult to precipitate sulfate completely from a solution containing chromic sulfate and chloride. If acetic acid is also added, precipitation of barium sulfate is more rapid and complete.[2] The method is carried out as follows: To

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[1] BAYLEY, W. J., *J. Electrodepositors' Tech. Soc.*, vol. 22, p. 121, 1947. STYLES, H. E., *J. Electrodepositors' Tech. Soc.*, vol. 22, p. 129, 1947.

[2] WILLARD, H. H., and SCHNEIDEWIND, R., *Trans. Am. Electrochem. Soc.*, vol. 56, p. 333, 1929.

a 10-ml sample in a 250-ml beaker are added 10 ml of concentrated HCl, 25 ml of ethyl alcohol (or isopropyl alcohol), and 40 ml of glacial acetic acid. (These three materials can be previously mixed and used as required.) The solution is boiled for 15 min, diluted with hot water to 150 ml, allowed to stand, and filtered to remove any suspended impurities. The filtrate is heated to boiling, and 10 ml of a 10 per cent solution of barium chloride, $BaCl_2 \cdot 2H_2O$, is added gradually, with stirring. The solution is then allowed to stand at about 70°C for 2 to 4 hr, after which the precipitate is filtered out, washed with hot water, ignited, and weighed as $BaSO_4$.

Example. If the precipitate of $BaSO_4$ from 10 ml of the bath weighed 0.0632 g, the solution contains

$$\frac{1,000}{10} \times 0.0632 \times \frac{SO_4}{BaSO_4} \text{ or } \frac{96}{233.4}$$

$$100 \times 0.0632 \times 0.41 = 2.59 \text{ g/l or } 0.35 \text{ oz/gal of } SO_4$$

The solution is

$$\frac{2.59}{48} = 0.054N \text{ in sulfate}$$

b. Centrifuge method. In this rapid method the $BaSO_4$ is precipitated in the presence of the chromic acid, with considerable HCl present to prevent precipitation of $BaCrO_4$. The solution and precipitate are then whirled in a centrifuge in a tube having a small graduated extension into which the $BaSO_4$ settles. The volume of $BaSO_4$ is measured. The tube is calibrated by means of a chromic acid solution with a known content of sulfate. With careful control of all conditions, the method yields results that are accurate to about ±10 per cent of the sulfate, which is often adequate for works control.

c. Turbidimeter method. In this procedure[1] the barium sulfate is precipitated in such a way that it remains in suspension. Its amount is then estimated from the measured turbidity of the solution.

IRON BATHS. In baths consisting mostly of ferrous sulfate or chloride, the principal determinations made are of ferrous iron and acidity. The latter can be controlled either by titrations or by pH measurements. Only occasional determinations of ferric

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[1] WILLARD, H. H., and SCHNEIDEWIND, R., *Trans. Am. Electrochem. Soc.*, vol. 56, p. 341, 1929.

iron or of added salts such as ammonium sulfate or calcium chloride are required, because their concentrations are not critical.

1. Ferrous iron. *a.* Permanganate method. If the bath consists principally of ferrous sulfate (or ferrous ammonium sulfate), the content of ferrous iron can be readily titrated with standard permanganate solution. A 5-ml sample is diluted to 50 ml, 10 ml of concentrated H_2SO_4 added, and the solution is titrated with $0.5N$ $KMnO_4$ to the appearance of a permanent pink color. The $KMnO_4$ may be standardized against sodium oxalate or for this purpose against pure crystallized ferrous ammonium sulfate, $FeSO_4, (NH_4)_2SO_4{\cdot}6H_2O$, which contains exactly one-seventh of iron.

Example. When a permanganate solution, containing 16 g/l of $KMnO_4$, was used to titrate 2.10 g of ferrous ammonium sulfate, 22 ml of $KMnO_4$ was required. One milliliter of the permanganate is therefore equal to

$$\frac{1}{22} \times 2.10 \times \frac{\text{Fe}}{\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4{\cdot}6\text{H}_2\text{O}} \text{ or } \frac{56}{392}$$

$$\frac{1}{22} \times 2.10 \times 0.143 = 0.0136 \text{ g of Fe}$$

If 5 ml of the plating bath required 30.4 ml of $KMnO_4$, the bath contained

$$\frac{1{,}000}{5} \times 30.4 \times 0.0136 = 82.6 \text{ g/l or } 11.0 \text{ oz/gal of Fe}$$

A normal solution of a ferrous salt contains $56/2 = 28$ g/l of Fe. Hence this bath is $82.6/28 = 2.9N$ in ferrous salt.

b. Dichromate method. If the bath contains ferrous chloride or any appreciable amount of a chloride, it is more conveniently titrated with potassium dichromate, using diphenylamine as an inside indicator. This titration is also convenient for sulfate baths. The calculations are similar to those above. The $0.5N$ dichromate is prepared by dissolving exactly 24.5 g of pure $K_2Cr_2O_7$ in 1 l.

2. Ferric iron. The presence of appreciable ferric iron in a bath is shown by a yellow color, which indicates the need for reduction of the bath with iron and acid. The most satisfactory method of determining the content of ferric iron is by first titrating for ferrous iron as above, then reducing a fresh sample (*e.g.*, with zinc), and titrating the total iron content. The difference between the two titrations corresponds to the ferric iron.

3. Acidity. *a.* Titration. The free acid may be titrated with standard alkali, using bromphenol blue as the indicator. If much

ferric iron is present, some of it may be included in the result of this titration.

4. Calcium. The content of calcium chloride in a bath containing only ferrous and calcium chlorides can be estimated from the specific gravity and the iron content (Table 23 in Appendix).

COBALT AND NICKEL BATHS. Most methods of analysis for these two metals and their baths are similar.

1. Metal content. *a.* Electrolytic. In the usual methods for the electrolytic determination, nickel and cobalt are deposited together and are not separated. In reporting such results it should be recalled that most nickel baths contain some cobalt and vice versa. The electrolytic method is carried out as follows.

To 25 ml of the bath, 5 g of ammonium sulfate $(NH_4)_2SO_4$, and 25 ml of concentrated ammonium hydroxide, NH_4OH, are added, and the solution is diluted to 200 ml. It is then electrolyzed with a platinum or copper cathode at 2 amp/dm^2 for about 1 hr if stirred or at 0.5 amp/dm^2 for several hours if not agitated. After the blue color of the solution has disappeared, a drop is removed and a drop of a 1 per cent alcoholic solution of dimethylglyoxime is added on a spot plate. Electrolysis is continued till no pink color appears in the tested drop. The cathode is washed with water and then with alcohol, dried, and weighed. The increase in weight represents nickel (plus cobalt if present).

If from 25 ml the deposit weighs 1.50 g, the solution contains

$$\frac{1{,}000}{25} \times 1.50 = 60.0 \text{ g/l or 8 oz/gal of Ni}$$

The solution is

$$\frac{60}{29.3} = 2.04N \text{ in nickel}$$

2. Nickel. *a.* Cyanide titration. This titration depends upon the reaction of nickel salts with sodium cyanide to form the nearly colorless soluble complex salt $Ni(CN)_2 \cdot 2NaCN$. Silver iodide is used to detect the presence of an excess of cyanide, which dissolves the silver iodide. Sodium pyrophosphate is added to keep any iron in solution and to prevent its reaction with the cyanide.

To 10 ml of the bath, 50 ml of a solution containing 50 g/l of $Na_4P_2O_7 \cdot 10H_2O$ is added. Ammonium hydroxide is added till the solution turns a clear dark blue, followed by 10 ml of a solution containing 8 g/l of potassium iodide, KI. A solution containing 25 g/l of sodium cyanide, NaCN, and 1.7 g/l of silver nitrate,

$AgNO_3$, is used for the titration. The presence of the silver nitrate ensures that the amount of silver iodide formed and dissolved is proportional to the volume of sodium cyanide used in the titration. The solution is titrated until the precipitate of silver iodide just dissolves. The cyanide solution must be standardized frequently against a nickel solution of known strength, *e.g.*, one made from pure crystallized nickel ammonium sulfate, $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$.

Example. If exactly 60 g of the nickel ammonium sulfate was dissolved in 1 l, the solution is $\frac{60}{197.5} = 0.304N$ and contains $0.304 \times 29.3 = 8.9$ g/l Ni; hence

$$1 \text{ ml} = 0.0089 \text{ g of Ni}$$

If in titrating 25 ml of this solution 24 ml of the NaCN was required, 1 ml of NaCN $= \frac{(25 \times 0.0089)}{24} = 0.0093$ g Ni. If 10 ml of the plating bath required 42 ml of the NaCN, the bath contained $\frac{1{,}000}{10} \times 42 \times 0.0093 = 39.1$ g/l or 5.2 oz/gal of Ni and the solution is $39.1/29.3 = 1.33N$ in nickel.

b. Colorimetric. It is possible to measure the nickel content of a bath by comparing its green color with that of a standard nickel solution. Because the eye is not very sensitive to changes in the intensity of green solutions, some colorimetric devices use a pink solution to neutralize optically the green color, *i.e.*, to produce a neutral gray. Presence of other salts, such as iron and tartrates or citrates, changes the color of the nickel salts and must be taken into account even in spectrophotometric methods.

3. Cobalt. *a.* Volumetric. The titration of cobalt solutions with cyanide requires a modified process, described by B. S. Evans.[1] This method depends upon the fact that in alkaline solutions cobalt tends to oxidize from Co^{++} to Co^{+++}. To ensure complete oxidation to Co^{+++}, the solution is treated with a measured excess of NaCN solution and air is bubbled through to oxidize the cobalt. The excess of NaCN is titrated with $AgNO_3$. In this titration the cobalt forms $Co(CN)_3 \cdot 3NaCN$.

b. Colorimetric. Cobalt can be conveniently determined with a spectrophotometer, making use of the blue color produced by cobalt and a thiocyanate. The reagent solution contains 200 g/l of NH_4CNS, 20 g/l of $K_4P_2O_7$, and 50 ml/l of acetic acid, all dissolved in a 1 to 1 mixture of acetone and water. Comparisons are made at a wavelength of 620 millimicrons.

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[1] *J. Electrodepositors' Tech. Soc.*, vol. 14, p. 141, 1938.

4. Ammonia. Volumetric. A 10-ml sample of the bath is distilled with an excess of sodium hydroxide, and the evolved ammonia, NH_3, is passed into and absorbed by a measured volume of standard hydrochloric acid, *e.g.*, 25 ml of $0.2N$ HCl. The unneutralized acid is titrated with standard alkali, using methyl orange as the indicator. The content of ammonia is calculated as follows:

Example. A 10-ml sample of a nickel bath was distilled into 25 ml of $0.2N$ HCl, and the excess required 8.4 ml of $0.2N$ NaOH to neutralize it. The evolved ammonia therefore neutralized

$$25 - 8.4 = 16.6 \text{ ml of HCl}$$

The concentration of ammonia (or of ammonium salt) is

$$\frac{16.6 \times 0.2}{10} = 0.332N$$

This is equivalent to

$$0.332 \times 17 = 5.6 \text{ g/l or } 0.75 \text{ oz/gal of } NH_3$$

or

$$0.332 \times 53.5 = 17.8 \text{ g/l or } 2.4 \text{ oz/gal of } NH_4Cl$$

or corresponding amounts of ammonium sulfate or other ammonium salts.

5. Chloride. Volumetric. A 10-ml sample is diluted to 50 ml, and if the pH is low, it is neutralized to about pH = 5. About 1 ml of a 2 per cent solution of neutral sodium chromate, Na_2CrO_4, is added. The solution is then titrated with $0.1N$ silver nitrate to the appearance of a faint permanent red precipitate.

Example. If 10 ml of the bath required 27 ml of $0.1N$ $AgNO_3$, the chloride concentration is $0.1 \times \frac{27}{10} = 0.27N$.

This is equivalent to

$$0.27 \times 35.5 = 9.6 \text{ g/l or } 1.28 \text{ oz/gal of Cl}$$

or

$$0.27 \times 53.5 = 14.4 \text{ g/l or } 1.93 \text{ oz/gal of } NH_4Cl$$

or

$$0.27 \times 119 = 32.2 \text{ g/l or } 4.31 \text{ oz/gal of } NiCl_2\cdot 6H_2O$$

6. Boric acid. Volumetric. There is no sample method of determining boric acid in the presence of fluorides. In the absence of fluorides, the boric acid can be titrated either before or after removal of the nickel (or cobalt).

To a 2-ml sample of the nickel bath are added a few drops of an indicator solution containing 0.2 per cent of bromthymol blue and 1 per cent of bromcresol purple in 93 per cent ethyl alcohol.

The solution is titrated with 0.5*N* NaOH till the color just changes from green to blue. Sufficient powdered mannitol is added to make a thick paste, the color of which is again green. The mixture is again titrated with NaOH to a blue color. The content of boric acid is proportional to the volume of alkali required in the last part of the titration.

In another method the nickel is removed by electrolysis (page 185) and any ferric hydroxide is filtered out. The filtrate is boiled with an excess of NaOH to destroy ammonium salts. A few drops of bromphenol blue are added, then a slight excess of sulfuric acid, and the solution is boiled to expel carbon dioxide. It is then exactly neutralized with standard NaOH. The burette reading at this point indicates the start of the titration. A few drops of phenolphthalein are added, and the solution is titrated with alkali until a pink color appears. About 5 g of mannitol (or 25 ml of glycerin) is added, which discharges the pink color. Titration is continued till a pink color persists after a further small addition of mannitol or glycerin. The volume of alkali used after the phenolphthalein addition corresponds to the boric acid in the equation

$$H_3BO_3 + NaOH = NaBO_2 + 2H_2O$$

i.e., one molecule of boric acid requires one NaOH. The mannitol or glycerin does not enter into the reaction but makes the end point distinct.

Example. If 10 ml of the nickel bath required 11 ml of 0.5*N* NaOH, the *molarity M* of the boric acid is $\frac{11}{10} \times 0.5 = 0.55M$.

This is equivalent to

$$0.55 \times 62 = 34 \text{ g/l or } 4.5 \text{ oz/gal of } H_3BO_3$$

7. Impurities in nickel baths. As part of an extensive research sponsored by the American Electroplaters' Society, methods have been published, principally by E. J. Serfass and his associates, on the determination of impurities in nickel-plating solutions.[1] As these methods are highly specific and the researches are still in progress, no effort will be made to include the details in this text. Most of the recommended methods involve the use of some form of colorimeter, such as a spectrophotometer. Methods have been

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[1] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 33, pp. 1073, 1189, 1946; vol. 34, pp. 320, 454, 1947; and *Am. Electroplaters' Soc. Research Rept.*, Serial No. 3, 1947. *Proc. Am. Electroplaters' Soc.*, p. 218, 1947.

described for determining small amounts of lead, iron, manganese, copper, cadmium, chromium, silica, zinc, calcium, aluminum, sodium, and ammonium in nickel baths. Very similar methods can probably be used in other baths. Only when reliable methods for such determinations are available is it possible to determine if and in what concentrations any impurity has significant effects in a given bath. These methods will then prove useful, especially in large plants, for controlling the contents of deleterious impurities.

PLATINUM GROUP METALS. 1. Platinum. *a*. Gravimetric. Before precipitating the platinum it is necessary to destroy the complex ammino phosphates or nitrites by boiling with sulfuric and nitric acid. The following procedure can be used:

To 100 ml of the plating bath add 25 ml of concentrated HCl, boil, and evaporate to a sirup. Add 10 ml of concentrated H_2SO_4, and evaporate to white fumes. Cool slightly, add a few milliliters of concentrated HNO_3 and again evaporate to fuming. Repeat the addition of HNO_3 and evaporation a few times to destroy the ammino complexes.

Finally add 10 ml of concentrated HCl, dilute to 200 ml, heat nearly to boiling, and pass in a rapid stream of hydrogen sulfide for 1/2 hr. The precipitate consists of platinum sulfide, together with any metallic platinum that may have been reduced during the evaporations. Filter, wash the precipitate with 1 per cent HCl solution, and ignite the precipitate in air in a porcelain crucible. Digest the residue with $6N$ HNO_3 to remove any included salts, filter, ignite, and weigh as metallic platinum.

In a more rapid, approximate method zinc dust is added to the heated solution containing hydrochloric acid. This precipitates metallic platinum. Nitric acid is added to dissolve the excess of zinc, and the precipitate of platinum is filtered out, washed, ignited, and weighed.

Example. If from 100 ml of the bath the platinum weighed 0.217 g, the bath contains

$$\begin{aligned} 10 \times 0.217 &= 2.17 \text{ g/l of Pt} \\ 2.17 \times 0.122 &= 0.264 \text{ troy oz/gal} \\ &= 5.28 \text{ dwt/gal} \end{aligned}$$

2. Rhodium. *a*. Gravimetric. If, as is likely to occur in a strongly acid solution, the rhodium bath has become contaminated with other metals such as iron, copper, and zinc, it is necessary to remove these impurities before precipitating the rhodium. This can be accomplished either by carefully controlled hydrolysis

or by precipitation with potassium ferrocyanide in a weakly acid solution.

The hydrolysis is conducted as follows: To 100 ml of the rhodium bath add 25 ml of concentrated HCl, boil for 10 min, and evaporate on a steam bath to a sirup. Dilute to 150 ml, and neutralize to a pH of 1.5 with NaOH, using thymol blue as the indicator, *e.g.*, on the end of a stirring rod. Heat the solution to boiling, and add gradually a 10 per cent solution of $NaNO_2$, which further decreases the acidity and causes the precipitation of any copper, zinc, nickel, or iron as hydroxides. Finally, add NaOH to produce a pH of 10, measured by the change of thymol blue from yellow to blue. Filter out the precipitate, and wash it with a 1 per cent solution of $NaNO_2$ adjusted to a pH of 10.

To the filtrate add 10 ml of concentrated HCl, evaporate on a steam bath, treat with HCl, and again evaporate. Add 10 ml HCl, dilute to 200 ml, heat nearly to boiling, and pass in a rapid stream of H_2S for 1/2 hr. Filter out the precipitate of rhodium sulfide, wash with 1 per cent HCl, and ignite in a porcelain crucible. Reduce the residue (rhodium oxides) with hydrogen, using a Rose lid and a quartz tube. Cool in hydrogen, and weigh as metallic rhodium.

Example. If from 100 ml 0.1590 g of rhodium was obtained, the bath contains

$$\begin{aligned} 10 \times 0.159 &= 1.59 \text{ g/l of Rh} \\ 1.59 \times 0.122 &= 0.194 \text{ troy oz/gal} \\ &= 3.88 \text{ dwt/gal} \end{aligned}$$

If ferrocyanide is used to precipitate the impurities, the bath sample should be diluted or neutralized to a pH of 3, as otherwise any copper is not entirely precipitated. The rest of the procedure is similar to that described for the hydrolysis.

b. Colorimetric. It is possible to determine rhodium colorimetrically by comparing the red color produced by bromide in acid solution with that of a standard rhodium solution. This method is often used for rapid control of the rhodium content of baths and is accurate to about 10 per cent, unless interfering impurities are present.

Alkaline and Cyanide Plating Baths. *General.* Most alkaline plating baths (except the stannate tin bath and the pyrophosphate baths) involve cyanides of sodium or potassium. In general, they contain (1) double metal cyanides, (2) an excess of alkali cyanide known as *free cyanide*, (3) alkali carbonate, and frequently (4) free sodium hydroxide. The methods of analysis are the same whether they are prepared from potassium cyanide, *e.g.*, gold and silver baths, or from sodium cyanide as in most other cyanide baths. The most common determinations for control are (1) free cyanide, (2) total cyanide (especially if the free cyanide is not readily estimated), (3) the pH or alkalinity, (4) carbonate, and (5) the metal content. All these methods except (5) are similar for different baths, with minor modifications that will be referred to.

Free Cyanide. Regardless of whether for a given bath the free cyanide is defined as the excess above a specified compound, *e.g.*, $KAg(CN)_2$, or as the excess above that required to maintain a clear solution of the existing composition, its titration is essentially empirical and must be defined for each bath. The titration of free cyanide is usually conducted with silver nitrate, which combines with alkali cyanide according to the equation

$$2\ NaCN + AgNO_3 = NaAg(CN)_2 + NaNO_3$$

The double silver cyanide is soluble. When an excess of $AgNO_3$ is added, it reacts with the double cyanide to form a white precipitate of AgCN, which may serve to detect the end point.

$$NaAg\ (CN)_2 + AgNO_3 = 2\ AgCN + NaNO_3$$

It has been shown[1] that the customary addition of potassium iodide, which forms a precipitate of silver iodide, AgI, at the end point, leads to more accurate results (especially in contaminated baths) because silver iodide is slightly less soluble than silver cyanide.

The titration of free cyanide in a silver bath is conducted as follows. To a 10-ml bath sample, 0.2 g of KI is added, *e.g.*, 10 ml of a solution containing 20 g/l of KI. The solution is diluted to 200 ml and titrated with $0.1N$ $AgNO_3$ to a faint opalescence, best observed against a black surface. Because 1 $AgNO_3$ reacts with 2KCN, $0.1N$ $AgNO_3$ is equivalent to $0.2N$ KCN.

Example. If 10 ml of a silver bath required 8.5 ml of $0.1N$ $AgNO_3$, the bath contains $8.5 \times 0.2 = 0.17N$ free KCN.

$$0.17 \times 65 = 11.1 \text{ g/l or } 1.47 \text{ oz/gal of free KCN}$$

If the bath contained free NaCN, its concentration would be

$$0.17 \times 49 = 8.3 \text{ g/l or } 1.11 \text{ oz/gal of free NaCN}$$

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[1] WICK, R. M., *J. Research Natl. Bur. Standards*, vol. 7, p. 913, 1931, RP 384.

The titration of free cyanide in gold and copper baths is similar to that in silver baths. In gold baths the free cyanide so titrated is that above $KAu(CN)_2$, exactly analogous to silver. In copper baths the titration corresponds to the excess above $Na_2Cu(CN)_3$ only if considerable KI, *e.g.*, 1 g, is present.[1] In titrating copper baths addition of a very small amount (not over 1 ml) of ammonium hydroxide sharpens the end point, probably by retaining in solution basic carbonates or similar compounds.

The titration of free cyanide in zinc and cadmium baths is unsatisfactory, because the results are influenced by the presence of free alkali and ammonia and the end points are uncertain. In a given plant it may be possible roughly to control such baths by arbitrary but consistent titrations of free cyanide, but the results do not have quantitative significance. It is therefore customary to determine the total cyanide and to compute the free cyanide from the metal content on the assumption that certain double cyanides are present.

Total Cyanide. DIRECT TITRATION. To titrate the total cyanide with silver nitrate, it is necessary to make such additions as will form soluble compounds with the metal present and will release the cyanide originally combined with the metal. For example, in a zinc bath, addition of an excess of sodium hydroxide forms soluble sodium zincate and liberates all the cyanide, which can then be titrated in the presence of potassium iodide.

$$Na_2Zn\,(CN)_4 + 4NaOH = Na_2ZnO_2 + 4NaCN + 2H_2O$$

In cadmium baths addition of an excess of ammonium hydroxide keeps the cadmium in solution and permits titration of the total cyanide.

Example. Total cyanide in a zinc bath. A 25-ml sample of a zinc bath was diluted to 250 ml, and a 25-ml sample was taken (equivalent to 2.5 ml of the original bath) and diluted to 200 ml; 5 ml of a 10 per cent solution of NaOH and 10 ml of a 2 per cent solution of KI were added, and the solution was titrated with $0.1N$ $AgNO_3$ (equivalent to $0.2N$ NaCN) to a faint permanent-yellow precipitate of AgI; 30 ml of $AgNO_3$ was required. The total cyanide in the bath is therefore

$$\frac{30}{2.5} \times 0.2N = 2.4N$$

Suppose that titration of the zinc (page 174) in this bath showed that the zinc content was $1.1N$. This is equivalent to $1.1N$ NaCN to form $Zn(CN)_2$

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[1] THOMPSON, M. R., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 18, May, 1931.

and an additional 1.1N NaCN to form $Na_2Zn(CN)_4$. Hence in this bath the calculated free NaCN is equal to 2.4 − (1.1 + 1.1).

$$2.4 - 2.2 = 0.2N \text{ free NaCN}$$
$$0.2 \times 49 = 9.8 \text{ g/l or 1.3 oz/gal of free NaCN}$$

Actually this value has little meaning unless the content of *free alkali* is also known.

Distillation. When NaCN or KCN is treated with dilute acid, hydrocyanic acid, HCN, is evolved. This operation is conducted in a distilling flask, and the HCN is distilled out and collected in an excess of sodium hydroxide to form NaCN. The latter may then be titrated with silver nitrate. If this procedure is applied to determine the total cyanide in plating baths, certain precautions must be observed. The CuCN or AgCN that precipitates on the addition of acid to the double cyanide is insoluble and not easily decomposed by the excess acid. The following procedure has been found to yield accurate results:[1]

A 5-ml sample of the cyanide bath is placed in a distilling flask and diluted with 50 ml of water. The outlet is arranged to distill into a flask containing about 70 ml of 0.4N NaOH. One hundred milliliters of a 1 to 10 HCl solution are poured into the distilling flask, and distillation is continued till about 50 per cent of the solution is distilled over. The solution in the receiver is then titrated with 0.1N $AgNO_3$ after the addition of KI. The result represents the total cyanide (including ferrocyanide) present in the bath sample.

The results for total cyanide as determined by distillation can be used to compute the free cyanide (page 191). Owing to uncertainties in the constitution of the double cyanides and to the possible presence of ferrocyanides, the computed values for free cyanide are somewhat indefinite. They may serve, however, for control of a given bath in continuous operation.

pH. All cyanide baths are alkaline, *i.e.*, have a pH above 7, because in aqueous solution the alkali cyanides hydrolyze according to the equation

$$NaCN + H_2O \rightarrow NaOH + HCN$$

The hydrocyanic acid, HCN, is chemically a very weak acid; hence the solution is alkaline. The cyanide present in the complex cyanides such as $NaAg(CN)_2$ is less readily hydrolyzed; hence a

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[1] Heiman, S., and McNabb, W. M., *Ind. Eng. Chem., Anal. Ed.*, vol. 10, p. 698, 1938.

pure solution of the double salt is slightly less alkaline than an equivalent solution of the alkali cyanide. To some extent, therefore, the pH is an indication of the content of free cyanide. However, the cyanide solutions always contain carbonate, formed either by absorption of carbon dioxide from the air, *e.g.*, by falling spray, or by saponification or oxidation of the cyanide. Sodium and potassium carbonate solutions are also alkaline as a result of hydrolysis. Many cyanide baths contain free alkali, either added as such or formed by dissolving zinc oxide or cadmium oxide in sodium cyanide.

Measurement and control of the pH of cyanide baths is now a common practice.[1] The colorimetric determination of pH in alkaline solutions is usually less satisfactory than in acid solutions, because the *salt errors* are larger and less consistent.[2] Errors also arise in glass electrode measurements of strongly alkaline solutions unless a special glass is used. The latter method is more reproducible than the colorimetric and with appropriate corrections serves to control the baths.

Alkaline Hydroxide. The total alkali in a zinc or cadmium bath can be approximately determined by first adding enough ferrocyanide to precipitate the zinc or cadmium (as determined by a previous titration). Sufficient silver nitrate is then added to precipitate all the cyanide present. The solution containing the precipitates is then titrated with $0.2N$ HCl, using phenolphthalein as indicator. This titration is equivalent to the total NaOH plus one-half the Na_2CO_3. If much carbonate is present, it should be determined and a correction made in the titration for total alkaline hydroxide.

In a sodium stannate bath the free alkali is determined by first adding a slight excess of barium chloride to precipitate the carbonate. Without filtration the solution is titrated with standard acid, using thymolphthalein as the indicator.

Carbonate. Because carbonate accumulates in cyanide baths and may require removal, its occasional determination is desirable. The method most commonly used involves precipitation of barium carbonate, which is filtered out, washed, and dissolved in standard acid, the excess of which is titrated.

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[1] HOGABOOM, G. B., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 24, p. 713, 1937.

[2] THOMPSON, M. R., *J. Research Natl. Bur. Standards*, vol. 24, p. 423, 1940, RP 1291.

To 10 ml of the cyanide bath, 1 ml of strong ammonium hydroxide is added, and the solution is diluted to 50 ml and heated nearly to boiling. An excess of barium chloride or nitrate is added. The precipitate of barium carbonate, $BaCO_3$, is filtered out and washed with hot water. The filter and precipitate are placed in a small flask with 50 ml of water, and a measured volume of standard HCl is added. After the precipitate has dissolved, the excess acid is titrated with standard NaOH, using methyl orange as the indicator.

Example. The precipitate of $BaCO_3$ obtained from 10 ml of the bath was dissolved in 25 ml of 0.2*N* HCl. The excess of acid required 12 ml of 0.2*N* NaOH to neutralize it. Hence the carbonate required

$$25 - 12 = 13 \text{ ml of } 0.2N \text{ HCl}$$

The carbonate in the bath was therefore

$$\frac{13 \times 0.2}{10} = 0.26N$$

This is equivalent to

$$0.26 \times \frac{106}{2} = 13.8 \text{ g/l or } 1.85 \text{ oz/gal of } Na_2CO_3$$

or

$$0.26 \times \frac{138}{2} = 18.0 \text{ g/l or } 2.41 \text{ oz/gal of } K_2CO_3$$

Metal Content of Cyanide Baths. PREPARATION OF SAMPLE. In order to determine the metal content of a cyanide bath, it is usually necessary first to destroy the cyanide. This is best accomplished by adding an excess of acid and evaporating in a hood to expel the hydrocyanic acid and most of the excess acid. Either hydrochloric or sulfuric acid will decompose the cyanides. Use of sulfuric acid is generally preferable, because it permits heating to higher temperatures and thereby destroys any organic matter. If, as in the Rochelle salt copper bath, considerable organic compounds are present, a mixture of HNO_3 and H_2SO_4 should be used. In any case if any dark color persists when the sulfuric acid is evaporated to fumes, a few drops of concentrated HNO_3 are carefully added and evaporation is continued. For most cyanide baths the following procedure is satisfactory.

To a 10-ml sample, add slowly 20 ml of 1 to 1 sulfuric acid. Evaporate in a hood till dense white fumes appear. If the residue is dark, add a few drops of concentrated HNO_3 and again evaporate to fumes. Cool and dilute carefully with water to 50 ml. The solution is then ready for most of the metal determinations, which may be carried out by regular methods such as the following.

COPPER. Iodide-thiosulfate titration (page 173).

SILVER. Thiocyanate titration. The silver is titrated with a sodium thiocyanate, NaCNS, solution, using ferric ammonium sulfate as the indicator, which gives a pink color when an excess of thiocyanate is present.

A solution containing about 10 g/l of NaCNS is standardized against 0.1*N* $AgNO_3$. To 10 ml of $AgNO_3$, diluted to 100 ml, 1 ml of a 2 per cent solution of ferric ammonium sulfate is added. It is then titrated with the NaCNS to the appearance of a pink color. The titration is made similarly of the diluted residue from the evaporation of a 10-ml sample of the silver bath with sulfuric acid.

Example. If 20 ml of 0.1*N* $AgNO_3$ required 19 ml of NaCNS, the latter is

$$\frac{20}{19} \times 0.1 = 0.105N$$

If 10 ml of the silver bath required 24.2 ml of NaCNS, the bath is

$$\frac{24.2}{10} \times 0.105 = 0.254N$$

$$0.254 \times 108 = 27.4 \text{ g/l or } \frac{27.4}{8.2} = 3.34 \text{ troy oz/gal of silver}$$

GOLD. 1. Precipitation. In the residue from the acid evaporation of a gold bath, the metal gold can be precipitated by the addition of ferrous sulfate or of hydrogen peroxide, filtered, washed, ignited, and weighed as gold. If evaporation is continued to white fumes of sulfuric acid, the gold is completely precipitated.

2. Fire assay. Gold can also be determined by a fire assay. A sample of the gold bath is evaporated and mixed with an excess of litharge, PbO; the mass is dried and heated to fusion in a clay crucible, producing a lead button that contains all the gold and silver. This lead button is oxidized in a muffle furnace in a *cupel* of bone ash. The resulting small bead that contains the gold and silver is weighed. If much silver is present (as in a green gold solution), the gold and silver are parted with nitric acid.

3. Iodine titration. If copper and iron are absent, the gold can be determined by titration with iodide and thiosulfate. In this process the gold is first reduced by the KI from the trivalent to univalent condition and iodine is liberated.

$$AuCl_3 + 3KI = AuI + I_2 + 3KCl$$

The liberated iodine is titrated with thiosulfate, using starch as the indicator. Because gold-plating solutions are usually dilute, 0.01*N* $Na_2S_2O_3$ is used and is standardized against a known amount of gold. An excess of $Na_2S_2O_3$ is added and is titrated back with 0.01*N* I_2 solution. It is preferable to dissolve the gold in aqua regia or to evaporate the gold bath with aqua regia and then with hydrochloric acid on a steam bath, avoiding overheating, which may decompose the auric chloride, $AuCl_3$.

Example. Exactly 0.04 g of pure gold was dissolved in aqua regia, evaporated with HCl, and diluted to 50 ml; 1 g of KI was added and a few drops of starch solution. Titration with 0.01*N* thiosulfate was continued till after the blue color disappeared, and then 0.01*N* iodine was added till the blue color just appeared. If 47.2 ml of the $Na_2S_2O_3$ and 5.8 ml of an exactly equivalent I_2 solution were used, the 0.04 g of gold was equivalent to

$$47.2 - 5.8 = 41.4 \text{ ml of the } Na_2S_2O_3$$

Therefore each ml of the $Na_2S_2O_3$ was equivalent to $0.040/41.4 = 0.00097$ g of Au.

If 25 ml of the gold bath required 42.6 ml of $Na_2S_2O_3$ and 3.6 ml of I_2 solution, the gold was equivalent to

$$42.6 - 3.6 = 39 \text{ ml of } Na_2S_2O_3$$

The bath therefore contained

$$\frac{1{,}000}{25} \times 39 \times 0.00097 = 1.51 \text{ g/l}$$

or

$$1.51 \times 2.44 = 3.7 \text{ dwt/gal}$$

or

$$1.51 \times 0.122 = 0.184 \text{ troy oz/gal of gold}$$

4. Colorimetric. The gold can also be determined colorimetrically after addition of orthotolidine (page 163) to the solution that has been evaporated with aqua regia to destroy cyanide. Since in this method a very small sample of the gold solution is employed, it is preferable to evaporate a larger sample, *e.g.*, 10 ml, with aqua regia and to dilute the residue, still containing some aqua regia, to, for example, 1 l. A small sample, *e.g.*, 10 ml (equivalent to 0.1 ml of the bath), is then carefully evaporated with hydrochloric acid in a stream of pure air to expel the acid without reducing any of the gold. If a spectrophotometer is available, it can be used both to determine the gold content of solutions and the thickness of gold deposits.

This method is used for determining gold in gold-alloy baths[1] in

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[1] NELL, K., *Plating*, vol. 35, p. 345, 1948.

a scheme of analysis that also includes methods for copper, nickel, phosphate, carbonate, and free cyanide in such baths.

Zinc. The zinc can be titrated with ferrocyanide (page 174) in the solution obtained after evaporation with sulfuric acid.

Zinc and Copper in Brass Baths. In the residue from evaporation with acid, copper may be determined electrolytically (page 172) after the addition of a few drops of nitric acid. The zinc is then titrated with ferrocyanide (page 174) in the residual solution.

Cadmium. 1. Volumetric. Cadmium may be titrated with ferrocyanide under the same conditions as zinc (page 174). Any zinc present in the bath is included in the titration. The ferrocyanide should be standardized against pure cadmium.

2. Electrolytic. Five milliliters of the bath is diluted to 80 ml, a slight excess of ammonia is added, and the solution is electrolyzed with platinum electrodes. With a rotating anode and a gauze cathode, at about 1.5 amp/dm^2, electrolysis is usually complete in 2 hr.

Tin. 1. Total tin content. *a.* Volumetric. This method depends upon the reduction of the tin in acid solution by sodium hypophosphite, of which the excess is destroyed by boiling. The resultant stannous tin is titrated with a standardized iodine solution, with care to exclude access of air which would reoxidize the stannous tin. The following reagents are employed.

Solid sodium hypophosphite.
Hydrochloric acid (1 to 1).
Mercuric chloride, saturated solution.
Citric acid, 50 g in 100 ml of water.
Potassium iodide, 40 g/l.
Starch solution, 1 per cent.
Standard iodine solution, 0.1*N*.

The titration is conducted in a 500-ml Erlenmeyer flask provided with a one-hole stopper, in which is inserted a glass tube drawn down to a fine tip.

To 5 ml of the plating bath add 20 ml of HCl (1 to 1), 5 g of hypophosphite dissolved in 80 ml of HCl (1 to 1), and 1 ml of mercuric chloride. The solution is boiled gently for 10 min. Five milliliters of KI solution, 1 ml of starch, and 50 g of citric acid are then added, together with a few pieces of marble, $CaCO_3$ (which on dissolving liberates CO_2 and so excludes air). The flask is stoppered and cooled quickly under running water. The tip of the burette is then inserted instead of the glass tube, and titration with the iodine is conducted to the appearance of a blue color.

Example. If 5 ml of the tin bath required 27 ml of 0.1N iodine solution, the bath is equivalent to $\frac{27}{5} \times 0.1 = 0.54N$ iodine. In the analysis the tin is first reduced to stannous tin, Sn^{II}, and then is oxidized by the iodine to stannic tin, Sn^{IV}. Hence one atom of tin is equivalent to two atoms of iodine, and this tin bath is $0.54/2 = 0.27M$ in tin. It therefore contains

$$0.27 \times 118.7 = 32.1 \text{ g/l or } 4.28 \text{ oz/gal of metallic tin}$$

b. Gravimetric. The total tin content can be determined by evaporating to dryness 10 ml of the bath with 10 ml of concentrated nitric acid. The insoluble residue of metastannic acid is filtered on a filter paper, washed with hot water, ignited, and weighed as SnO_2, which contains 78.76 per cent of tin.

2. Stannous tin content. *a.* Volumetric. A 25-ml sample is acidified with HCl and titrated quickly with 0.1N iodine solution. The calculation is similar to that for total tin content. If much stannous tin is present, it should be subtracted from the total tin content to give the stannic tin.

CHAPTER VII

PREPARATION FOR ELECTROPLATING

GENERAL PRINCIPLES

Prior to the application of electroplated coatings it is essential that the surface of the basis metal be cleaned. The common foreign materials likely to be present on metal surfaces may be roughly divided into three major groups. The first class, often designated as *grease* or *soil,* includes all greasy, oily compounds that may have been applied to prevent corrosion during storage (such as *slushing* compounds), those applied during machining operations (*cutting* compounds), and those greases and waxes present in the polishing and buffing compounds used to smooth the metal surfaces. Even if the latter are so-called "greaseless" compounds containing abrasive, glue, and a preservative, they may, for convenience, be included in this major group, since they have lubricating properties.

The second class of contaminants includes all foreign particles that are not derived from the basis metal. These include the abrasive constituents of polishing and buffing compounds as well as any other dust or particles of metal that may adhere to the greasy surfaces. In general, the removal of the greasy materials, except with organic solvents, loosens and detaches these solids unless the latter are firmly attached to the surface. An extreme case of firm adhesion is represented by particles of sand or steel that may be embedded in the metal surface as a result of sand or shot blasting or rolling.

The third class of contaminants consists of those metal compounds, usually oxides, which are formed or left on the metal surface as a result of casting, rolling, machining operations, and heat-treatment. In specific cases, other substances such as graphite and sulfides may be present on the metal surfaces.

In general, it is essential to remove all foreign substances from a metal surface prior to plating. In fact, it was formerly considered axiomatic that adherent, impervious coatings could be applied only to metal surfaces that were *perfectly clean.* Recent proposals to produce an oxide film on aluminum or a phosphate film on steel prior to plating involve deliberate contamination of the metal surface. If such procedures yield adherent coatings, and if the compounds are actually still present to any great extent between the basis metal and the coating, these usages appear to furnish the proverbial exception to the rule that a metal surface should be clean before plating. Apparently the adhesion of plated coatings to anodized aluminum depends on the intentional production of pores in the oxide film through which adhesion occurs. The phosphate coatings on steel are largely removed during the plating operation.[1]

Under any commercially practicable procedures, the metal surfaces are unlikely to be absolutely clean, especially because solid, liquid, and gaseous substances may be adsorbed on them. In a comprehensive paper on this subject Ernest H. Lyons, Jr.,[2] developed the thesis that for practical purposes no surfaces are absolutely clean before plating and that the production of adherent coatings depends upon the elimination of *objectionable* films, in some cases by substituting harmless films. This paper and its discussion represent a very timely and instructive résumé of our knowledge (and ignorance) of the factors involved in the preparation of metals for plating. We must therefore fall back on the somewhat equivocal statement that all harmful substances must be absent from the metal surface to ensure adherent plated coatings.

In a recent summary of the principles of preparing metal surfaces for electroplating Walter R. Meyer[3] defines a clean metal surface as one on which there are no interfering films that are thicker than the order of magnitude of the atomic spacing of the basis metal and deposited metal. If thicker films are present, they prevent the atoms of the deposited metal from approaching those of the basis metal closely enough to permit the attractive forces of adhesion to be exerted.

One serious obstacle to exhaustive research on the cleaning of metals is the difficulty of defining when a surface is *clean*. The criteria most commonly applied are (1) the absence of a *water break*, *i.e.*, the complete wetting of the surface when it is rinsed in water; (2) freedom from any loose *smut* that can be rubbed

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[1] *Trans. Electrochem. Soc.*, vol. 84, p. 335, 1943.

[2] *Trans. Electrochem. Soc.*, vol. 88, p. 281, 1945.

[3] Presented at Wayne University, Detroit, in 1948.

off; and (3) the production of continuous, adherent coatings. None of these tests furnishes quantitative evidence of the degree of cleanness of the surface. As will be seen, most solutions for final removal of grease are alkaline and have a low surface tension. Such solutions are very difficult to rinse off, owing to adsorption of alkali on the metal surface. This residue of cleaning solution may cause the film of water to bridge over small areas of grease and hence may yield fictitious evidence of freedom from water break. If such a surface is pickled in acid, the alkaline film is neutralized and the presence of any grease is revealed by failure to pickle uniformly on those areas. For this reason, freedom from water break is a valid evidence of cleanness only if the surface has been dipped into acid, preferably hydrochloric, and again rinsed. Even then, freedom from water break is no proof that finely divided smut may not be present, as shown by production of a hazy deposit in a bright-nickel bath.

The ability of a steel surface to receive an adherent coating of copper by immersion in copper sulfate may serve as a test for the cleanness of the surface.[1]

As explained in Chap. V, there are at present no entirely satisfactory nondestructive tests for adhesion and no quantitative methods that can be applied to plated articles. Hence the most that can be said of a given cleaning procedure is that it does or does not yield sufficiently adherent coatings to meet particular requirements.

Proposals have been made to test the efficiency of cleaning procedures by initially applying a suitable oil and then exposing the cleaned surface to ultraviolet light, which causes fluorescence of any residual oil. Such a test may be helpful to compare the periods of time required by different materials or procedures to remove practically all the oil. It is unlikely to furnish evidence regarding the presence of the very minute quantities of oil that may still affect the adhesion of subsequently applied coatings.

There is a need for more fundamental studies on the presence, composition, removal, and effects of films on metal surfaces. The application of new research tools such as X ray, electron diffraction, and the electron microscope may throw light on these difficult problems.

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[1] HOGABOOM, G. B., *Proc. Am. Electroplaters' Soc.*, p. 215, 1948.

REMOVAL OF GREASE AND SOLIDS

Definitions. Most of the greasy or oily compounds that may be present on metal surfaces can be divided into two classes: those which are and those which are not *saponifiable*, according to whether or not they react with alkalies to form soaps. The simplest saponifiable compounds are the *fats*, represented by stearin, which is used in some buffing compounds. Stearin is an *ester*, *i.e.*, an organic salt, known as *glycerin stearate*, formed by the combination of glycerin (glycerol), which is an alcohol, and stearic acid, which is a fatty acid. When stearin reacts with an alkali, such as sodium hydroxide, it is *saponified*, *i.e.*, is converted into a soap, with the liberation of glycerin. This reaction, used in making soap, may be represented as

$$\underset{\text{stearin}}{\text{Glycerin stearate}} + \text{sodium hydroxide} = \underset{\text{soap}}{\text{sodium stearate}} + \text{glycerin}$$

Similar reactions occur between alkali and other common fats, such as those derived from oleic and palmitic acids, which are present in many greases and oils. One important distinction between fats and the alkali soaps derived from them is that the former are insoluble and the latter are soluble in water. In the usual short time in alkaline cleaning solutions, very little saponification of fats occurs.

Many of the unsaponifiable oils and greases consist of hydrocarbons, *i.e.*, compounds of hydrogen and carbon, which may be derived from petroleum. These hydrocarbons may vary in consistency from very light liquids such as gasoline to lubricating oils and solid waxes such as paraffin. These substances are practically unaffected chemically by alkaline solutions, and hence their removal is accomplished by physical methods.

Various types of waxes are applied to metals, either in buffing compositions or as stop-offs, including natural waxes, such as beeswax, carnauba and candelilla wax, and artificial waxes. If the latter contain chlorine, they may under certain conditions react with water to liberate hydrochloric acid, which may corrode the metals. Waxes usually contain some constituents that are saponifiable and some that are not.

The use of alkaline solutions for cleaning metals usually involves some saponification of any fats present on the metal or in some cases of added fats, such as rosin, to form at least a small amount of soap. The soap aids in the removal of greases of all kinds by lowering the surface tension (page 85) of the solution and thus fostering the formation of an "emulsion," in which fine oil particles are held in suspension in the aqueous solution. An emulsion (such as cream, a suspension of fat particles) is similar to a colloidal solution except that the suspended particles are liquid instead of solid. Formation of emulsions is fostered by the presence of polar compounds, such as soap, which consist of large molecules, usually oriented in chains. One end of such a molecule is more strongly attracted to water, *i.e.*, is *hydrophilic*, and the other to oil, *i.e.*, is *hydrophobic*. Consequently, the surface tension of the solution containing such substances is lowered, and the oil or grease tends to break up into small particles that may remain suspended in the water solution, forming an "oil-in-water" emulsion. The formation of stable or permanent emulsions is undesirable, as it is better to permit the oil to separate and be skimmed off.

Most modern cleaning mixtures contain *surface-active materials*, *i.e.*, wetting agents (page 85). These improve the detergent action by changing the surface tension of the solution and thereby displacing oil films on the metal surface and deflocculating, *i.e.*, taking into suspension, the solid dirt particles.

There are three principal methods for removing oils and fats, each with numerous modifications. The first is by means of organic solvents, in which almost all oils, fats, and waxes dissolve to some extent. This method is known as *solvent cleaning* or *vapor degreasing*. In the second method, known as *emulsion cleaning*, the surface is treated with an oil containing a wetting agent that forms with the grease present an emulsion which can be readily rinsed off. In the third method cleaning is accomplished by means of alkaline solutions, with or without the passage of current. When current is used, it is designated as *electrolytic cleaning*.

In most processes of preparation for plating, the major part of the grease is removed by organic solvents or emulsifiers and the final cleaning is accomplished by electrolytic cleaning in alkaline solutions. Small articles to be barrel-plated are usually cleaned by immersion in suitable alkaline solutions.

Organic Solvents and Vapors. Almost any organic liquid has some solvent action on greases and waxes. The solvents used in cleaning metals are limited to those which most nearly meet certain requirements. It is desirable that they be (1) nonflammable, (2) nontoxic, (3) noncorrosive, (4) volatile, and (5) capable of dissolving the greases or waxes present. Gasoline and similar volatile hydrocarbons are so flammable that their use is seldom justified. Higher boiling hydrocarbons, such as kerosene, are less readily flammable but are less volatile and have less solvent power. They are therefore not used much except in connection with emulsion cleaners, to be discussed shortly. Mixtures of gasoline (naphtha) with chlorinated solvents such as carbon tetrachloride are nonflammable and are sometimes used for cleaning.

In recent years the most commonly used organic cleaner is trichloroethylene, C_2HCl_3, which is used especially in so-called "vapor degreasing." Frequently tetrachloroethylene or perchloroethylene (*perchlor*) is employed, because it has a higher boiling point, which permits better solution of certain greases or waxes.

In vapor degreasing advantage is taken of the solvent power of the compound and its relatively low boiling point. In most of the devices used for such cleaning three stages are involved. In the first step the greasy articles are immersed in the liquid, which is kept boiling, usually by heat from steam coils or electric heaters. In this way the largest part of the grease is removed and is retained in the compartment that holds the contaminated solvent. In the next step the articles are dipped in the clean condensed liquid to cool them. Next they are suspended in the vapor from the boiling liquid. As long as the temperature of the articles remains below that of the vapor, the latter will condense on the metal surface and will run back into the first liquid compartment. This condensed liquid dissolves and carries away the grease left on the surface but may leave solid particles, *e.g.*, of buffing abrasive, or of metallic dust, in cracks or corners. The articles are allowed to drain well before being brought into the air for the last solvent to evaporate.

Two important factors govern the details of such operations. The toxicity of this and other chlorinated solvents demands that as little as possible escape into the room atmosphere and that good ventilation be provided. Special care must be used when cleaning out such apparatus, including at all times the use of suitable gas masks.

In the pure state the chloroethylenes are not corrosive to metals, but if moisture is also present, at high temperatures the solvent hydrolyzes to form small amounts of free hydrochloric acid, which may corrode the articles or the containing equipment. For this reason it is desirable to exclude moisture as much as possible, *e.g.*, by keeping the apparatus closed, especially in humid weather, when the moisture of the air can condense on the inner cooled walls of the chamber. If aluminum is present and aluminum chloride is formed by incipient corrosion, it may hydrolyze and still further accelerate corrosion. Because it is not practicable to exclude moisture entirely, it is customary to add to the chloroethylenes certain *inhibitors*, usually organic amines. These both retard decomposition of the solvent and neutralize any hydrochloric acid that is set free. By their use it is possible to operate for long periods in equipment made of galvanized steel.

While solvent degreasing removes practically all greases and some waxes, it does not remove all solid particles, and hence it does not leave the surface clean enough for plating. It is therefore always followed by electrolytic cleaning.

Emulsion Cleaning. In *emulsion* cleaning, advantage is taken of the fact that, especially at high temperatures, most greases are soluble in oils or high-boiling hydrocarbons such as kerosene, which are much cheaper than chlorinated solvents. As these hydrocarbons are not very volatile, it is difficult to remove them from the metal surface. If, however, suitable wetting agents (including soaps) are present, which foster emulsification of the solvent, the latter, together with the grease, can be readily removed by an aqueous solution in a subsequent operation. Just as with vapor degreasing, emulsion cleaning is usually a *precleaning* step, to be followed by electrolytic or immersion cleaning.

Two procedures are used in emulsion cleaning. In one, the metal articles are immersed at room temperature in a solution consisting of a solvent and a wetting agent. This penetrates into and softens or dissolves the greases or resins present. Especially when caked polishing compound adheres to the metal, the emulsion can be sprayed onto the surface at a sufficient pressure to loosen the soil. The articles are then rinsed off with a stream of very hot water, which may be made slightly alkaline and which forms an emulsion with the mixture on the surface and thereby carries it away. This process is similar to the common practice of removing lampblack or other pigments from the hands by first rubbing them with a mineral oil and then washing in soap and water.

In the other process the oil, wetting agent, and solvent are mixed directly with an alkaline cleaner or with water only, and the mixture is heated and agitated. The emulsion thus formed serves to loosen the grease and dirt.

One of the principal advantages of emulsion cleaning is that it removes solid particles more effectively than do organic solvents. In the presence of an emulsion, especially one of oil particles suspended in water, most of the finely divided solids present pass into the *interface* between the oil and water and are thereby carried away from the metal surface.

Alkaline Solutions. *Composition.* As previously explained, grease can be removed from a metal surface by alkaline solutions. If the sole purpose were to render water alkaline, addition of a strong alkali, such as caustic soda or potash, would be the simplest and most effective method, especially if saponification were the principal step in cleaning. The early use in the plating industry of strong potash solutions rested on this misconception. Even if all the oil to be removed were saponifiable, formation of a small amount of soap would serve to remove the remainder by emulsification.

Addition of sodium or potassium hydroxide is usually desirable, but there is no advantage in using high concentrations. If, however, a dilute solution of sodium hydroxide only were used, it would be rapidly consumed, *e.g.*, by saponifying grease or by absorbing carbon dioxide from the air.

All modern alkaline cleaners involve the use of salts that hydrolyze in aqueous solution to form alkaline solutions, *i.e.*, with a pH distinctly above 7. Such hydrolysis of a salt occurs whenever the base is stronger, *i.e.*, is more dissociated, than is the acid combined in the salt. The hydrolysis of typical salts used in alkaline cleaning may be illustrated by the following equations, which indicate that the reactions are reversible. Hence, liberation of a little alkali stops the hydrolysis, and addition of more free alkali will reverse the process, *i.e.*, re-form the salt.

$$\underset{\substack{\text{sodium}\\\text{carbonate}}}{\mathrm{Na_2CO_3}} + \underset{\text{water}}{2\,\mathrm{H_2O}} = \underset{\substack{\text{carbonic}\\\text{acid}}}{\mathrm{H_2CO_3}} + \underset{\substack{\text{sodium}\\\text{hydroxide}}}{2\,\mathrm{NaOH}}$$

$$\underset{\substack{\text{trisodium}\\\text{phosphate}}}{\mathrm{Na_3PO_4}} + \underset{\text{water}}{\mathrm{H_2O}} = \underset{\substack{\text{disodium}\\\text{hydrogen}\\\text{phosphate}}}{\mathrm{Na_2H\,PO_4}} + \underset{\substack{\text{sodium}\\\text{hydroxide}}}{\mathrm{NaOH}}$$

$$\underset{\substack{\text{sodium}\\\text{metasilicate}}}{\mathrm{Na_2SiO_3}} + \underset{\text{water}}{2\,\mathrm{H_2O}} = \underset{\substack{\text{metasilicic}\\\text{acid}}}{\mathrm{H_2SiO_3}} + \underset{\substack{\text{sodium}\\\text{hydroxide}}}{\mathrm{NaOH}}$$

Such a salt is frequently referred to as an *alkali*. It serves as a *reservoir* from which a small amount of free alkali is released and is replenished if it is used up. Consequently, such a solution tends to maintain a nearly constant pH. Depending on the salt concentration and the temperature, the resultant pH is usually from 8 to 11. To obtain a pH above 12, free alkali must be added. Each salt has, however, specific properties that influence its detergent action, apart from the pH.

The desirable and permissible pH of a cleaner depends partly upon the metal to be cleaned. Steel and iron are practically unattacked by strong caustic solutions; hence the pH of these cleaners may be high. (Iron is, however, attacked by caustic if made anodic at high current densities.) Copper, brass, and similar alloys are more likely to be tarnished by strong alkalies; hence a pH from 10 to 11 is preferable. Because aluminum, tin, zinc, and lead all dissolve in alkalies, the pH of solutions for cleaning these metals should be no higher than is necessary to achieve cleaning, *e.g.*, from 9 to 11. If sodium silicate is added, somewhat more alkaline solutions may be used without attack of aluminum.

If the resultant pH were the only consideration, there would be little choice in the selection of compounds for cleaners. Of more practical importance are the surface tension and the deflocculating power, which depend on other factors as well as pH. In recent years the use of complex phosphates, such as tetrasodium pyrophosphate, $Na_4P_2O_7$, and hexametaphosphate, $(NaPO_3)_6$, has increased because they are more effective deflocculators than the orthophosphates. However, much of this advantage is lost in cleaning solutions that are used for long periods, as is customary in the plating industry, because in hot aqueous solutions all forms of phosphate revert to orthophosphate.

While it is essential that the cleaning solution have emulsifying properties, it is not desirable to produce too stable emulsions, as the solutions then become contaminated and fail to clean. On cooling, the oil or grease separates and can be skimmed off, partly as a result of *salting out*, thus increasing the effective life of the cleaners.

The four alkaline compounds most commonly used in cleaners are (1) sodium hydroxide, (2) sodium carbonate, (3) sodium phosphate (in some form), and (4) sodium silicate (usually metasilicate). The concentrations and proportions of these constituents are varied to meet specific requirements, such as the basis metal to be cleaned and the type of *soil* to be removed. A high concentration of sodium hydroxide is usually included only for cleaning steel. Use of sodium silicate is undesirable if complete rinsing is not feasible, *e.g.*, in screw holes or lapped joints, because any residual silicate may be converted to *silica gel* in subsequent pickling operations. As this gel cannot be readily removed by rinsing, it may later leak out and cause poor adhesion and staining. The total concentration of compounds is usually from 4 to 8 oz/gal (30 to 60 g/l).

When dry-cleaning mixtures are prepared for distribution, it is necessary to avoid caking as a result of moisture absorption. Sodium carbonate (soda ash) is a useful addition to prevent caking. If the cleaning solution is made up from the separate compounds, any desired proportion may be used. A simple cleaner may contain 3 oz/gal (23 g/l) each of sodium carbonate and trisodium phosphate, 1 oz/gal (8 g/l) of sodium metasilicate, and 1 to 2 oz/gal (8 to 15 g/l) of caustic soda, especially if steel is to be cleaned. Some wetting agent may also be added.

The extensive use of hot, strong soap solutions, *e.g.*, in the *soap soak* frequently employed depends upon the fact that soap solutions have low surface tension. Soap solutions may be effective through their emulsifying action or, more commonly, through their displacement of oil films and dirt particles, even when no permanent emulsion is formed. They are commonly used to remove the bulk of the grease and are followed by electrolytic cleaning.

Electrolytic Cleaning. All hot alkaline solutions have a cleaning action on metals, but the time required to produce a clean surface varies with the composition of the cleaner and the type of grease to be removed. It was early learned that electrolytic cleaning is more rapid than immersion, and some form of electrolytic cleaning is now almost universally used as the final cleaning operation before plating. In general, this process involves passage of current through a hot alkaline solution (at 180 to 200°F or 75 to 90°C) with the articles to be cleaned constituting one of the electrodes. Electrolytic cleaning is not conveniently applied to bulk articles to be barrel-plated. Hence, immersion cleaning is most commonly employed for such products.

Until recent years cathodic cleaning was always used; *i.e.*, the objects were made cathodic, with either the steel tank or separate steel plates serving as the anode. This usage was based partly (but erroneously) upon the fact that at the cathode 2 volumes of hydrogen are evolved for each volume of oxygen at the anode; hence there is more violent stirring at the cathode. At the cathode free alkali is liberated and may slightly accelerate cleaning. On the other hand, any metallic impurities dissolved in the cleaner, especially any lead, tin, or zinc, are likely to be deposited on the cathode in the form of films that may cause poor adhesion. Especially in the cleaning of brass and other nonferrous metals, it was therefore customary to employ cathodic cleaning, followed by a short reversal of current to dissolve anodically traces of precipitated metals. These steps should always be conducted in separate tanks.

In recent years, especially in large-scale plating operations, anodic cleaning of steel usually follows or replaces cathodic cleaning, and for some purposes their combination has proved effective. Surface-active materials tend to migrate to the anode. Another favorable factor of anode cleaning is that at the anode oxygen is evolved and may oxidize or destroy traces of certain organic compounds which may be present on the steel surface. By the same process, however, there may be slight oxidation of the steel to form "passive" films; in fact, this is one method of treating a steel surface to foster subsequent separation of a deposit in electroforming. Prior to electroplating of adherent deposits an acid dip or pickle always follows alkaline cleaning, so any trace of oxide produced by anodic cleaning is thereby removed. Use of anodic cleaning prevents deposition of any dissolved metals and also of any suspended oxides of silicon or iron that would normally migrate to the cathode. Anodic cleaning is not suitable for cast iron, probably because the silicon present may be oxidized to silica, SiO_2.

Anodic cleaning of nonferrous metals is also practiced. The periods of cleaning are shorter than for steel, because most nonferrous metals, especially those containing tin, zinc, lead, or aluminum, tend to dissolve anodically in alkaline solutions and hence to be etched. To some extent this etching can be retarded by the use of compounds such as silicates, phosphates, or carbonates that tend to produce insoluble films on the specific metals. In such cases an acid dip must follow in order to yield a clean metallic surface.

In general, the same types of compounds are used in electrolytic cleaning solutions as for immersion cleaning. They should be selected to yield well-conducting solutions. Another important factor is the avoidance of compounds such as soaps or wetting agents that produce large amounts of foam. Accumulation of such foam, necessarily filled with hydrogen and oxygen, may lead to explosions from the sparks produced in attaching or detaching racks from the bus bars. Even though such explosions seldom cause structural damage, they may scatter hot alkaline solutions and injure the workmen.

The current density used in electrolytic cleaning is often determined by the available voltage. For most purposes, current densities of 5 to 10 amp/dm^2 or 50 to 100 amp/ft^2 are employed for cathodic cleaning and lower current densities for anodic cleaning. Too high a current density, especially anodic, may cause *smut* on both steel and brass. The tank voltage required is usually from 4 to 6 volts.

REMOVAL OF OXIDES

General. The processes above described serve principally to remove the soil, including grease and other organic materials, from the metal surface, together with solid particles that are retained by the grease. After the surface has been so cleaned, there is usually a film of oxide, which must be removed prior to plating. With steel, this oxide may consist of red rust produced by atmospheric corrosion, heavy black scale produced in rolling and forging operations, a thin blue film formed in heat-treating and machining, or an invisible oxide film that is usually present on apparently clean steel as a result of forming operations, as well as on other metals such as aluminum, magnesium, zinc, lead, and copper.

The methods used for removal of oxides generally involve their solution by means of an acid. The type and concentration of acid, its temperature, and the time of treatment vary with the kind and amount of oxide to be removed. Removal of heavy scale on steel or brass may require long, drastic treatments. Thin films, *e.g.*, on blued steel, can be removed in 1 or 2 min. Apparently bright steel, *e.g.*, cold-rolled steel, usually receives a 10- to 20-sec dip into dilute acid, which also serves to neutralize any residual alkaline film. In general, the term *pickling* refers to severe or continued treatment, while the term *dipping* refers to a short treatment, *e.g.*, for less than 1 min.

Pickling Steel. *General.* On steel the principal acids used are hydrochloric and sulfuric. In general, hydrochloric acid is more effective, because it dissolves the iron oxide more rapidly and its salts are more soluble, but it is more expensive. Hence for large-scale pickling, sulfuric acid is more commonly used. For many pickling operations solutions approximately 2*N* are used, although more concentrated hydrochloric acid is more rapid and effective. To produce 2*N* solutions, 1 vol of concentrated hydrochloric acid (sp gr 1.18) is mixed with 5 vol of water; *e.g.*, 1.25 pt of HCl is diluted with water to form 1 gal; or 1 vol of concentrated sulfuric acid (sp gr 1.84) is mixed with 15 volumes of water, *e.g.*, 0.5 pt of H_2SO_4 is diluted with water to form 1 gal.

Sodium acid sulfate, $NaHSO_4$, or *niter cake*, a by-product of the manufacture of nitric acid, is sometimes substituted for sulfuric acid. Even when the same concentration of "free" sulfuric acid is present, the pickling action is slower than with sulfuric acid.

Hydrofluoric acid, HF, is used to remove silica (sand) left in castings or embedded by sand blasting, and from alloys containing silicon. A concentration of about 2*N*, corresponding to 0.5 pt of the 50 per cent commercial HF to 1 gal, is often used, generally with the addition of some sulfuric acid.

In the pickling of steel it is desirable to accelerate the solution of the oxides but to retard that of any exposed steel. The latter action represents a waste of acid and of the steel. Some attack of the steel is desirable to provide evolution of hydrogen, which may detach the scale, and sometimes to provide a slight etching of the steel. Substances known as *inhibitors* are often added to hydrochloric or sulfuric acid to retard attack of the steel and also to form a scum on the liquid surface, which cuts down the loss of acid by spray. They are usually organic compounds or mixtures, which may contain or give rise to colloids. While the action of inhibitors is not fully understood, it may involve the migration of colloids or of strongly polar groups to the bare steel surface and an increase in the overvoltage of hydrogen, whereby the reaction of the acid on the steel is retarded. When acid containing an inhibitor is used to pickle steel, it may leave a very thin film of inhibitor (or its products) on the surface. It is therefore desirable to follow the pickling by a brief anodic cleaning in alkali to remove any inhibitor film.

Electrolytic Pickling. Occasionally, electrolytic pickling of steel is employed, especially for strip steel or wire. Both direct and alternating current have been employed, and with direct current, the articles may be made either cathodic or anodic. In cathodic pickling, the use of the current serves to keep the steel cathodic, so that it is not appreciably attacked by the acid, which, however, continues to dissolve the oxide. Successive cathodic and anodic picklings are often used on steel, *e.g.*, on strip steel, and prior to brass plating for rubber adhesion.

Anodic pickling of steel before plating is more commonly used in Europe than in the United States. For this purpose about 70 per cent H_2SO_4 is commonly employed, although more dilute solutions are also used. The purpose of the strong acid is not so much to remove oxide as to remove smut and to etch the surface in a manner and degree that will promote adhesion of subsequently deposited coatings, especially heavy deposits used for building up worn parts. Nickel-silver (or nickel-brass) for tableware is cathodically pickled in sulfuric acid (32°Bé, or 1.28 sp gr, equivalent to 37 per cent H_2SO_4). When electrolytic pickling is employed, it is inadvisable to use those inhibitors or wetting agents which tend to form excessive foam that may cause explosions. Certain wetting agents are acceptable.

Embrittlement of Steel by Pickling (and Plating). In the pickling and cathodic cleaning of steel, some hydrogen is always evolved and some is dissolved in the steel. The presence of this hydrogen is believed to be chiefly responsible for the embrittling of steel, especially high-carbon spring steel, as a result of pickling and plating operations. This effect is most pronounced and significant in steel parts that are subjected in use to alternating stresses, as in airplanes, and it may lead to serious structural failures. While many studies have been conducted on this subject, the causes and effects of this embrittlement are not well understood, partly because of the difficulty of devising laboratory tests that yield reproducible and significant results. The evidence thus far obtained leads to the following tentative conclusions:

The principal cause of brittleness is the absorbed hydrogen. This is evolved gradually on standing at room temperature and more rapidly at temperatures from 100°C (212°F) to 200°C (392°F). After standing or heating, the brittleness is entirely removed, except that which results from deep etching of the steel. The use of sodium acid sulfate and of certain inhibitors in pickles or of anodic pickling may reduce the absorption of hydrogen and the embrittlement.

The effects produced in plating operations are less definite.[1] Plating of zinc or cadmium from cyanide baths may produce em-

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[1] Zapffe, C. A., and Haslem, M. E., *Trans. Am. Soc. Metals*, vol. 39, p. 341, 1946.

brittlement of high-carbon steel, but their relative effects have not been definitely established. The embrittling effects of chromium plating may involve the absorption of hydrogen, the mechanical *notch* effect of the cracks, and stresses present in the hard, brittle chromium coatings. One effect of zinc coatings, whether produced by plating or hot-dipping, is associated with the continued use of the zinc-coated steel parts at high temperatures, *e.g.*, 500°C (900°F), under which conditions the zinc tends to cause intergranular disintegration of the steel.

Pending more exhaustive and conclusive studies of this embrittlement, it is expedient, especially with high-carbon steel, to (1) reduce the period of acid pickling, (2) use plating baths with relatively high cathode efficiencies, and (3) bake the plated parts at least 1 hr at about 200°C (392°F).

Pickling and Dipping of Copper Alloys. The removal of heavy scale, consisting of cuprous and cupric oxide, from brass is usually accomplished in brass mills by a mixture of sulfuric acid and dichromate. The removal of lighter scale produced by brazing or hard soldering is generally done by treatment with dilute sulfuric acid, *e.g.*, about 60 g/l or 8 oz/gal of H_2SO_4. This process is often followed by a *black boil*, *i.e.*, treatment with a solution made by adding about 5 fl oz/gal of HNO_3 and 0.025 fl oz/gal of HCl to a spent *bright dip* (see below). If this leaves a smut on the brass, it can be removed with a bright dip.

Some copper alloys received for plating or other finishing require a bright dip. The solution contains sulfuric and nitric acid, a very small amount of hydrochloric acid, and sometimes finely divided carbon, *e.g.*, lampblack. The latter produces more uniform action, possibly by selective absorption and subsequent release of hydrochloric acid. The solution is kept in stoneware jars surrounded by running water, to keep the temperature below 40°C (104°F).

The composition of bright dips depends upon the alloy to be treated and the surface desired. The data in the following table are derived from an article by A. K. Graham.[1] These formulas are adapted for bulk dipping and are slightly more dilute than those used for individual pieces, which can be removed and rinsed more quickly. The volume relations have been computed on the assumption that there is no change in volume on mixing, but

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[1] *Trans. Am. Electrochem. Soc.*, vol. 52, p. 289, 1927.

actually the final volume is 3 to 5 per cent less than the sum of the constituents.

DIPS FOR BRASS

Compounds	Scaling dip					Bright dip		
	Sp g	°Bé	g/l	ml/l	fl oz/gal	g/l	ml/l	fl oz/gal
H_2SO_4	1.84	66	700	380	49	800	435	55
HNO_3	1.38	40	100	72	9	100	72	9
HCl	1.18	22	5	4	0.5	2.5	2	0.25
H_2O	......	......	544	544	68	491	491	63

Solutions have also been developed for the *chemical polishing*, *i.e.*, bright dipping, of aluminum alloys.

Pickling Zinc and Die Castings. In the preparation of zinc die castings for plating, it is customary to use dilute hydrochloric acid and to reduce the pickling time, for example, to 10 to 15 sec. Overpickling of zinc alloys tends to remove the more dense surface *skin* of chilled zinc, thereby exposing possibly less dense metal as well as forming a scum of the metal constituents other than zinc, especially copper. For the same reason overcleaning of zinc in alkaline solutions should be avoided.

Pickling of other metals involves use of appropriate acids. For aluminum and its alloys nitric acid is usually employed. For lead the use of fluoboric acid, HBF_4, has been suggested, because both HCl and H_2SO_4 leave insoluble salts and HNO_3 is too active.

Electropolishing. In recent years methods of anodically pickling metals have been developed that leave the surface bright and may thus serve as a substitute for mechanical polishing. These methods, known as *electropolishing*, have been developed for several purposes, including (1) preparation of specimens for microscopic examination; (2) producing a uniformly bright surface on finished unplated articles; (3) as a *taking-off* tool, *i.e.*, to change the dimensions, in some cases preparatory to plating with another metal to the original dimensions; (4) to provide a bright clean surface to be electroplated; and (5) to brighten plated surfaces. At present, application (2), brightening of metal surfaces, especially stainless steel, is the most extensive application of electropolishing and does not have any necessary direct relation to electroplating. It is probable, however, that electropolishing will find important applications for brightening of plated metal surfaces and also as a step in the preparation for plating. Because of these varied possible uses and of the relation of electropolishing to other methods of electrolytic pickling, it is included in this chapter.

A comprehensive summary of electropolishing was published by C. L. Faust,[1] in which numerous references to papers and patents are cited. In 1947, at the Third International Conference on Electrodeposition, four papers on electropolishing were presented, some of which contain extensive bibliographies. With few exceptions, these processes involve anodic treatment of the metals at high current densities in relatively concentrated acid baths. When brightening is thereby accomplished, it is the result of the more rapid attack of the elevated portions of the rough surface than of the depressions. The process does not usually obliterate scratches or pits of appreciable depth, although it may round them off. The net result is to produce a surface that is *microscopically* smooth and therefore bright, but not necessarily a perfectly smooth or plane surface, since some waviness is usually present.

While no complete theory of electropolishing has yet been developed, all the available evidence indicates that its success depends upon the presence or formation of viscous high-resistance films, which tend to fill in depressions and thereby reduce the anodic current density that would otherwise prevail in these depressions. Because there is more opportunity for removal and replenishment of the film on the high spots or peaks, as a result of the higher current density and gas evolution there, the attack is more rapid on these high spots. To achieve this goal, it is necessary that the solution be relatively concentrated and hence viscous and that the salts produced in the reaction be relatively insoluble, so that they assist the formation and retention of viscous films in the depressions. To avoid local pitting, it is essential that the solutions do not become dilute (*e.g.*, by absorption of water) and that the relatively high required current density is maintained over the entire surface, if necessary by the use of auxiliary cathodes. Because the solution resistance and anode polarization are relatively great, higher tank voltages are required than in most plating, *e.g.*, up to 12 volts. Because the solutions are viscous, there is a tendency for streaks to appear on the polished surfaces. This action can be prevented by mild uniform

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[1] *Proc. Am. Electroplaters' Soc.*, p. 49, 1946; p. 223, 1948. Also WERNICK, S., "Electrolytic Polishing and Bright Plating of Metals," 1948; and JACQUET, P. A., *Metal Finishing*, vol. 47, p. 48 and 83, 1949.

agitation. Rapid agitation is usually undesirable because it counteracts the desired effect of the high viscosity. The use of elevated temperatures usually decreases the viscosity, and the temperature must therefore be carefully maintained at the preferred value for a given bath.

The most commonly used baths for electropolishing contain sulfuric, phosphoric, chromic, nitric, or citric acid or a combination of these. A mixture of perchloric acid and acetic anhydride is very effective, but its use involves a serious explosion hazard (illustrated by a disastrous explosion in Los Angeles on Feb. 20, 1947). This mixture should not be used except on a small scale, as in metallographic polishing, and then only if extreme care is used to avoid elevation of the temperature or contamination with deleterious substances, especially organic matter.

Mixtures of sulfuric and phosphoric acid are effective for polishing most types of stainless steel as well as many plain-carbon steels. In a solution containing 40 to 43 per cent of H_2SO_4 and 40 to 46 per cent of H_3PO_4 at 180 to 200°F (82 to 93°C) an anode current density of 250 to 500 amp/ft^2 (27 to 54 amp/dm^2) is employed. Addition of a small amount of chromic acid to this bath retards tarnish of the polished steel after it is rinsed.

Another bath used for stainless steel contains 55 to 60 per cent of citric acid, 15 to 20 per cent of sulfuric acid, and 20 to 30 per cent of water. The anode current density is 75 to 145 amp/ft^2 (8 to 16 amp/dm^2).

Electropolishing of brass involves more difficulties than does that of stainless steel, including more tendency for formation of streaks and dark stains. In one process[1] a solution of approximately the following composition is recommended for electropolishing rolled brass parts prior to plating with bright nickel and chromium:

ELECTROPOLISHING BRASS

	M	g/l	oz/gal
Phosphoric acid, H_3PO_4 (sp gr 1.75)	1.8	200	27
Chromic acid, CrO_3	1.8	180	24
Sodium dichromate, $Na_2Cr_2O_7 \cdot 2H_2O$	1.4	420	56
Sulfuric acid, H_2SO_4	0.9	90	12
Hydrofluoric acid, HF	0.25	5	0.7
Propionic acid, $HC_3H_5O_2$	1.6	120	16
Water, to make	1/l	1 l	1 gal

Temperature, 24°C (75°F)

Current density, 140 to 350 amp/ft^2 (15 to 37 amp/dm^2)

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[1] BERGER, P., *Proc. Third Intern. Electrodeposition Conf.*, p. 33, 1947.

Electropolishing of nickel deposits can be accomplished in 73 per cent sulfuric acid or in a solution containing 15 per cent H_2SO_4 and 63 per cent H_3PO_4. In the former solution A. W. Hothersall and R. A. F. Hammond[1] employ a current density of 250 amp/ft^2 (27 amp/dm^2) at about 30°C (86°F) for a very short period. This treatment has been suggested for brightening regular dull nickel deposits and also semibright nickel or even bright nickel that may require light buffing on some areas. For such uses Faust suggested the term *electrobuffing.*[2]

When electropolishing is applied to plated coatings, consideration must be given to the solution of the coating, *e.g.*, nickel, during the electropolishing, and sufficient metal must be deposited to yield the desired thickness after polishing. Because the *throwing power* of the polishing may exceed that of the plating process, such computations should be based on the thinnest part of the deposit, which is commonly designated in specifications. If proper allowances are made for thickness, the electropolishing does not increase the porosity of the coatings.

Much further study of electropolishing is required to realize its full possibilities in the plating industry. For example, it is not now known to what extent the use of electropolishing prior to plating will affect the adhesion or porosity of a particular deposit on a specified basis metal.

Mechanical Cleaning. The use of mechanical operations to prepare metals for plating includes such processes as blasting with sand or steel shot, tumbling with various materials to *debur* or burnish the surfaces, and the various types of polishing and buffing operations. It is not feasible in this text to describe these processes and equipment or even to discuss their principles. It is important to note that these operations may have important effects upon the appearance, adhesion, and porosity of the subsequently plated coatings. Many of these operations may not only change the contours of the metal surfaces but may also produce profound changes in the structure of the metal on the surface, *e.g.*, by producing a weak or brittle "work-hardened" layer. One of the purposes of dipping, pickling, or electropolishing operations prior to plating is to remove such weakened layers. On the other hand, excessive pickling, *e.g.*, of steel or zinc-base die

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[1] *J. Electrodepositors' Tech. Soc.*, vol. 16, p. 83, 1940.

[2] For electropolishing of silver, see GRAY, D., *Proc. Am. Electroplaters' Soc.* p. 241, 1948.

castings, may be detrimental because it may remove the denser, sounder layer produced by rolling or casting and expose more porous metal and also release insoluble impurities as a scum on the surface.

Typical Cycles for Preparing Metals for Plating. In an effort to coordinate and emphasize the essential steps in the preparation of metals for plating, certain "recommended practices" have been prepared and published by the ASTM. It should be recognized that these methods are still in a *tentative* stage and that, even after further revision, they cannot cover all types of basis metal and of coatings for all possible purposes. They may serve, however, as a guide for the selection of those cycles which will meet more specific requirements. Among these is a tentative recommended practice[1] for plating on low-carbon steel. A similar recommended practice for preparing high-carbon steel is in preparation by ASTM.

Other typical cycles for plating on brass[2] and on zinc-base die castings[3] have been published.

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[1] *ASTM Standards*, Part I-B, p. 769, 1946.

[2] Blum, W., and Strausser, P. W. C., *J. Research Natl. Bur. Standards*, vol. 24, p. 443, 1940, RP 1293.

[3] Nixon, C. F., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 34, p. 298, 1947.

CHAPTER VIII

PREPARATION FOR ELECTROFORMING AND ELECTROTYPING AND FOR DEPOSITION ON PLASTICS

Electroforming, as first defined by one of the authors, is "the production or reproduction of articles by electrodeposition." Its most important applications are electrotyping and similar methods of making printing plates, the production of phonograph matrices and of sheets, tubes, or other shaped articles by electrodeposition. One essential feature of these processes is that they involve separation of the deposit from the form or base on which it was produced. Even though most of these processes involve relatively thick metal deposits, there is no justification for applying the term electroforming to the production of thick, adherent metal coatings that may be used to build up worn or overmachined parts. The term *building up* more accurately describes this process.

Because electroforming is often conducted on nonmetallic molds, including plastics, some of the operations are similar to those for plating permanent deposits on plastics. Hence the latter subject is included for convenience in this chapter. Typical modern applications of electroforming are described in recent articles.[1]

PRODUCTION OF METAL MOLDS

In order to produce or reproduce an article by electrodeposition, it is necessary to have a form on which to deposit, preferably a *negative* of the desired product, as only thus can an accurate reproduction be made. Occasionally, when no high accuracy of dimension or surface finish is required, it is possible to use a *positive*, but underdimensioned form as the mold.

Whenever it is feasible to employ a metal mold, its use is advantageous as the surface is electrically conductive and requires no treatment except to permit separation of the subsequent deposit.

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[1] SAVAGE, F. K., FIANDT, R. M., REID, D. B., and PFEFFERLE, P. R., *Proc. Am. Electroplaters' Soc.*, p. 173, 1944. KASDAN, ALFRED S., *Proc. Am. Electroplaters' Soc.*, p. 115, 1947. SAFRANEK, W. H., DAHLE, F. B., and FAUST, C. L., *Electroplating*, vol. 35, p. 39, 1948.

Metal molds can be made by casting, pressure molding, machining, or electrodeposition.

For producing cast-metal negative molds, use of low-melting alloys is advantageous because these can be cast in metal, plaster, or even wood or plastic positives that do not withstand high temperatures, and the alloys can be subsequently melted out of the electroformed *shells*. The lowest melting common alloy is "Wood's metal," which contains 50 per cent of bismuth, 25 per cent of lead, and 12.5 per cent each of tin and cadmium and melts at about 70°C (158°F). In recent years two low-melting alloys known as *Cerrobase* and *Cerrotru* have been developed, the former being an alloy of bismuth and lead, melting at 125°C (255°F), and the latter of bismuth and tin, melting at 139°C (281°F).

The principal production of metal molds by pressure is the lead molding for electrotypes (page 234). In certain cases, such as the production of sheets or tapered tubes, the molds can be made by mechanical operations such as machining and surface grinding or lapping until the desired finish is obtained. For this purpose, chromium steels are advantageous because they foster separation.

The use of electrodeposited negatives is advantageous when accurate reproduction and large numbers of similar electroformed products are required, as then the electrolytic negatives can be used repeatedly. (Cast or pressed molds are generally used only once.) By electrodepositing the negatives, it is possible to reproduce accurately the finest lines and details that can be observed with a microscope. Two good examples of electroformed negatives are in the reproduction of engraved printing plates at the U.S. Bureau of Engraving and Printing and the production of phonograph record matrices. In the first of these processes a negative, or *alto*, of an engraved steel plate (a *basso*) is made by first treating the steel with graphite and water, rinsing, treating with a dichromate solution, and then depositing a layer of nickel, followed by a thick deposit of iron. This alto is separated and used as a form on which basso plates are deposited.

The production of phonograph matrices involves an original recording in wax or other plastic material. The surface of this plastic recording is made conductive, *e.g.*, by means of an evaporated gold film or a chemically deposited silver coating, after which copper is deposited to produce a negative shell, known as a *master matrix*. On this plate a number of *master records*, or *mothers*, (which are positives) are deposited. These serve as forms on which the *pressing matrices*, or *working masters* or *stampers*, are deposited. The latter may have an initial nickel surface and are usually plated with chromium to increase their resistance to abrasion during the molding. By such processes several "generations" of plates may be reproduced with no detectable loss in accuracy.

TREATMENT OF METALLIC SURFACES TO PERMIT SEPARATION

It is necessary so to treat the metal surface that it is still conducting but will not produce any firm bond with the deposited metal. In effect, a uniformly *unclean* surface is desired. It is usually necessary to have a slight bond so as to prevent premature separation.

Mechanical Films. It is possible but difficult to apply very thin films of grease, *e.g.*, by treating the metal surface with a dilute solution of a grease or wax in a volatile solvent such as gasoline. This is more practicable on plane surfaces than on those with lines or depressions, where too much grease may be retained.

The use of finely divided graphite is often satisfactory. It may be applied in the form of dry powder or as a mixture with water. In either case it is brushed on vigorously and the excess is removed with a powerful stream of water. Measurements of the gain in weight indicate an average thickness of graphite of not over about 0.000002 in., which does not affect the contour or design.

Chemical Films. In principle, these methods involve the formation on the metal surfaces of films of chemical compounds that are somewhat conductive, usually because they are so thin. The simplest (chemically) of such coatings are the *passive* films that are naturally present on chromium and nickel and many of the alloys containing one or both of these metals. These films probably consist of adsorbed or chemically combined oxygen. They are advantageous because they are generally very thin and uniform. They are not usually effective if the deposition involves any steps, such as use of acidified chloride solutions, that may remove the passivity. The use of stainless steel and chromium-nickel alloys such as *Inconel* warrants consideration whenever permanent rigid molds can be used.

When plain-carbon steel or nickel is used as the mold, it can be made passive by (1) treatment with an oxidizing agent such as a chromate or (2) making it anodic in an alkaline solution, *e.g.*, dilute sodium hydroxide. Both of these treatments may also be helpful on the chromium alloys to ensure that the surfaces are passive.

Another method involves the formation of sulfides by treatment of the metal surface with any soluble sulfide, such as sodium sulfide, Na_2S, or polysulfide, Na_2S_x. This will react with most metals, including iron, nickel, lead, bismuth, silver, and copper, to form corresponding sulfides, which are somewhat conducting (especially silver sulfide). One practical problem is that it is difficult so to control the rate of reaction as to avoid too thin or too thick a film, which will lead, respectively, to sticking or to premature separation. For lead, bismuth, and copper, a solution containing 1 oz/gal (7.5 g/l) of Na_2S is used, and for nickel, a stronger solution.

Soluble chromates, dichromates, or chromic acid, *e.g.*, Na_2CrO_4, $Na_2Cr_2O_7$, or CrO_3, react with lead or silver to form insoluble chromates. About 0.5 oz/gal (4 g/l) can be used.

When the metal employed does not readily lend itself to separation, a very thin coating of another metal may be deposited on it and subsequently treated to yield separation. A good example is the use of silver iodide on copper phonograph matrices and map plates. The copper is treated with a silver cyanide solution such as the following:

		N	g/l	oz/gal
	Silver cyanide, AgCN	0.3	37.5	5.0
or	Silver chloride, AgCl	0.3	40	5.3
	Sodium cyanide, NaCN	1.8	90	12.0

This solution is poured or brushed onto the clean copper surface, preferably mixed with an inert powder such as whiting ($CaCO_3$) to form a thin paste. A thin film of silver is thus produced on the copper by displacement. This is treated with a dilute solution of iodine, which can be prepared by diluting 1 fl oz of pharmaceutical tincture of iodine with water to make 1 gal. Tincture of iodine has the formula

	g/l	oz/gal
Iodine, I_2	70	9
Potassium iodide, KI	50	7
Water, H_2O	50 (ml)	7
Alcohol, C_2H_5OH, balance		

This treatment produces a thin film of silver iodide, AgI, which permits deposition and separation of the deposited metal.

TREATMENT OF NONMETALLIC SURFACES

Before depositing metals on nonmetallic substances such as glass, rubber, wax, plastics, leather, or wood, it is necessary to render the surface conductive. If the material is porous, *e.g.*, plaster, leather, or wood, it must first be rendered impervious to the plating solution.

Making Surfaces Impervious. One of the best means is to soak the object in melted wax, usually kept at a temperature slightly above 100°C (212°F) so as to expel most of the water as well as the air present in the pores. The soaking should continue till the evolution of bubbles of steam or air has almost ceased. Too high a temperature (over 71°C or 160°F) should not be used for materials such as leather that are rendered brittle at high temperatures. Almost any wax is effective. For leather, paraffin is preferred, and for other materials higher melting waxes such as beeswax and ceresin are preferable. After the articles are well soaked, they are removed and allowed to drain and cool.

For large objects that cannot be readily immersed in wax, treatment with a solution of wax in a solvent such as carbon tetrachloride can be employed. In that case sufficient time should be allowed, preferably at a slightly elevated temperature, for all the solvent to evaporate.

Another treatment, applied especially to leather, involves the use of several coats of a waterproof varnish, lacquer, or shellac. A good spar varnish or a melamine lacquer is generally satisfactory.

Rendering Surfaces Conductive. When wax or varnish is employed, copper powder or graphite can be used to make a conducting surface. The copper powder should be free of the grease in which it was ground. If grease-free powder is not obtainable, the regular powder should be treated with a solvent such as benzol. The dry powder is brushed on the surface of the wax or on the varnish when the last coat is just *tacky*. Graphite is cheaper than copper powder and is used in large-scale operations such as electrotyping (page 230).

For industrial metal deposition, *e.g.*, on wax, glass, and plastics, chemically deposited silver films are commonly applied by methods similar to those used for silvering mirrors. In all these processes the production of the silver film is brought about by mixing, just when required, an ammoniacal solution containing a silver salt and one containing a reducing agent. Information on several of these processes, as applied to mirrors, is summarized in a publication from the National Bureau of Standards.[1]

The silver solution is prepared by adding just enough ammonium hydroxide (sp gr 0.90) to a silver nitrate solution *A* to redissolve the precipitate of silver oxide, Ag_2O, that was first formed by the addition of either KOH or NH_4OH. If too much ammonia is added, subsequent silver deposition will be prevented, and too little ammonia leaves a precipitate that may cause faulty silver films. It is customary to prepare a separate solution of silver nitrate *B*, which should be carefully added to combine with any excess of ammonia and to produce a slight darkening of the solution.

Caution. It is very important to note that, when ammoniacal silver solutions evaporate to dryness, the residues are explosive and may cause serious accidents. For this reason all waste solutions should be at once disposed of, *e.g.*, by adding hydrochloric acid, which precipitates silver chloride that may be recovered. Bottles containing the solution should be kept closed to prevent evaporation.

Among the reducing agents that can be used are (1) sucrose (cane sugar) $C_{12}H_{22}O_{11}$ (or more strictly, the invert sugars, dextrose and levulose, $C_6H_{12}O_6$, which are formed by treating sucrose with dilute acid); (2) Rochelle salt and sodium potassium tartrate, $NaKC_4H_4O_6 \cdot 4H_2O$; (3) formaldehyde, HCHO; and (4) hydrazine, N_2H_4 (or its salts). The following formulas are typical for some of these processes.

BRASHEAR (SUGAR) METHOD

	g/l	oz/gal
1. Silver solutions:		
A. Silver nitrate, $AgNO_3$	50	7
Potassium hydroxide, KOH	25	3.5
B. Silver nitrate, $AgNO_3$	65	9
Solution *A* rendered ammoniacal as above		
2. Reducing solution:		
Granulated sugar	90	12
Nitric acid, HNO_3 (sp gr 1.42)	4 (ml)	0.5 (fl oz)

No. 2 solution should be boiled for 5 min and allowed to cool or it can be allowed merely to stand for 1 week before use. About 175 ml/l of ethyl alcohol can be added to preserve the solution. One

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[1] *Natl. Bur. Standards, Circ.* 389, 1931.

part by volume of reducing solution is mixed with 4 parts of the ammoniacal silver solution.

ROCHELLE SALT METHOD

1. Silver solutions:	g/l	oz/gal
A and *B*. Silver nitrate, $AgNO_3$	100	13
Solution *A* rendered ammoniacal as above		
2. Reducing solution:		
Silver nitrate, $AgNO_3$	2	0.27
Rochelle salt, $NaKC_4H_4O_6 \cdot 4H_2O$	1.7	0.22

Equal volumes of the ammoniacal silver solution and reducing solution are mixed as required.

FORMALDEHYDE METHOD

1. Silver solutions:	g/l	oz/gal
A and *B*. Silver nitrate, $AgNO_3$	20	2.7
Solution *A* rendered ammoniacal as above		
2. Reducing solution:		
Formaldehyde, 40 per cent solution	200 (ml)	27 (fl oz)

One volume of reducing solution is required for 5 vol of the ammoniacal silver nitrate.

It is customary to mix the silver and reducing solutions just as they are poured onto the surface to be silvered, *e.g.*, by allowing them to run in from adjacent stopcocks. In one method, applied especially for silvering plastic electrotype molds, the two solutions are mixed and applied as a spray. For silvering small objects such as plastic buttons, they can be rotated in the mixed solution in a small stoneware barrel.

Prior to silvering, the surface must be perfectly clean. The suitable procedure will depend upon the material to be coated. Glass can be cleaned with alcohol or other solvent to remove grease and then with concentrated nitric acid, which should be thoroughly rinsed off, after which the glass is kept in distilled water to prevent it from drying. For plastics, solvents must be selected that will not appreciably soften or attack the particular plastic but will slightly roughen it.[1] For plastic electrotype molds, solvents should be used that do not roughen the surface. Mild alkaline cleaners can be used for the final cleaning.

Just before silvering it is necessary to *sensitize* the surface in order to foster the uniform deposition of silver. The most commonly used reagents are stannous chloride, $SnCl_2 \cdot 2\ H_2O$ (*e.g.*, 10 g/l + 40 ml/l of concentrated HCl), and stannous sulfate, $SnSO_4$ (*e.g.*, 25 g/l + 10 ml/l of concentrated H_2SO_4 + 150 ml/l of

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[1] NARCUS, H., *Trans. Electrochem. Soc.*, vol. 88, p. 371, 1945.

C_2H_5OH). When the cleaned glass or plastic surface is treated for about 1 min with such a solution and rinsed, a very small amount of the reducing agent is probably adsorbed on the surface. This may furnish reducing nuclei that initiate reduction of the silver and thus cause more uniform silver films.

It is possible to deposit other metals such as copper[1] and gold on nonmetallic surfaces by chemical reduction, but these methods have not been extensively applied.

Another effective method of metalizing surfaces is by *vacuum evaporation.*[2] In this process the metal to be vaporized is supported on and heated by a wire of tungsten or molybdenum through which current is passed. The heater and the object to be coated are enclosed in a glass vessel that is evacuated to a pressure of less than 0.001 mm, *i.e.*, so low that there is insufficient oxygen to oxidize the deposits. When the heating coil reaches a sufficiently high temperature, the enclosed metal evaporates and is deposited on all adjacent surfaces, including the one to be coated. Many metals, including copper, silver, gold, and aluminum, can be so deposited. For subsequent plating, gold or silver films are often used, *e.g.*, in the phonograph industry.

Cathode sputtering may also be used to coat nonconducting materials with metals but is less convenient than evaporation. This process is also conducted in an evacuated vessel, in which the article to be coated is made anodic or is placed between the anode and cathode and the cathode consists of the metal to be deposited, *e.g.*, platinum or gold. A potential up to 10,000 volts can be used.

Another method used to metalize glass or porcelain involves the application of a paint consisting of very fine silver powder and flux suspended in a suitable drying oil. When the paint is dry, it is heated to a sufficient temperature to burn off the oil and to flux the coat of silver, on which additional silver or other metals may be deposited.

For some purposes, a conducting paint is made by suspending copper powder in a lacquer which has been so diluted with thinner that, when it dries, there is insufficient solid material left to insulate the copper particles from each other. Commercial conducting lacquers containing, for example, silver dispersed in an organic medium are now available.

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[1] NARCUS, H., *Metal Finishing*, vol. 45, p. 64, 1947; and *Proc. Am. Electroplaters' Soc.*, p. 157, 1948.

[2] BURNS, R. M., and SCHUH, A. E., "Protective Coatings for Metals," Reinhold Publishing Corporation, New York, 1939.

Still another method sometimes applied to leaves and flowers (previously rendered impervious) is to dip them into a solution of silver nitrate, allow them to dry, and then expose them to hydrogen sulfide gas, which produces a conducting film of silver sulfide.

The choice of methods and materials depends upon the products to be plated. Specific examples will be given for electrotyping and the plating of plastics.

PREPARATION FOR ELECTROTYPING

Electrotyping involves the reproduction of surfaces to be used for printing. The original form may consist of (1) type (locked in a "chase"), usually an alloy of lead, tin, and antimony; (2) photoengraved half-tone or line-cut plates, usually of zinc or copper; (3) previously produced electrotype plates, used as patterns; (4) engraved copper or steel plates, such as are used for intaglio printing; or (5) a combination of any or all of these subjects. For present purposes all the steps up to the electrodeposition will be considered as *preparation*.

Because the original plates are *positives*, *i.e.*, are the same as the desired printing plate, it is necessary first to prepare a negative mold on which the final printing surface is deposited. Four methods of molding are now used in electrotyping for letterpress, or surface, printing, *viz.*, (1) wax molding; (2) use of waxlike "plastic" sheet molding material, backed with metal foil, *e.g.*, a product known as *tenaplate*, (3) sheet plastic molding; and (4) lead molding. Methods (1) and (4) have long been used, while (2) and (3) are more recent developments.

Wax Molding. The essential steps in wax molding are as follows: The wax is melted in a steam-heated kettle and is then poured over flat sheets of electrotype backing metal or aluminum, known as *cases*, that rest on a flat-rimmed *wax table*. The layer of wax, about 1/8 to 1/4 in. (3 to 6 mm) thick, is heated with a flame to remove air bubbles before it is allowed to solidify. After cooling, the surface is *shaved* by a machine to yield a smooth surface and a definite thickness (about 1/16 in. or 1.5 mm). Before molding, the subjects are slightly warmed, *e.g.*, to 100 or 110°F (38 to 43°C), in a heated cabinet. The surfaces of the wax and also of the subject are brushed with molding graphite to prevent sticking of the wax and subject. The subject is laid face downward on the wax, and a pressure of about 1,000 to 1,500 lb/in.^{2} (70 to 105 kg/cm^2) is applied in a hydraulic press. The molded case is lightly shaved to remove wax forced above the surface and is carefully heated with a small flame to remove burrs and slightly round the edges. (The printing faces of the letters are in the bottoms of the depressions and hence are unaffected by these treatments.) The wax mold is rendered conducting by means of graphite, usually applied in a so-called "emulsion," actually a suspension of graphite in water.

It is difficult to define quantitatively the properties of a suitable molding wax. It must have such hardness at slightly elevated temperatures that it can be molded at reasonable pressures and yet be hard enough at room temperature to retain its shape. It must be *plastic* and not *viscous; i.e.*, it must not flow unless some minimum pressure is applied. This distinction is illustrated by the behavior of wax and pitch. If a thin rod of each of these materials is supported at two points, the plastic wax will scarcely bend, while the viscous pitch, even though it may be much harder, will sag and continue to do so for long periods. If a viscous wax were used for molding, it might flow at room temperature and thereby lose the details of the impression or cause serious dimensional changes. In addition the wax must not be sticky, as this would cause difficulty in separating it from the type form. The coefficient of expansion should not be too high, as then the wax may crack on cooling or may cause a *concave face*, a difficulty sometimes observed with beeswax. The wax should have very fine crystals, *i.e.*, be *microcrystalline*, in order to avoid crystal boundaries on the surface, especially in impressions of fine half tones.

It is possible to measure the *penetration hardness* by means of a penetrometer, used for testing asphaltic products. A few unpublished tests on a satisfactory electrotypers' wax with a 150-g load for 15 sec yielded at 25°C (77°F) values from 25 to 33. The hardness value of 35°C (95°F) (about the molding temperature) should be about one-half that at 25°C. Wax with a higher ratio, *e.g.*, three times as hard at 25°C as at 35°C, proved to be quite unsuitable because its hardness changed too rapidly with temperature.

In earlier years Austrian ozokerite was the principal wax used in electrotyping, but during the First and Second World Wars it was unavailable. Early attempts to use American ozokerite (found in Utah) were unsuccessful, but subsequently suitable mixtures were prepared. In recent years molding waxes that closely approach ozokerite in behavior have been developed from petroleum.

When the green or brown ozokerite was employed, additions of paraffin or petrolatum were usually made and also of some resin, *e.g.*, white pine pitch, Burgundy pitch, or Venice turpentine. One advantage of the waxes obtained or synthesized from petroleum is that suitable substances can be added by the producer to yield consistently the desired properties.

The temperature of the wax in the steam kettle should not exceed 110°C (230°F), as otherwise the wax composition will change rapidly by volatilization of some constituents.

Application of Graphite. Although wax molding of electrotypes is rapidly being superseded by other methods, it is still in extensive use. It is possible to render the surface of wax molds conductive by the use of silver films (as used on plastic molds); however, graphite is most commonly used on wax. It may be applied for two purposes: (1) to facilitate the molding, for which a *molding graphite* is used, and (2) to make the surface conductive. For the latter purposes the graphite can be applied dry, or wet in a suspension in water, often but erroneously called an *emulsion*.

The principal properties of graphite that determine its usefulness are (1) purity, (2) fineness, and (3) conductivity, which is related to (1) and (2). The purity can be determined by burning off a sample in oxygen and weighing the ash. The loss in weight is assumed to represent graphite but will include any other forms of carbon that may be present.


FIG. 43. Frame used to determine the rate of covering of nickel on a graphited wax surface.

The fineness is measured by means of standard mesh sieves, *e.g.*, with 100, 200, or 325 meshes per linear inch (40, 80, and 130 meshes per centimeter). A weighed sample, *e.g.*, 10 g, is placed on the 325-mesh sieve, mixed with water, and stirred with a fine brush while a fine stream of water enters the sieve. When no more graphite passes through, the residue is dried and weighed. It is then treated similarly on the 200- and 100-mesh sieves, although water is not necessary for the latter.

The effective conductivity of the graphite is conveniently determined by measuring the time required for nickel to deposit over a given area under specified conditions. A frame such as in Fig. 43 is filled with wax, shaved to a plane surface, and coated with the graphite to be tested either dry or wet. An area exactly equal to 2.5 by 15 cm (1 by 6 in.) is obtained by scraping the edges. Contact is made to the graphite through a brass strip connected to the hanger. A solution containing 0.5*N* nickel sulfate (70 g/l or 9 oz/gal of $NiSO_4 \cdot 7HO$) and 0.1*N* ammonium chloride (5.3 g/l or 0.7 oz/gal of NH_4Cl) is used at a pH of 5.6 and a temperature of 25°C (77°F). The anode and cathode are 10 cm (4 in.) apart, and a potential of 3.0 volts is applied. The period required for the nickel to cover the graphite completely is designated as the *covering time.*

Laboratory tests and plant observations led to recommendation of the specifications listed in the following table, which have been closely followed by industry.

SPECIFICATIONS FOR ELECTROTYPING GRAPHITE

Type	Fineness, minimum per cent through sieve No.			Carbon content, minimum per cent	Time of covering, maximum min
	325	200	100		
Dry polishing.......	50	75	99	92	8
Wet lead...........	50	95	99	92	10

The graphite for wet leading should readily mix with water to form a suspension containing about 2 lb of graphite per gallon of water (240 g/l).

The adhesion of graphite to wax when an aqueous suspension is applied illustrates the selective effect brought about by differences in surface tension. Because the surface tension between wax and graphite is less than that between water and graphite, the latter is *attracted* to the wax. If, however, a mixture of chalk (calcium carbonate) and water were applied to the wax, very little chalk would adhere to the wax. One advantage, especially of natural graphite, is that it is usually in fine flakes that overlap and thus foster continuous contacts. A few tests have shown that the average thickness of a film of graphite applied dry to wax is about 0.00002 in. (0.0005 mm) and if applied wet it is only about half that thick.

Oxidizing of graphited wax cases produces a thin film of copper that increases the conductivity of the surface and shortens the covering time. In this process the graphited surface is covered with a dilute, slightly acid solution of copper sulfate and very fine iron powder. The solution is then agitated by shaking the case, moving it with a brush, or whipping a fine spray of water over the surface. Each of these iron particles sets up with the graphite a small local cell, in which the iron dissolves and deposits a film of copper on the graphite. The term *oxidizing* applied by electrotypers to this process is technically correct, since the iron is oxidized and the copper is reduced.

Waxlike Sheet-molding Material. As explained on page 234, the use of lead molds in electrotyping is not generally applicable to type-metal forms because the required pressures would deform the type metal. On the other hand, the plates produced from wax molds may require a great deal of finishing, partly because there is so much opportunity for the wax to flow. A kind of molding sheet known as *Tenaplate*, which has been in successful use for about 15 years, represents a composite of a metal and a wax mold. It consists of a thin sheet of a fairly soft metal such as aluminum or copper, on the surface of which is a relatively thin layer of a special waxlike mixture coated with a thin layer of molding graphite. When a type form is molded in such a sheet, the metal deforms to a considerable extent, but the exact impression is taken by the wax surface. The net result is a mold that is a more accurate reproduction of the original type face, and bench operations are minimized.

The surface of such a mold must be rendered conductive. In the early years of this process graphite was applied, but with the development of methods for silvering plastics (page 234) the Tenaplate molds are now usually silvered, after which deposition of nickel or copper is conducted in the regular way. Tenaplate permits greater flexibility of handling, storing, shipping, and revising than is possible with wax molds.

Plastic Molds. Probably the most important and novel development in electrotyping in recent years is the use of sheet plastic in place of other mediums for molding and of silvering in place of graphite to render the surface conducting. The elimination of wax and graphite makes it possible to keep an electrotyping plant *clean* and more hygienic than formerly. Plastic molding is so rapidly replacing wax and lead molding in the electrotype industry that in a few years the older processes may disappear entirely. Plastic molds can be readily shipped, with a saving in transportation costs.

Most successful results have thus far been obtained with sheets of a copolymer of vinylacetate and vinylchloride such as is sold commercially under the trade name of *Vinylite,* although efforts are being made to employ plastics that have a somewhat lower molding temperature and lower coefficient of expansion than Vinylite. The Vinylite is obtained in the form of sheets about 0.03 in. (0.8 mm) thick, which have been colored, *e.g.*, white, green, or black, by a suitable dye or filler. The color aids the inspector to detect any flaws in the impression. A dull, slightly matte surface is now preferred.

In plastic molding, the type form is first warmed to a temperature of about 130°F (54°C) on an electrically heated platen. The plastic sheet is then laid face downward on the form, and the plastic is warmed to a temperature of about 250°F (123°C), after which the assembly is placed in the molding press. A relatively low pressure, *e.g.*, 500 lb/in.^2 (35 kg/cm^2), is required. The mold and form are then allowed to cool under light pressure, *e.g.*, 10 lb/in.^2 (0.15 kg/cm^2), after which the mold is removed from the form.

The face of the mold is then coated with silver by one of the methods described on page 234 to render it conductive. Spraying of the silvering solutions is especially effective on electrotypes, because it ensures complete coverage of the surface, including the sides of dots and letters.

Nickel or copper as required is then deposited on the silvered mold, *e.g.*, about 0.001 in. (0.025 mm) of nickel followed by 0.006 in. (0.15 mm) or more of copper for nickel electrotypes or merely about 0.008 in. (0.2 mm) of copper for copper electrotypes. The shell is then held flat by a suction device while the mold is pulled off. One distinct advantage of plastic molds is that, unlike wax, Tenaplate, or lead molds, they can be resilvered and used repeatedly to make duplicate plates. They may also be heated, pressed flat, and used to mold other forms. In order to prevent sticking of the electrotype metal to the silvered face of the shell during the backing operation, the shell can be treated with a solution of sodium sulfide and soap, which produces a thin black film of silver sulfide. This is also advantageous in assisting the finisher to make the printing surface plane.

Lead Molds. Lead molding was formerly used extensively in electrotyping of fine half tones to obtain fine reproductions. Because of the high pressures required (8,000 lb/in.^{2} or 560 kg/cm^2), this process cannot be employed for molding subjects containing type metal. It is, however, sometimes used for making molds of previously fabricated electrotypes that contain type matter.

A thin, smooth sheet of lead about 0.04 in. (1 mm) thick is used. In some cases this has on the surface a very thin layer of tin, which prevents oxidation of the lead during storage. This tin-faced lead is not recommended for copper electrotypes, as the acid copper bath attacks the tin. To prevent the lead mold from sticking to the form, both are lightly dusted with molding graphite. In some cases a dilute solution of a grease in a solvent is applied instead of graphite.

In order to permit separation of the electrotype shell from the lead mold, the latter is first treated with a very dilute solution of sodium or potassium dichromate, *e.g.*, about 1 g/l or 0.13 oz/gal of $Na_2Cr_2O_7$. This produces a very thin film of lead chromate, $PbCrO_4$, on the lead surface.

PLATING ON PLASTICS

Most of the principles of the steps required to plate metals on plastics are referred to previously in this chapter. The term *plating* is justified because it is desirable to obtain adherent coatings. Actually the degree of adhesion of metal deposits on plastics is not equal to that on metals, (1) because there is no strong bond between metal and plastic and (2) because, if such a bond existed, the tensile strength of the plastic is usually much less than that of the metal coating. The two procedures that lead to fair adhesion of coatings on plastics are (1) the customary practice of plating the complete surface, which leaves no edges to start peeling, and (2) sufficient roughening of the plastic surface to produce some mechanical bond of the metal. One factor that tends to disclose any relatively poor adhesion on plastics is the usual higher coefficient of expansion of the plastic than of the metal coating. If, therefore, the plated object is heated, *e.g.*, in buffing or in subsequent use, the plastic expands and may stretch the metal coating and cause the latter to blister when the temperature returns to normal.

A good résumé of methods of plating on plastics was published by H. Narcus.[1]

The principal essential steps are as follows:

1. Slight roughening of the surface to remove the *glaze*, or *skin*, and also any burrs from the surface. This can be accomplished by (*a*) tumbling with pumice and water, (*b*) blasting with fine alundum, or (*c*) chemical etching in either an acid or alkali that will slightly attack the surface of that plastic.
2. Cleaning in a mild alkali such as trisodium phosphate or $0.1N$ (0.4 per cent) sodium hydroxide.
3. Sensitizing the surface, *e.g.*, by dipping for 1 or 2 min in a solution containing stannous chloride, $SnCl_2 \cdot 2H_2O$, 10 g/l, and concentrated hydrochloric acid, 40 ml/l.
4. Application of the silver film, *e.g.*, by the formaldehyde method (page 226).
5. Deposition of copper. An initial coat from a bath containing copper sulfate, $CuSO_4 \cdot 5H_2O$, 75 g/l (10 oz/gal), and H_2SO_4, 2.5 g/l (0.3 oz/gal), followed by deposition from a bath containing 250 g/l (33 oz/gal) of $CuSO_4 \cdot 5H_2O$ and 40 g/l (5 oz/gal) of H_2SO_4.
6. Deposition of other metals as desired.

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[1] *Trans. Electrochem. Soc.*, vol. 88, p. 371, 1945.

CHAPTER IX

ELECTRICAL EQUIPMENT

SOURCES OF CURRENT

Generators. Obviously the most essential requisite for electrodeposition processes is a source of low-voltage direct current. As it is not practicable to distribute current to any great distance at as low an emf as 6 to 12 volts owing to the excessive cost of the large copper conductors which would be necessary to minimize transmission losses, it is customary for electroplating and electrotyping plants to generate their electric power or to transform it from a commercially transmitted emf, (usually 220 or 440 volts) to that required. A low-voltage generator[1] is frequently employed, driven from a shaft operated by steam power or by a motor impelled by the commercial current. In the latter case the shafts of the motor and generator are usually connected together, or the motor is assembled on the generator shaft, forming a *motor-generator set,* such as is now used extensively in the electrodeposition industries. Rectifiers are also used (page 241).

The fundamental principle of the generator is that, when a coil of wire is rapidly rotated in a magnetic field in such a way that it cuts lines of force, a current is produced in the wire. Conversely, when a current is passed through a movable coil placed in a magnetic field, there is a tendency for the coil to rotate to a position in which the maximum number of lines of magnetic force will be enclosed. This latter effect is the basis of the electric motor. In principle, therefore, a motor and a generator may have exactly the same construction. Such an arrangement becomes a generator if the coil is rotated by some external mechanical force or a motor if a current is passed through the coil by the application of an emf from an external source. The four most essential electrical parts of a d-c generator (or motor) are the armature, field magnets, commutator, and brushes. The armature, which carries

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[1] The word *dynamo,* which is frequently but incorrectly used in place of *generator,* is a contraction of *dynamo electric machine* and may therefore refer to either a motor or a generator.

the moving coils, consists of a cylindrical stack of thin disks of silicon steel. The coils of insulated wire are wound in slots running lengthwise of the armature. The field magnets, usually four or more in number, consist of soft iron cores, magnetized by the passage of a current through coils of wire surrounding them so that the inner ends are alternately of north and south polarity. The commutator is the device for collecting and reversing the current. It consists of segments of copper insulated from each other and from the shaft by thin sheets of mica. The terminals of the armature coils are connected to the commutator bars in such a way that, as each coil leaves one pole and approaches the next one, which is of opposite polarity, the connections between the coil and the external circuit are also reversed, and hence the direction of the current outside the machine is the same at all times. The brushes are the terminals of the current leads, which *pick up* the current from the commutator and transmit it to the leads and thence to the bus bars.

The most essential differences in the types of generators used for electrodeposition are in the relation between the current passing through the field and through the armature. The four arrangements that have been used in plating generators are represented diagrammatically in Fig. 44.

The most important consideration in the choice of winding for such generators is the maintenance of a constant voltage when the load in the tanks changes greatly. Any one of the arrangements may yield a constant voltage as long as the load in the tanks remains constant.

The current that passes through the field coils may be derived from the generator itself, in which case the generator is said to be *self-excited.* The residual magnetism of the field magnets is sufficient to produce the initial field required to start the generator. In the *self-excited shunt-wound* generator, the field coils are in parallel with the armature and only a part of the generated current passes through the field coil. Suppose that with such a generator the amount of work in the plating tanks is increased. This decreases the tank resistance, and the voltage at the generator brushes decreases because of the increased voltage drop in the armature. The current in the shunt fields therefore decreases, and the voltage at the generator terminals drops and can be maintained only by changing the field rheostat. Such a machine therefore has a drooping voltage characteristic.

The *self-excited compound-wound* generator has two separate field windings: one of which is in parallel with the armature as in a shunt-wound generator and the other a winding of low resistance in series with the armature and called the *series winding*. As the load in the tank increases, the current through the series winding also increases. This raises the generated voltage. If this just offsets the decrease which would occur with the shunt winding only, the generator has a flat voltage characteristic. If it more than compensates for the decrease due to the shunt winding, the generator is *overcompounded* and the voltage tends to build up as the load increases. Small machines are generally self-excited compound-wound.

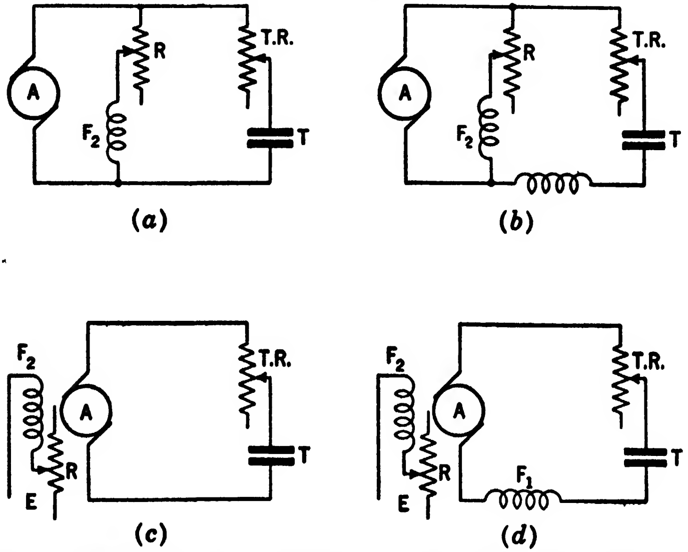

FIG. 44. Typical generator windings. (*a*) Self-excited, shunt-wound. (*b*) Self-excited, compound-wound. (*c*) Separately excited, shunt-wound. (*d*) Separately excited, compound-wound. *A*, armature. F_1, series field coil. F_2, shunt field coil. *E*, exciter. *R*, field rheostat. *T.R.*, tank rheostat. *T*, tank.

In *separately excited* generators the current required for the field coils is furnished from an outside source, *e.g.*, direct current at 110 to 220 volts from a power line, or from a separate small generator installed to furnish the exciting current. The so-called "separately excited shunt-wound" generator is simply a generator in which the entire field current is furnished from outside. Strictly speaking it is not "shunt-wound," but the above expression has come into common use, probably in contrast to the term *separately* *excited compound-wound.* The latter has a winding of low resistance in series with the armature. Although it is difficult to handle very high currents through the series coils, many large generators are compound-wound. Separately excited shunt-wound generators are frequently used on large machines if a wide range of voltage control is required.

The type of motor to be employed to operate the generator is determined by the source of current available and by the required power output and efficiency of the generator. If alternating current is applied, an a-c motor must be installed, in which case the motor-generator set serves both as a rectifier and transformer. The approximate size of the motor required may be calculated as follows: Suppose that it is desired to operate a generator to yield 2,000 amp at 6 volts. The power output will then be 2,000 × 6 = 12,000 watts, or 12 kw. If we assume a generating efficiency of 80 per cent, it will be necessary to supply to the generator 100/80 × 12,000 = 15,000 watts. The motor must therefore be able to deliver that amount of power to the generator, *i.e.*, it must be a 15-kw motor, or (since 1 hp equals 746 watts) it must deliver 15,000/746 = 20.1 hp. In such a case a 20-hp motor should usually be installed unless the generator will frequently be subjected to overloads.

The *power efficiency* of the generator set is equal to the product of the motor efficiency and the generator efficiency. In the above case if the motor has an efficiency of 85 per cent, the motor generator set will have an efficiency of 0.80 × 0.85 = 68 per cent. The motor transmits to the generator only 85 per cent of the power furnished to it, and the generator in turn yields only 80 per cent of that amount. In order to secure 12,000 watts, it will therefore be necessary to supply to the motor 100/68 × 12,000 = 17,600 watts, or 17.6 kw or 23.5 hp. The same result is obtained if we calculate from the power requirement and efficiency of the motor, *i.e.*, 100/85 × 15,000 = 17,600 watts. Even though the power consumption represents a very small part of the cost of the electroplating operations, consideration should be given, especially in large plants, to the possible losses arising from defective design or faulty operation of generators. Thus even with the above moderate-sized generator, an increased expense of 5 per cent over a period of 300 working days of 9 hr each, with electricity at $0.05 per kilowatt-hour, would represent an annual loss of about $119.

The size and number of generators to be used in any plant will depend upon conditions of operation. In those rather unusual cases where continuous operation is essential, it may be advisable to provide at least two generators to permit occasional overhauling and repairs. In such an installation each generator should have a current capacity slightly in excess of the normal requirement so that it will not be overloaded when the entire burden is placed upon it. When both generators are available, however, the load should be divided so as to have each operating with a wide margin. Even when continuous operation is not essential, in all plants requiring over 1,000 amp the expense of two generators is usually warranted by the greater freedom from shutdowns, the ability to take care of "peak loads," and especially the greater freedom of voltage adjustment. Thus, for example, in a plant with a maximum requirement of 1,500 amp, much greater flexibility can be obtained with two 1,000-amp generators than with one 1,500- or even one 2,000-amp set.

A generator with two commutators is advantageous; in fact it is common practice to design all generators except in very small sizes with two commutators. Such generators are now built with four terminals, which can be connected in such a way as to give 6 or 12 volts or to give both voltages at once on a three- or four-wire system. Such a generator is cheaper and more efficient than two separate generators of the same total power output and is nearly as flexible, except for the possibility of shutdowns for repairs. For most cases it will be found preferable to have the two commutators similar, *e.g.*, each generating 6 volts. In special cases it is possible to have different voltages on the two commutators, *e.g.*, 10 and 5 volts. Such an arrangement does not, however, permit the full output of the generator to be secured at any one voltage.

The principal factors in the care of plating generators are the lubrication of the bearings and the care and adjustment of the brushes and commutators. Of the several types of brushes used, those consisting of a mixture of graphite, carbon, and copper, commonly called *metal graphite*, are most satisfactory. For plating generators it is necessary to have as low an electrical resistance as possible and a low friction coefficient. The exact adjustment of the brushes depends upon the machine design, but in any case sparking should be reduced to a minimum. Dust from the air or from the brushes should be blown away from the commutators and armature at frequent intervals. The commutators should be kept smooth and clean and ordinarily should not be lubricated. The formation of a chocolate brown film on the commutator generally indicates good operation, and this film should not be removed.

Rectifiers. As electrical energy is distributed to plants in the form of alternating current (ac) at 110 or 220 volts, it is necessary for use in electroplating to *rectify* it, *i.e.*, to change it to direct current (dc), and also to use a *step-down transformer* to reduce the voltage, usually to 6 or 12 volts. As previously noted, a motor-generator set operated with alternating current serves as both a rectifier and a transformer. During the past fifteen years extensive use has been made in the plating industry of other devices, known as *metal rectifiers*, in place of motor generators. Associated with such a rectifier is a step-down transformer, which reduces the voltage of the alternating current from, for example, 220 volts to the voltage required to yield the desired low voltage from the rectifier.

All these rectifiers involve a boundary surface through which current will pass readily in one direction but with difficulty, if at all, in the other direction. If then to such a boundary, an alternating current is applied in which the current flows alternately in two directions, *e.g.*, with 60 complete cycles per second, only the half of the current that flows in the appropriate direction will continue to flow through the boundary, which serves as a barrier to the other half of the current. Since the portion that passes through goes in only one direction, it results in a direct current that is not continuous but pulsating. This is illustrated in Fig. 45, in which *a* represents the curve for direct current if only one half the current is rectified. If, however, both sides of a single-phase current are rectified so as to pass in the same direction, a curve such as *b* for full-wave rectification is obtained, which is continuous but not uniform in voltage. A current represented by *b* can be used in many plating operations, but it has been reported to be unsatisfactory for critical processes such as chromium plating. It is preferable therefore to employ three-phase alternating current, which with full-wave rectification yields a curve such as in *c*, in which there is a *ripple* of only about 7 per cent in voltage, with a frequency of 360 cycles/sec. This ripple is of about the same magnitude and frequency as that present in direct current obtained from a motor generator. There is no evidence that this slight ripple yields any different results in electrodeposition from those obtained with a continuous uniform current from a battery.

At present three types of rectifiers are in common use in the plating industry, in which the surface of the rectifying plates consists respectively of (1) cuprous oxide, Cu_2O; (2) magnesium and cuprous sulfide, Cu_2S; and (3) selenium. Each of these types possesses advantages and limitations, the exact definition of which may require longer years of experience.

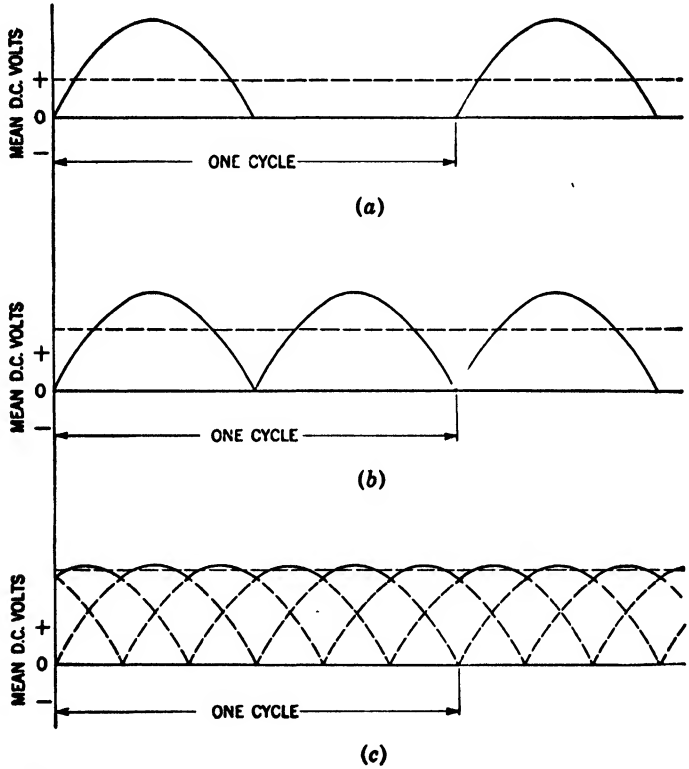

FIG. 45. Typical rectification curves. (*a*) Half-wave rectification. (*b*) Full-wave, single-phase rectification. (*c*) Full-wave, three-phase rectification.

The initial electrical efficiency of these rectifiers at full load is relatively high, *e.g.*, 70 per cent, but it decreases somewhat with time. The operating efficiencies of some types of rectifiers are less than 50 per cent if account is taken of the entire electrical input, including losses in transformers and controls. Because considerable heat is generated in the passage of current through rectifier plates and their efficiency is decreased at high temperatures, it is necessary to provide cooling. This is most commonly done by blowing a stream of clean cool air through by means of ventilating fans. This air should preferably be drawn directly from outside in order to avoid dust and fumes, which reduce the efficiency. Oil cooling has also been employed, but it may introduce certain fire hazards.

It is difficult at this time to decide upon the relative advantages and disadvantages of rectifiers and motor-generator sets. During the Second World War, a large number of rectifiers were introduced into plating in the United States. Experience with these as well as the longer experience with rectifiers in England should make it possible to define the fields for which each source of power is best suited. The following factors should be taken into consideration.

1. Because rectifiers have no moving parts except the ventilating fans, their maintenance requires less attention than that of generators, in which bearings must be lubricated and brushes adjusted or replaced.

2. Rectifiers are commonly constructed in relatively small units, *e.g.*, of 500 amp at 6 volts, any number of which can be readily connected in series or parallel to suit the current requirements of a given process. Their use is therefore somewhat more flexible than that of generators, which are less conveniently operated in series or parallel.

3. The efficiency of a rectifier at full load is less than that of a large motor-generator set, but at lower loads, *e.g.*, at 25 per cent load, the efficiency of the rectifier is likely to be better than that of a generator set, in which considerable energy is required to operate the motor at even zero load.

4. As at present constructed and rated, rectifiers will not withstand so heavy or continuous overloads as will generators. This difference may, however, be based primarily on the margins allowed in the ratings of the two types of equipment.

Storage Batteries. One other source of direct current that should be considered is the storage battery, which may prove very useful to electroplaters for (1) small-scale experiments, (2) electroanalysis of solutions, and (3) occasional plating with gold, silver, or platinum. The principal type of commercial storage battery is the lead peroxide battery, often designated as the lead accumulator or the *chloride accumulator*. The Edison battery, which contains iron, nickel oxide, and caustic soda solution, is less used but is especially valuable for occasional service, as it does not deteriorate rapidly on standing.

Electrical batteries are usually classified as *primary* and *secondary*, which classes are illustrated, respectively, by the simple Daniell cell and the storage cell. In each form electrical energy is produced as the result of a chemical reaction. The essential difference between the two types of batteries is that in the secondary cells the chemical reaction is reversible but not (efficiently) in the primary cells. A secondary or storage cell, when charged, is in no way essentially different from a primary cell. When it is discharged (or preferably only partly discharged), it is possible, by the application of a current of opposite direction from an external source, to reverse the chemical action that has taken place and thus to reproduce the compounds that were present in the originally charged cell. Such a cell therefore serves as a reservoir for electricity, since it is capable of being successively charged and discharged. It is important to note, however, that in such a cell the stored energy is present in the form of chemical compounds, capable of undergoing a chemical reaction that under favorable conditions will produce a current. It is not stored in the same simple sense that electrical energy is stored in a statically charged object such as a condenser.

When fully charged, the ordinary storage cell consists of two kinds of plates or grids constructed of lead and containing in the interstices of the one (the positive plates) lead peroxide, PbO_2, a brown powder, and in the other (the negative plates) a sponge of metallic lead. These grids, arranged alternately, are immersed in an electrolyte consisting of sulfuric acid and water. When this cell is discharged, *e.g.*, by allowing the current to flow between the terminals attached to the two plates, the following reaction in the cell as a whole occurs from left to right:

$$PbO_2 + Pb + 2H_2SO_4 \leftrightarrows 2PbSO_4 + 2H_2O$$

This may be considered as occurring in two steps, thus:

$$PbO_2 + Pb \leftrightarrows 2PbO$$
$$2PbO + 2H_2SO_4 \leftrightarrows 2PbSO_4 + 2H_2O$$

The reactions occurring at the two plates may be represented as follows:

Positive plate:

$$PbO_2 + H_2 = PbO + H_2O$$
$$PbO + H_2SO_4 = PbSO_4 + H_2O$$

Negative plate:

$$\mathrm{Pb + O = PbO}$$
$$\mathrm{PbO + H_2SO_4 = PbSO_4 + H_2O}$$

In effect, the lead peroxide plate is reduced and the lead plate is oxidized, in each case forming lead monoxide (PbO, litharge), which in the presence of the sulfuric acid forms water and lead sulfate, a white powder. When the cell is fully discharged, each of the plates is covered with lead sulfate and so much of the sulfuric acid has been combined that the concentration of sulfuric acid in the electrolyte has been reduced, as may be shown by a simple hydrometer reading. For satisfactory operation it is necessary to avoid the formation of *inactive* lead sulfate, as it is difficult to recharge a cell that is badly *sulfated.* In every case lead sulfate is formed during the discharge of the cell, but under proper conditions this is in a crystalline form which is readily acted upon during recharging. If, however, the battery is allowed to stand uncharged, the plates become *sulfated*, *i.e.*, the lead sulfate is dense and hard, and the cell cannot be easily recharged.

When a cell is recharged, the opposite reactions occur; *i.e.*, all the above reactions take place from right to left. There are, however, secondary reactions during both charging and discharging, which therefore reduce the efficiency of the cells below the theoretical 100 per cent.

Storage batteries should never be used to furnish a current above their specified discharge rate or beyond their rated capacity. When fully charged, the lead batteries should have an emf of about 2.2 volts, and the electrolyte should have a specific gravity at 25°C (77°F) of about 1.28. Distilled water should be added at intervals to replace that lost by electrolysis (evolution of hydrogen and oxygen), but no sulfuric acid should be introduced unless there has been actual mechanical loss. The batteries should never be allowed to discharge below 1.8 volts and preferably not below 2 volts. In any case they should be recharged at intervals of a few weeks whether they have been discharged or not.

It is a simple matter to recharge batteries by current from an electroplating generator. For each cell to be charged, an emf of about 2.5 volts is necessary. A generator designed for 6 volts may be used for two cells by adjusting the field rheostat so as to produce 5 volts for two cells, or when the generator is not otherwise in use, it is frequently possible to secure, for the small currents required, an emf of 7 to 7.5 volts, *i.e.*, sufficient to charge three cells in series. The rate (in amperes) for charging and discharging and the total capacity are specified for each type and size of battery. To prevent reversing the polarity of the generator, a relay should be provided, which opens the circuit if the current is reversed.

TYPES OF CURRENT

As previously stated, electrodeposition of metals is conducted almost exclusively with direct current. In recent years modifications have been proposed in which the current is interrupted or reversed. Such modifications may influence the anode or cathode polarization and hence the electrode efficiencies and may change the structure or appearance of the deposits.

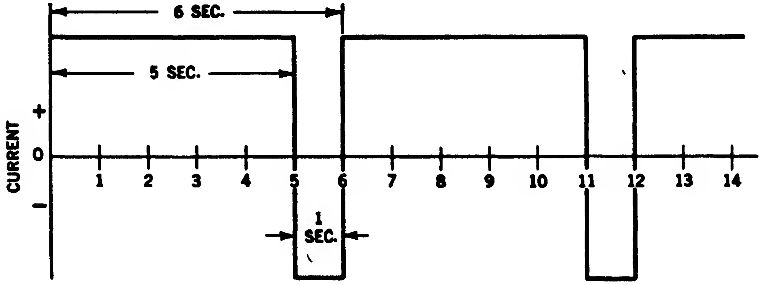

FIG. 46. Typical current-time curve for periodic reverse current plating.

Periodic Reverse Current. In one process, known as *periodic reverse-current plating*,[1] the current is reversed for 10 to 50 per cent of the period used for direct-current plating, *e.g.*, with 5 sec direct and 1 sec reverse current (Fig. 46). If the anode and cathode efficiencies were equal and were unchanged by the cyclic process, one-fifth of the metal deposited by the direct current would be dissolved by the reverse current and the actual cathode efficiency would be four-sixths, or 67 per cent, of that obtainable with the same total current as direct current. Actually it is claimed that, because of the replenishment of metal ions at the cathode surface during the reversal periods, the d-c cathode efficiency may be higher than normal, in which case the over-all efficiency may be greater than 67 per cent. It should be emphasized that, whenever any appreciable part of the current is reversed, the over-all cathode efficiency must be less than 100 per cent.

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[1] JERNSTEDT, G. W., *Metal Finishing*, vol. 45, p. 68, 1947; and *Plating*, vol. 35, p. 708, 1948.

In this particular process, it is reported that, especially in cyanide copper baths, smoother and denser thick deposits are obtained in a shorter time, because a higher current density can be used. Probably during the reversed part of the cycle, a process similar to electropolishing occurs (page 215).

Interrupted Direct Current. In another process the direct current is merely interrupted for short intervals, so that the current is always passing in the same direction but not continuously. This process has been suggested as a means of obtaining smoother or brighter deposits. If, for example, the direct current flows for 5-sec intervals and is interrupted for 1 sec between periods of flow, there is a greater opportunity for replenishment of the cathode film to occur through diffusion and convection. Thereby the cathode polarization is decreased, and the cathode efficiency may be increased. In consequence a higher current density can be used and a given weight of metal can be deposited in a shorter total period, even though the current is not flowing continuously.

Superposed Alternating Current. For many years specific studies have been made upon the effects of a superposed alternating current upon the processes of electrodeposition, but no exhaustive researches have been published, and few advantages have been conclusively established. If, for example, the maximum value of the alternating current applied was exactly equal to that of the direct current, the net result would be an interrupted, variable, direct current, in which the maximum value was the sum of the alternating current and direct current and the minimum was zero. If, instead, the alternating current were greater than the direct current, a periodic reversal would occur. In either case it may be expected that the anode and cathode polarizations would be decreased and the electrode efficiencies increased. However, a decrease in throwing power would be expected because of the decrease in polarization. In certain zinc baths it has been reported that a combination of superposed alternating current and an appropriate addition agent yielded results not obtainable with either one alone.

One of the few industrial processes in which superposed alternating current is employed is the Wohlwill process for refining gold. The use of the alternating current tends to loosen the silver chloride that is formed on the impure gold anodes and hence reduces the anode polarization.

Far more study is required to understand and predict the effects of these various types of current in a given deposition process. Their use must be justified by improvements in quality of the product that compensate for the additional current and equipment which may be employed. However useful they may prove, they do not now constitute a panacea or a revolution in plating.

Bipolar Electrodes. Sometimes it is more convenient to plate the interior of a hollow object by an arrangement known as a *bipolar electrode*, or an *intermediate electrode.* In this process an electrode is placed between the anode and cathode, without being electrically connected to either. The end nearest to the regular anode becomes cathodic, while the other end becomes anodic, and current passes from it to the cathode to be plated. This principle is illustrated in the well-known *series* process of copper refining, illustrated in Fig. 47. In a suitable tank, current passes from an anode at one end of the tank to a cathode at the other end. Between these two primary electrodes are placed a large number of plates consisting of impure copper and not connected electrically to either electrode. The current from the primary anode deposits copper on the near side of the adjacent intermediate electrode, from the other side of which copper dissolves and deposits on the next electrode. The net result is to replace impure copper with pure copper on each intermediate electrode.

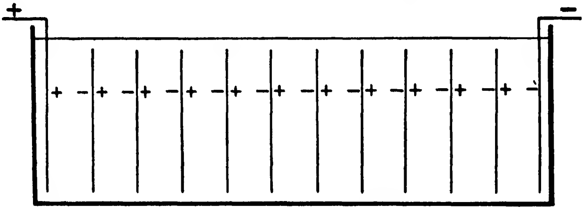

FIG. 47. Diagram of tank and electrodes used in series copper refining.

In one of the few papers on the applications of this principle to electroplating F. K. Savage[1] gives examples of the use of bipolar electrodes to deposit metal into recessed portions of a cathode. This application is illustrated diagrammatically in Fig. 48.

In such an arrangement current passes from the anode *A* to the portion *D* of the bipolar electrode, which may be relatively large and serve as a *collector* of current, all of which must then pass through the projecting arm *E* and through the solution to the

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[1] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 29, p. 301, 1942.

inside of the article *C*, connected to the cathode bar *B*. If *A* is a soluble anode, metal dissolves from it and deposits upon *D* and must be removed at intervals. If *E* is soluble, it dissolves and must be replaced at intervals. If *E* is insoluble, *e.g.*, steel in a cyanide bath, it can be used indefinitely. For certain applications *E* may be a rod of the metal to be plated, with no extension *D*. In that case one end of *E* becomes larger from deposition of metal and the other becomes smaller. By merely reversing this electrode at intervals it can be used indefinitely.

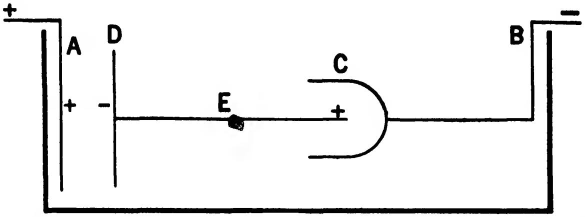

FIG. 48. Diagram illustrating the use of bipolar electrodes in electroplating. *A*, anode. *B*, cathode connection. *C*, cathode. *D*, collector end. *E*, discharge end of bipolar electrode.

In special cases it is possible to have *D* consist of an article that is to be plated on only one side or on only the outside, in which case it is plated simultaneously with *C* and is replaced at intervals.

The principal advantage of the bipolar electrode for certain purposes is that it avoids the necessity of separate connections that are required for a regular inside anode. It also makes it possible to collect and direct into a cavity a larger current than can conveniently be carried by a regular anode. The use of a bipolar electrode usually involves the application of a higher bath potential, which must be justified by its advantages.

CURRENT DISTRIBUTION

Conductors. In dealing with small currents derived, for example, from storage batteries, any ordinary conducting wires can be used. With currents of 100 amp or more, as commonly used in electroplating and electrotyping, the size of the conductors becomes an important consideration. The two factors that govern the minimum size of conductors are the loss in available potential due to the resistance and the heating of the conductors. The chief reason for using low-resistance conductors is that the available emf is usually limited, and if there is an appreciable resistance in the line, this is equivalent to reducing the generator voltage by an amount proportional to the product of the current and resistance, *i.e.*, the *IR drop*. Thus if a current of 100 amp is passed through a conductor with a resistance of 0.01 ohm, the potential drop through this conductor is 100 × 0.01 = 1 volt. If, therefore, the emf at the generator is 6 volts, that at the tanks will be only 5 volts.

The power lost in the conductor is equal to I^2R; therefore in the above case there would be a loss of 100 × 100 × 0.01 = 100 watts. This power is all converted into heat, which is objectionable because of the inconvenience and danger of overheated conductors and because the resistance and hence the voltage loss increases as the temperature is raised. The actual temperature that is reached in the conductor is determined by the size (or weight) of the bar, by the surface exposed to radiation, and by the temperature of the surroundings.

All the above considerations show the importance of using conductors of the proper material, size, and shape. The metal most commonly used is copper, since it has the best conductivity of any metal with the exception of silver and, moreover, it is relatively resistant to acids and alkalies.

Aluminum has been suggested for bus bars. It has a volume resistivity about 1.5 times that of copper; hence to carry a given current an aluminum conductor should have 1.5 times the cross section of a copper conductor. As, however, the density of aluminum is less than one-third that of copper, the larger aluminum conductor will weigh only about one-half as much as the copper. Their relative prices at a given time will determine which is cheaper. Aluminum is fairly resistant to atmospheric corrosion, but because it always carries a slight oxide film, more care is required to obtain and maintain a low resistance at the places where aluminum bus bars are bolted together. Aluminum is more susceptible than copper to corrosion by acids and salts and is therefore not very suitable for tank bars or hangers.

The size of the copper conductors should be such that for short runs not more than 1,000 and preferably not over 750 amp should be carried per square inch of cross section. Every effort should be made to reduce the length of the bus bars, but where for any reason it is necessary to make runs of over 20 ft, the cross section should be increased so that not over 500 amp/in.^{2} will be carried. With a run of 20 ft and return, making 40 ft in all, with a copper conductor carrying 1,000 amp/in.^{2}, there will be a minimum voltage drop of over 0.3 volt, *i.e.*, over 5 per cent of that usually generated (6 volts). By doubling the cross section so as to carry only 500 amp/in.^{2}, the voltage drop will be reduced to about 0.15 volt. Where large installations are involved, it is a simple matter to calculate, from the cost of power and of copper, what is the most efficient size of conductors. This is reached when the annual interest on the copper cost is equal to the annual cost of the power lost in the conductors. Heretofore there has been a great tendency in plating and electrotyping plants to use round conductors of annealed copper. Experience shows, however, that flat bars are much better for several reasons. They expose a greater area for radiation; they can be readily mounted on walls; two or more bars can be used to build up conductors of any desired capacity; and they can be readily bolted to each other or to branch bars. Two convenient sizes are 1 by 1/4 in., which will carry up to 200 amp, *i.e.*, as much as is commonly used on a small electroplating tank, and 2 by 1/4 in., which latter can be used to build up conductors of any desired capacity. These bars can be purchased in lengths of, for example, 20 ft, and used to construct almost any distribution system. Where the bars overlap, it is desirable to increase the cross section, in order to make up for the increased resistance of the joint and of the brass bolts.

The bars on the tanks are required not only to carry the current but also to sustain the weight of the anodes and cathodes. In such cases hard-drawn copper should be employed, as it is stronger and its resistivity is only slightly greater than that of soft annealed copper. In many plants, especially when the tank bars are very long, brass bars are employed instead of copper. There is no objection to this if the brass bars are large enough to have a resistance no greater than that of copper of the necessary conducting size. Brass is not suitable, however, for acid copper solutions as used in electrotyping, as it may be appreciably attacked and may contaminate the solutions. In most cases the wires used for suspending the work need not be of large size. Simple observation of whether or not they become appreciably heated will serve as a guide. Copper is usually employed, although iron wires may be entirely satisfactory if of proper size, and their use may simplify salvage of the metal deposited upon the wire. Where a large rack is used in electroplating or a hanger in electrotyping, consideration should be given to the current that it is required to carry, which may amount to 100 amp or more.

Contacts. Even more important than the size of the conductors is the method of making contacts throughout the circuit. The resistance of a single poor contact may be several times as great as that of the bus bars. Wherever possible, therefore, connections between bars, etc., should be made permanent, either by soldering the contacts or at least by bolting together the cleaned surfaces. It is a common practice to connect bus bars by the use of standard bus bar clamps, which ensure a good tight contact without the necessity of drilling holes through the bars. By amalgamating or silver-plating the cleaned surfaces, or inserting tin foil before bolting them together, a better contact is secured and the joint is protected against corrosion. In a well-designed system it is possible to have (except for switches) continuously soldered or welded lines from the generators to and including the tank bars.

This still leaves possibilities of poor contacts in the anode and cathode hooks. Too often the assumption is made that round tank bars are preferable because by twisting a wire around them or by supporting a curved hanger upon them a large contact area is secured. Actually, it will be found that, even if, as is usually not the case, both surfaces are very well cleaned, actual contact is made at only a few points. Such a contact is satisfactory provided there is a sufficient mass of conducting metal immediately adjacent. If, then, we wish to assure positive contact at a few points, this can probably be better secured upon bars with sharp edges than upon rounded bars. Thus, for example, if a hook is suspended upon or a wire is twisted around a square bar, it is practically certain to make a good contact on at least two or three points, whereas a few particles of dirt or oxide upon a round bar may cause complete insulation of the wire. Tank bars of hard-drawn copper 3/4 by 3/4 in. (19 by 19 mm) in cross section have been used very successfully and will sustain considerable weights on spans of over 3 ft (92 cm). For electrotyping, special hangers might be found preferable, but even the regular hanger with a curved section can be used with square bars.

The anode hooks should, wherever possible, be cast, driven, screwed, or soldered into the anodes so as to make permanent contacts. Copper anodes for acid copper solutions usually have the hook connected to the anode by pouring lead (or type metal) around the hook connection, which also serves to prevent the hook from being dissolved off at the top of the solution. Nickel anodes are usually supported by nickel or monel metal hooks.

Of these, the pure nickel is least likely to be corroded, and if it is, it will not contaminate the solution. Unless such hooks are used, it is preferable to have small lugs or projections upon the anodes extending above the solution level.

The switches and fuses employed on the service lines are of the customary types, as the current used (*e.g.*, 220 volts) is generally small. On the low-voltage lines, however, with currents amounting often to as much as 3,000 or 5,000 amp, line switches would be quite large and correspondingly expensive. For this reason switches for over 1,000 amp are very rarely installed, and usually no switches are used on the tanks except in connection with the rheostats. This is entirely satisfactory, since with 6 or even with 12 volts there is very little danger of damage except from a *dead short*. This is best guarded against by the installation of fuses or circuit breakers in the motor circuit or of circuit breakers of appropriate capacity in the low-voltage line.

Rheostats. Similarly, it is usually desirable to avoid as much as possible the installation of rheostats in the line to regulate the voltage, as rheostats for over 500 amp are expensive and troublesome and are necessarily inefficient, since they do not in any way reduce the power required to operate the motor-generator set. Where more than one kind of work is involved, requiring different tank voltages, it is preferable to regulate the generator voltage by the field rheostat so as to secure the maximum voltage required for any work and to employ rheostats on each of the tanks requiring lower voltages.

Rheostats are constructed of suitable resistance wire, such as nickel, nichrome, silchrome, or constantan. Two types of rheostats are in use, in which, respectively, the resistance coils are in series and in parallel, represented diagrammatically in Fig. 49.

Suppose that in each case there are five coils, which have resistances of 0.01, 0.02, 0.03, 0.04, and 0.05 ohm, respectively, and that the generator voltage is 6 volts. Then, disregarding the resistance of the tank and lines, the current secured by various adjustments of the rheostats can be calculated as follows:

In a series rheostat, the resistance at any point will be equal to the sum of the resistance up to that point; *e.g.*, at point 3, the resistance will be $0.01 + 0.02 + 0.03 = 0.06$ ohm and the current will be $6 \div 0.06 = 100$ amp. By similar calculations it can be shown that for the five steps the currents will be respectively 600, 200, 100, 60, and 40 amp. With the simple form of series rheostat no greater number of adjustments can be made than there are coils. By using two moving contacts, greater flexibility can be secured. It should be noted that with series rheostats, as more coils are put into circuit, the current is decreased. Therefore, the coil of lowest resistance must be large enough to carry the maximum current desired.

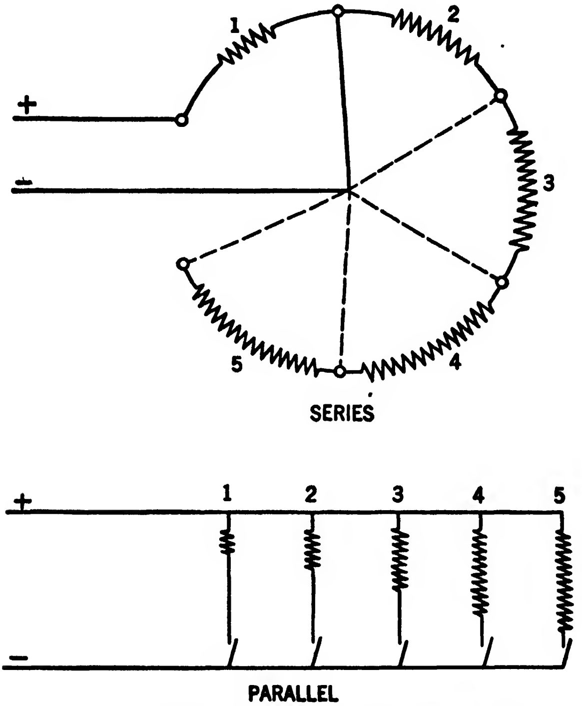

Fig. 49. Diagram of series and parallel rheostats.

In a parallel rheostat the resistance is decreased and therefore the current is increased as additional coils are introduced into the circuit. Hence all the coils are in use when the maximum current is to be carried. The number of adjustments is equal to the number of combinations that can be made. It is possible by means of five coils, with resistances in the proper ratios, to secure a large number of adjustments between the lowest and highest resistances. It will be recalled (page 37) that the resistance of two or more coils in parallel is less than that of either of the single coils. The reciprocal of the total resistance is equal to the sum of the reciprocals of the separate resistances, or $1/R = 1/R_1 +$

$1/R_2 + 1/R_3$, etc. This can be more readily recalled if we remember that the conductance is equal to the reciprocal of the resistance. It is quite obvious, therefore, that, if two coils of equal conductance are in parallel, the current can pass twice as readily as through one coil; in other words, the conductance is equal to the sum of the two separate conductances.

With parallel coils having the resistances above specified, the current that will pass when any one coil is in circuit is equal to the emf (in this case 6 volts) divided by the resistance of that coil, therefore, respectively, 600, 300, 200, 150, and 120 amp. Suppose now that coils 1 and 2 are in the circuit; then the resistance and current can be calculated thus:

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{0.01} + \frac{1}{0.02} = 100 + 50 = 150$$

therefore

$$R = \frac{1}{150} = 0.0067$$

$$I = \frac{E}{R} = \frac{6}{0.0067} = 900 \text{ amp}$$

With a given emf (omitting the tank resistance) in a parallel rheostat the current carried by the two coils is equal to the sum of that carried by each of the coils separately. The resistance of the coils should therefore be selected so as to yield conductances (and not resistances) that can be added together like the weights in a set. Instead of having the resistances in the ratio of 1, 2, 2, 5, 10, etc., their reciprocals should be in such ratios. The resistances will then be in the proportion of 1, 2, 5, 5, 10, etc.

The effective resistances of rheostats are usually expressed in terms of their *voltage drops* when their rated current is passed. Thus, a coil with a resistance of 0.01 ohm and a current of 300 amp will have a voltage drop (IR) of

$$300 \times 0.01 = 3 \text{ volts}$$

A very simple form of parallel rheostat for experimental work, with commercial current of 110 or 220 volts, can be made by arranging a *bank* of incandescent lamps in parallel. No switches are necessary, as the lamps can be screwed in or out as desired.

Another form of rheostat which is useful for experimental work is the *carbon rheostat*, which consists of plates of carbon in a frame with a screw for adjusting the pressure. The resistance is decreased by screwing the plates closer together and vice versa. The carbon rheostat has the advantage of permitting continuous instead of stepwise adjustment, but the disadvantage is that the resistance changes decidedly if the plates are shaken or wet or if they become heated by the passage of heavy currents. For general use, therefore, parallel rheostats, such as can be readily constructed from suitable coils and switches, are preferable. If it is desired to cut out all resistance in the line, a separate switch must be provided to short-circuit the rheostat.

CURRENT MEASUREMENT

Electrical Instruments. The purpose of an *ammeter* is to measure the current flowing in a circuit at any given instant, while a *voltmeter* is used to measure the potential difference between two parts of a circuit. Both instruments depend upon the same principle. When a current is passed through a coil of wire surrounding the core of a fixed permanent magnet, the coil tends to rotate. If this rotation is opposed by any force, such as a spring or the torsion in a wire, or by gravity, the angle of rotation is determined by the number of turns in the wire and the current passing through it. With a given coil of definite resistance, the rotation of the coil, as indicated by a needle attached to it, may serve as a measure of the current or of the voltage, since the magnitude of the former is determined by that of the latter. There are two principal types of instruments used. In the D'Arsonval type the magnet is fixed in position and the coil is free to move on an axis, while in the *soft-iron* type the coil is fixed in position and the piece of soft iron is moved by the passage of the current. The latter instruments are cheaper but somewhat less accurate and reliable than those of the D'Arsonval type and are therefore rarely used.

The essential difference between an ammeter and a voltmeter as actually constructed is that the ammeter has a very low resistance and the voltmeter a very high resistance (up to several thousand ohms). The reason for this difference is clear if we consider the positions in which these instruments are placed in a circuit (Fig. 50). The ammeter is always placed in series with the tank, *i.e.*, in the main circuit, so that all the current passes through it or, as will be explained later, through it and the shunt connected with it. If, therefore, the ammeter (including the shunt) has a resistance comparable to that of the tank, it will materially reduce the current passing through the latter. Its resistance is hence made very low by the use of a few coils of relatively large wire. The voltmeter, on the other hand, is always connected across the tank, *i.e.*, in parallel with it. In such an arrangement, if the voltmeter has a low resistance a relatively large proportion of the current will pass through it and hence be deflected from the tank. For this reason the voltmeter usually has a coil consisting of a large number of turns of fine wire.

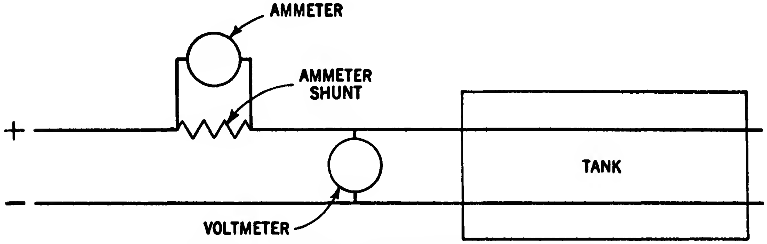

FIG. 50. Position of ammeter and voltmeter.

If an appreciable current were passed through the ammeter coil, it would produce excessive heating. It is customary, therefore, to pass only a definite part of the current through the coil. This is accomplished by arranging in parallel with the ammeter coil another coil or shunt of lower resistance, which bears a definite ratio to that of the ammeter coil. Thus if the two resistances are in the ratio of 9 to 1, 9/10 of the current passes through the shunt. The graduations on the ammeter scale will in that case be so numbered as to indicate ten times the current that actually passes through the ammeter coil and therefore to denote the entire current to be measured. For portable instruments of moderate range, such shunts are often contained in the case with the ammeter, but for larger ranges, outside shunts are provided which are connected in series in the main circuit in which the current is to be measured. These shunts are simply conductors of definite resistance, to the ends of which the ammeter leads are attached. Since the accuracy of the readings depends upon the ratio of the resistance of the shunt to that of the ammeter including the leads, the latter should not be exchanged or altered in length. For small currents ammeters are often provided with three ranges, *e.g.*, 1.5, 5, and 15 amp, secured by means of appropriate self-contained shunts and corresponding binding posts.

The great similarity between an ammeter and a voltmeter may be illustrated by the fact that they can be used interchangeably, with proper adjustments. Thus a sensitive voltmeter (*e.g.*, a millivoltmeter) can be used to measure the current passing through a copper bar of definite cross section by simply applying the two terminals to points a definite distance apart on the bar. Suppose that the terminals of a millivoltmeter are applied to two points 12 in. (30 cm) apart on a round copper conductor 1 in. (2.5 cm) in diameter. Such a bar has a cross section of 1,000,000 *circular mils*.[1] From a table of conductivities, such as are given in many electrical handbooks, it will be found that the resistance of 12 in. of such a bar is approximately 0.00001 ohm. If, therefore, the potential drop indicated by the millivoltmeter is 0.002 volt (2 millivolts), the current may be calculated:

$$I = \frac{E}{R} = \frac{0.002}{0.00001} = 200 \text{ amp}$$

Even when it is not important to know the exact current on a given bar, such measurements may be very useful in determining quickly if the same current is flowing through each of several bars or tanks. To make these measurements it is convenient to have the two voltmeter leads attached to a small board, so that the wires make contacts at a definite distance apart, *e.g.*, 12 in. This method may be used to measure the actual or relative currents flowing on any bars without disturbing the connections in any way.

In any case measurement of the current on a tank or even on a given bar indicates only the rate of flow of electricity and not the *current density*, which is the factor that determines the rate of deposition in any tank. This can be approximately calculated if the area of the work is known. With complicated shapes it is, however, difficult to compute this area, and where racks are used their areas must also be taken into account. Even when all these calculations are made, the result gives only the *average* current density and is no indication of the actual thickness of deposit upon different parts of an object. With irregular shapes or objects with deep recesses the current density and thickness of deposit may be more than five times as great on some parts as on others. It is partly for these reasons that the

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[1] A circular mil is defined as the area of a circle 0.001 in. (1 mil) in diameter. A round bar 0.5 in. (500 mils) in diameter has a cross section of 500 × 500 = 250,000 cir mils.

ammeter is not more generally used in electroplating. It is possible to reproduce current conditions on a given class of work simply by regulation of the voltage, *provided* the composition of the solution, the temperature of the solution, and the anode and cathode areas and polarizations remain constant. Such an assumption is, however, never warranted, and therefore the ammeter and voltmeter should both be used to ensure uniformity of operation.

Where it is desirable to measure and control with considerable accuracy the actual weight of metal deposited, *e.g.*, in silver or gold plating, this can be accomplished by means of an *ampere-hour meter*. This measures the actual quantity of electricity that passes in a given interval. In many cases the ampere-hour meter for electroplating is so devised that a bell is rung when a certain number of coulombs have passed. It is important to remember that this instrument measures the quantity of electricity and not the weight of metal deposited, which is proportional to it only if the cathode efficiency remains constant. Thus if on two different days, owing to differences in the temperature or composition of the solution or to a change in current density, the cathode efficiency of a silver bath is 90 and 99 per cent, respectively, 10 per cent more silver will be deposited on the latter day than on the former by the same quantity of electricity, as measured by an ampere-hour meter. The instrument does not, therefore, ensure a definite weight of metal even when so calibrated, although it does aid in securing uniform results. Actually, however, the cathode efficiencies in silver baths are so nearly 100 per cent that no appreciable error is likely to occur. In chromium plating, the cathode efficiency varies so greatly with the current density that readings with an ampere-hour meter give no indication of the weight or thickness of chromium deposited.

Where it is desired to determine the cathode efficiency in an electroplating bath, this can be calculated approximately by weighing the cathodes before and after plating and noting the current and period of plating. Any such results are, however, only a rough approximation, due to the possible fluctuations in the current strength or to errors in the ammeter calibration, the measurement of the time, and the accurate weighing of the cathodes. For such purposes it is therefore preferable to make observations upon a smaller scale, using a copper (or silver) coulometer (page 32) to measure the quantity of electricity.

LOCATION OF EQUIPMENT

In the installation of electrical equipment in a plating plant, it is often necessary to compromise between the considerations of protection and convenience of equipment. At best, the atmosphere of a plating plant is certain to have a high humidity and more or less acid fumes or alkaline spray. It is therefore necessary to protect the generators and instruments so that they may preserve their efficiency and accuracy. If, however, this effort at preservation results in the location of the generator where it is inaccessible and is therefore neglected or of the ammeters at a point where they are never consulted, more harm than good is accomplished.

The generator should be mounted on a solid base, preferably of concrete, and should be bolted rigidly in place. It should be as close to the plating tank as is feasible and preferably at a point intermediate between the tanks, so as to avoid excessively long bus bars. It should be protected as much as possible from dust and fumes and should be provided with good ventilation either from a window or by a fan. In many cases these conditions may be met by housing the generator on one side of a plating room, with a wood and glass partition around it. The occasional practice of supporting a generator near the ceiling is questionable, as it is thereby made inaccessible and is also subject to the action of the heated vapors that rise toward the ceiling. By placing the generator upon a concrete base, raised, for example, 6 in. above the floor level, it is protected against damage from spilled solutions, overflow of water, etc.

Rectifiers should be kept away from heat and fumes, and should be provided with an ample supply of clean, cool air.

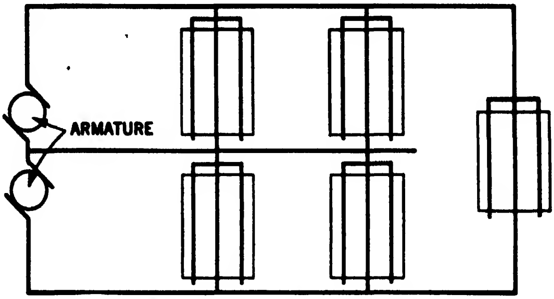
The starting switches, circuit breakers, field rheostat, and main voltmeter and ammeter should be located upon a switchboard close to the generator but facing the plating room. Thus, for example, the switchboard can be made a part of the partition of the generator housing. The tank rheostats, voltmeters, and ammeters are preferably located close to the tanks, so that they can be read or adjusted as work is introduced or removed. Where a considerable number of tanks are placed close together, it is sometimes convenient to have the voltmeters and ammeters mounted upon a single switchboard, which may be the same as that for the generator. In such a case it is possible to use a *multiple switch* for the voltmeter, by means of which the voltage on each tank may be read. If the generator is working at nearly its full capacity, a change in the load on one tank may change the generator voltage and thus necessitate adjustment of the field rheostat or of the other tank rheostats. This can be accomplished more readily if all are on one panel board.

The bus bars from the generator to the tanks are usually run overhead. Where the plating room is located above the basement floor, it is often an advantage to run the bus bars down through the floor and along the ceiling of the room beneath. Connections to the tanks are then made through waterproofed openings in the floor. If the latter is of cement, the openings may be surrounded by a ring of cement. If wooden floors are used, asphalt may be placed around the duct through which the bars pass. In any case they should be as completely accessible as possible. Two advantages of running below the floor are that usually the distance is thereby shortened, and the space above the tanks is more free. This is an especial advantage where mechanical conveyors of any type are to be used, as is often feasible in large plants.

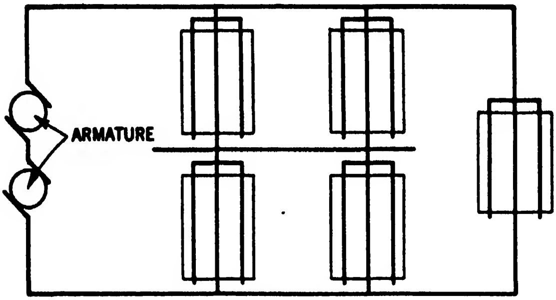
In practically all electroplating plants the tanks are arranged in parallel. Such a plan is justified by the fact that there is seldom sufficient work of a similar size and shape to permit that balancing of cathode areas which is necessary for successful series operation. As the actual emf required in many plating baths is not over 3 volts, it is possible to operate two tanks in series with the customary 6-volt generator, but not usually practicable, for the above reason.

In electrotyping plants it is customary to operate two acid copper tanks in series. This is possible because the forms are usually of similar size or at least of only a few sizes and the voltage required to produce current densities even from 50 to 75 amp/ft^2 (5.5 to 8 amp/dm^2) is usually less than 3 volts. In unusual cases, where the work is very uniform and where solutions of high conductivity and large copper conductors are used, it is possible to operate three acid copper tanks in series on a 6-volt generator and secure 50 amp/ft^2 (5.5 amp/dm^2). This practice is not, however, adapted to general conditions.

Where a considerable variety of work is involved, as in a plating plant requiring, for example, 6 volts on plating tanks and 12 volts on plating barrels, or in an electrotyping plant operating copper tanks at 3 volts and nickel tanks at 6 volts, it may be advantageous to employ the three-wire system, which is based upon the use of a generator with a double commutator. In this system, as shown in Fig. 51, it is desirable approximately to balance the currents used on the two sides of the line but not so closely as in a simple series arrangement. A slight modification is made in the *false neutral* system also illustrated in Fig. 51.



TWO AND THREE WIRE SYSTEM



FALSE NEUTRAL SYSTEM

FIG. 51. Typical tank arrangements for two-armature generator.

CHAPTER X

TANKS AND THEIR EQUIPMENT

Under this heading may be considered the apparatus used for preparing, containing, and operating plating solutions. The first consideration is the material of which the tanks are to be constructed, which in any given case is determined principally by (1) resistance to attack by the solutions concerned, (2) mechanical strength for the loads involved, and (3) cost, including investment, upkeep, and depreciation. Other factors, such as electrical and thermal conductivity, may also influence the choice of materials.

MATERIALS OF CONSTRUCTION

The materials that have been used or suggested for the construction of plating tanks include wood, iron (or steel), stoneware, concrete, and soapstone and for small or experimental tanks, glass, enameled iron, and plastics. No one of these materials possesses all the desired properties. Their relative advantages and disadvantages will be discussed in the light of the above-mentioned considerations. For general purposes we may consider all the solutions as (1) nearly neutral, *e.g.*, water and nickel-plating solutions; (2) acid, *e.g.*, pickles and acid copper solutions; and (3) alkaline, *e.g.*, cleaning solutions and cyanide copper, brass, or silver-plating solutions. Where the materials do not possess the desired chemical resistance, appropriate linings will be considered.

Wood. In the past by far the greatest number of plating tanks were constructed of wood, lined if necessary with other materials. This general use of wood was due not so much to its cheapness or special fitness for the purpose as to the fact that it is usually accessible and can be fabricated by mechanics with customary training and equipment. Wood is not so resistant to the action of solutions as are many other substances, and with present lumber prices a well-made wood tank may cost as much as one made of other materials.

The essential constituent of wood is cellulose, a substance that is not appreciably acted upon by either dilute acids or alkalies. The disintegrating action of such solutions upon wood is therefore due primarily to the removal of the constituents that bind the fibers together. (In the manufacture of paper pulp from wood, hot solutions of alkali or of salts are used to remove the constituents other than cellulose.) The desirable properties of wood for plating tanks are therefore impermeability and freedom from readily soluble constituents. The woods that have been found most satisfactory are cypress, maple, and redwood, all of which are extensively used.

The initial action of solutions upon wood results in the extraction from the wood of certain constituents, such as tannins (from oak or chestnut) and resins (from pine, etc.), the removal of which not only weakens the wood but may also result in serious contamination of the solutions. Where wooden tanks are to be used without linings, it is therefore advisable to soak them for several days with a solution of similar reaction, *e.g.*, with water or with dilute sulfuric acid, and to discard this solution.

The life of a wood tank depends largely upon its construction. It is necessary to use good workmanship to ensure tight joints, which are usually *tongue and grooved.* The tanks should be reinforced not only with monel bolts at the ends but also with rods running through the boards at intervals of 18 to 24 in., *e.g.*, one in each end and three in each side and three in the bottom of a tank 3 by 6 by 3 ft deep. The thickness of the boards will depend principally upon their length; *e.g.*, for a length of 3 ft or less, 2-in. stock will suffice; for 3 to 6 ft, 3-in. stock is used. As most plating tanks are not over 3 ft deep, there is not much hydrostatic pressure developed.

Linings for Wood. For water or for nearly neutral solutions, *e.g.*, nickel-plating baths, wood tanks can be used without any linings. This practice has the advantage of keeping the boards wet and swelled, thus maintaining tight joints. For acid solutions they must, however, be lined with some acidproof material. Wood tanks are not suitable for strongly alkaline solutions even when lined, as the wood is readily attacked by even occasional contact with alkali. All wood tanks should be painted on the outside, preferably with a bituminous paint.

For many purposes bituminous linings prove very satisfactory. Asphalt, tar, or petroleum products can be used successfully.

For this purpose the material should have a melting point of at least 200°C (390°F), it should not soften or flow at temperatures up to 75°C (135°F), and it should be hard but not brittle at ordinary temperature. It should be applied in a molten condition, either by means of swabs or by pouring it on the surface and spreading it with a suitably sized board. The tanks should be first cleaned and dried, and a coat of a bituminous primer applied with a brush. Such a primer can be purchased or can be made by dissolving some of the solid bitumen in benzene (benzol). The priming coat should be allowed to dry to a slightly "tacky" condition before applying the hot asphalt or tar.

For weakly acid baths the inside of wood tanks can be painted with varnishes containing synthetic plastics.

Another type of lining that has been suggested but not extensively used is made of rubber applied to the wood in such a way as to adhere firmly. As rubber is flexible and not readily attacked by dilute acids, such linings may prove very useful for electroplating tanks. It is not suitable for strongly alkaline solutions, as these may extract sulfur from it.

For acid copper solutions used in electrotyping, lead-lined tanks are extensively employed. Such a tank is, in effect, a lead tank supported by the wood tank. The lead should be fairly thick, at least equal to 6-lb lead (weighing 6 lb/ft^2), which is approximately 1/10 in. (2.5 mm) in thickness. It must be united at the joints and corners entirely by *lead burning*, which is accomplished by melting the edges together with a blowtorch, an operation requiring great skill and experience. Where tanks are over 3 ft deep, it is desirable to anchor the lead to the walls at several points. In any case it should be fastened along the top edges by brass screws. As the lead is scarcely attacked by dilute sulfuric acid, it makes a very durable though rather expensive lining. Its chief disadvantage is its electrical conductivity, giving rise to occasional short circuits, which not only cause a loss of current but also result either in deposition of metal on the linings or in the liberation of acid in the solution according to whether the lining becomes the cathode or anode. For this reason it is customary in electrotyping plants to cover the lead lining with a thin wood or plastic lining, which serves only to prevent the electrodes from touching the lead. Efforts to coat the lead with a bituminous covering have not been very successful, as the coating tends to peel off and expose the metal.

Iron and Steel. For alkaline solutions, iron or steel tanks are almost exclusively used. They should be of heavy-gage metal, as otherwise they are readily deformed or may be corroded through from the outside. They are usually welded by means of either acetylene or arc welding, preferably with a double lap weld. The principal precaution to be observed in this welding is that the metal should not be *burnt; i.e.,* there should be no oxide inclusions in the weld. In several cases leaks in iron tanks have been traced to the presence of oxide in the welds. Iron oxide may be readily dissolved by alkaline cyanide solutions, especially if, as in electrolytic cleaning, the tank is made the anode. Steel plating tanks possess the same disadvantage as lead, of being conductive and therefore tending to cause short circuits. This conductivity, however, is frequently utilized in electrolytic cleaning by making the tank serve as the anode.

Rubber and Plastic Linings. Extensive use is made of rubber-lined steel tanks for acid and neutral baths. Rubber of suitable quality is very resistant to such solutions, and its good insulating properties prevent short circuits to the tank.

Prior to the Second World War, rubber-lined tanks were almost exclusively used for bright-nickel-plating solutions. It was then found that some of the materials used to vulcanize the rubber were extracted in sufficient amounts to contaminate the nickel baths and yield unsatisfactory deposits. Through experience, accelerators for the rubber vulcanization were found that had no harmful effects. In selecting a rubber lining, care should be exercised to ensure that it is suitable for the solution to be used.

During the past five years great advances have been made in the production of synthetic rubber of various types. It is reported that some of these are even more resistant to pickling and plating solutions than is natural rubber. For example, certain synthetic rubbers have been successfully used with cyanide baths. Experience with these new types of rubber is needed to define their advantages and limitations.

Among the many plastics that have come into use in the last decade, some appear promising for lining plating tanks, including those for chromic acid baths. Here again the experience is too brief to warrant definite conclusions at this time. The important point is that entirely new substances are now available for the construction of tanks and other plating equipment and should receive careful consideration, especially in making new installations.

For chromium plating, steel tanks are generally employed. They should not be used without linings, because under these conditions, considerable iron may dissolve, especially if the tank becomes anodic. For this reason it is a common practice loosely to insert linings of reinforced glass. Lead-lined iron tanks are most extensively used for chromium plating, in some cases with an additional glass lining, or better, with a plastic lining such as polyethylene.

Fused-glass-lined tanks, such as are used in many chemical operations, are also satisfactory for chromium-, silver-, and gold-plating baths.

Stoneware. Vitrified stoneware is very resistant to dilute acids and may therefore prove useful for plating tanks. It is usually glazed, but stoneware of high quality does not depend upon the glaze for resistance to acid. It is attacked, however, by hydrofluoric acid. In most cases where hydrofluoric acid is used in plating solutions, *e.g.*, in lead and occasionally in nickel solutions, it is combined with boric acid to form fluoboric acid, which has only a very slight action on stoneware. For such solutions, however, the stoneware should be coated with asphalt as a precaution. For small installations, *e.g.*, up to 100 gal, stoneware tanks are very satisfactory for chromium plating.

Stoneware is slightly attacked by dilute alkalies and markedly so by strongly alkaline solutions and is therefore not suitable for use for cleaning solutions. The chief advantages of stoneware tanks are their resistance to the chemical action of many solutions, their low electrical conductivity, and high thermal conductivity. The last property is an advantage when it is necessary to keep the solutions cool, *e.g.*, in summer. Their principal disadvantage is their relative fragility and consequent danger of breakage in transit and in use. The latter danger can be minimized by the use of suitable wooden guards at corners where the tanks are likely to be hit, and by resting them on sand.

Concrete. Reinforced concrete tanks have been used occasionally for plating and electrotyping. They can be built of cheap, readily available materials and in any size or shape that may be desired. They are, however, not usually portable and must therefore be destroyed if the plant location is changed. Concrete is not very resistant to acids and alkalies, and consequently the tanks must be lined, *e.g.*, with asphalt. They also are subject to cracking from heavy impacts.

Soapstone. A variety of soapstone, known as *alberene*, has been employed very largely for sinks used in chemical laboratories. This material when free from imperfections is fairly resistant to dilute acids and alkalies. The chief difficulty in its use for plating tanks is that of securing satisfactory joints. These are usually formed by means of metal dowel pins, and a cement (*e.g.*, litharge and glycerin) is used to fill the cracks. Such a cement is likely to be attacked by continued exposure to acids or alkalies. If attacked, the result is not only leakage of the joints but also exposure of the metal dowel pins, which then corrode and by expansion crack the stone. If alberene tanks are used, the joints at least should be thoroughly coated with a plastic material.

Glass, Hard Rubber, and Enameled Iron. For small experimental tanks, *e.g.*, up to 1 gal (4 l), rectangular glass battery jars are most convenient. They are reasonably cheap, are practically unacted upon by acids or alkalies, and permit observation of the position and condition of the electrodes. If heated gradually, they can be used to contain hot solutions, although at times they are poorly annealed and may crack most unexpectedly. Even for larger sizes they are very useful, but the danger of breakage is greater. For this reason rubber or plastic jars are sometimes preferable. Rubber is quite resistant to acid solutions but not to alkaline. It softens at high temperatures and cannot, therefore, be used safely at temperatures much above 40°C (104°F). Enameled iron has practically the same resistance to acids and alkalies as has glass but has the disadvantage that after long use the enamel is likely to chip off. Enameled iron tanks and also stainless steel tanks are used for gold and platinum plating.

Greater consideration should be given to the size of plating tanks. In general, it is desirable to have them as large and especially as deep as conditions justify. A large volume of solution is advantageous in reducing the effect of changes in concentration or composition that may occur during the operations. A relatively deep plating tank is desirable because it facilitates the settling of suspended matter. The added investment for the larger volume of solution required in large or deep tanks is usually justified.

INSULATION

In any case, but especially when using metal or metal-lined tanks, it is necessary to use some insulating material to support and separate the bus bars along the edge of the tanks. Except for the presence of moisture or of the solutions, there would be no difficulty in securing suitable material, as with an emf of only 6 or at least 12 volts, there is little chance for *direct* electrical leakage. The principal difficulty is that of securing insulating materials which will not absorb or be attacked by the solutions. If the insulating strips become impregnated with the solutions, they become *electrolytically* conductive. Under such conditions there is not only a loss of current but also an attack of the bus bars. The most common practice is to use wood strips or blocks and to replace them when they show disintegration. It is advantageous to impregnate the wood by dipping it into heated wax or asphalt. Frequent coating with shellac also prolongs the usefulness of the wood. Other materials are, however, preferable to wood. Hard rubber, bakelite, and other plastics are very suitable, and the greater expense will probably be balanced by the increased resistance to attack. Stoneware strips or tiles and porcelain tiles are resistant but somewhat fragile and subject to chipping if hit by the heavy anodes. Alberene stone resists neutral or slightly acid solutions, but when subjected constantly to conditions that permit the concentration of acid solutions by evaporation, it is rapidly disintegrated. Glass is satisfactory in all respects except its fragility. There is need for the development of an inexpensive insulating material that will be nonabsorbent and will resist the action of acids and alkalies. Among the new plastics, polyethylene is very promising.

In connection with insulation it is important to prevent any pipes used in the tanks from getting into the circuit. This can be most readily accomplished by connecting each pipe with an insulated joint consisting of hard rubber. A simple insulated joint consists of several inches of rubber steam hose.

In recent years the need for insulating certain parts of the plating racks has arisen, especially in connection with automatic plating and with chromium plating. In such cases it is desirable to avoid the loss of current and of metal upon the rack itself. In principle the rack should be insulated entirely, except where it makes contact with the cathode bar and with the articles to be plated. The ideal insulating material for this purpose should resist both alkalies and acids as well as the plating bath, so that the racks can pass through the cleaners and pickles without injury. Certain new plastic coatings fully meet these requirements. For many purposes rubber coatings are satisfactory.

They are, however, attacked by strong alkalies and by chromic acid. Vitreous enamel resists moderate concentrations of most acids and alkalies but is so brittle that cracks soon develop and permit corrosion of the underlying metal.

In connection with insulation, the *stopping off* of certain areas of the cathode may be considered. This procedure is especially useful in producing thick deposits, *e.g.*, in building up certain surfaces, or in electroforming. Some new plastic substances are suitable for general use in acid and alkaline baths and in hot and cold solutions. Up to temperatures of about 40°C (104°F) certain waxes such as paraffin and ozokerite are generally useful, and higher melting synthetic waxes can be obtained now. Their adhesion to metal surfaces can be increased by the addition of a small amount of a resin. For acid solutions bituminous coatings are quite useful and can be obtained with relatively high melting points, *e.g.*, above 100°C (212°F). Bituminous paints or enamels, especially after baking, are more resistant but more brittle and may be difficult to remove subsequently. Certain plastic lacquers are useful for stopping off in chromium plating and can be colored to define their area better. They are often applied in the form of tapes.

AGITATION

Air Agitation. It is frequently desirable to agitate depositing solutions, thereby fostering uniformity of composition and permitting the use of higher current densities than would otherwise be possible. In electrotyping this is accomplished by means of compressed air delivered through perforated lead pipes, preferably so placed as to have the maximum degree of agitation between the anodes and cathodes. Where air agitation is used, it is essential that the air be freed from oil by means of suitable traps or scrubbers, as even very faint traces of oil in these solutions may be detrimental. Air agitation has the advantage of adaptability, as it can be introduced into any part of the tank and the degree of agitation can be controlled by simple valves. The disadvantage is that by the introduction of air an oxidizing atmosphere is maintained in the solutions and secondary (and possibly deleterious) chemical reactions may be accelerated. Thus it is well known that the use of air agitation in acid copper solutions is in part responsible for the consumption of sulfuric acid and the accumulation of copper sulfate that almost always occur. This effect is accounted for by the fact (page 291) that there is a tendency for the copper to pass into solution in the cuprous state (Cu^+) and the oxidation to the cupric state (Cu^{++}) is fostered by the presence of oxygen. Aside from the accumulation of copper sulfate (which may prove very troublesome) there is no definite evidence that the use of the air agitation is detrimental in such solutions. It is possible with air agitation to secure high cathode efficiencies and to produce dense copper deposits of desirable physical properties. With other metals, such as lead and zinc, however, air agitation results in distinctly inferior deposits. With nickel, the effect of the air is uncertain. This form of agitation is used very generally in nickel electrotyping baths with beneficial results, but in electroplating and even in electrotyping with some solutions such agitation is apparently harmful. As electrodeposition at the cathode is essentially a process of chemical reduction, the maintenance in the solution of oxidizing conditions appears, on general principles, to be contradictory. Air agitation is occasionally used in chromium plating, especially to equalize the temperature in the bath. It probably reduces the cathode efficiency. Air agitation in cyanide solutions is objectionable because it increases the formation of carbonates, both through oxidation and through absorption of carbon dioxide. Much work remains to be done upon the effects of air in plating solutions.

Mechanical Agitation. Mechanical agitation of solutions on a commercial scale often involves practical difficulties. It can be accomplished either by movement of the anodes or the cathodes or of the solution by stirrers not in the circuit. Where the cathodes or racks are circular or symmetrical, they can often be rotated as, for example, was formerly done in the plating of flatware. If the cathode is a hollow cylinder, it is often possible to rotate the anode within the cathode. This has been done successfully in lead-plating the interior of ordnance shells. In some cases, as in plating spoons, the cathode rods are moved mechanically.. Where, however, the cathodes are large and flat or of irregular shapes, it is difficult to move them rapidly or even to move the solution adjacent to them. If the latter operation is accomplished by means of moving stirrers or paddles, difficulty is experienced in securing materials that will not be attacked by the solutions. Plastics are most commonly used for this purpose.

Whatever method is used for agitation, there is danger of particles from the anodes being kept in suspension and giving rise to roughness on the cathodes. This condition is not very objectionable in electrotyping, as slight roughness on the back of electrotype shells is not a serious defect. In electroplating, however, it is the layer of metal last deposited that determines the appearance of the coating. Therefore, it is not generally feasible to employ violent agitation in plating solutions. The roughness can be overcome in part by the use of bags around the anodes or by frequent or continuous filtration of the solutions. Continuous circulation and filtration produce moderate agitation.

There are various mechanical plating devices in which the cathodes are conveyed through the solution by means of a chain conveyor or upon arms from a central axis. In addition to providing a mild form of agitation, many such machines serve as laborsaving devices by automatically cleaning, pickling, plating, rinsing, and drying the work. The degree of agitation secured as a result of the movement of the cathodes is helpful in permitting the use of current densities slightly higher than normal but by no means equal to what might be secured by more rapid agitation were such feasible. There are great possibilities of increasing the current density by improved methods of agitation, especially for large-scale production of similar articles.

In *barrel plating*, which is used for small articles, such as nuts, bolts, screws, and washers, a high degree of agitation is secured, *e.g.*, by the rotation of the work in a cylinder immersed in the plating solution. One reason that this agitation does not cause roughness from suspended particles is that during the operation the articles are subjected to a slight continuous burnishing action, which counteracts any tendency to roughness.

The simplest form of plating barrel consists of an open cylindrical tank which rotates upon an axis inclined at about 45 deg. The anodes are hung directly in the solution. The articles are placed directly in the barrel, making contact with the cathode by suitable bars attached to the barrel. By the rotation of the barrel the objects tumble over each other and thus continually expose a fresh surface for plating. This type of barrel has the advantage of simplicity of construction but the disadvantage that, in order to remove the work from the barrel, the solution must be emptied into some other receptacle. It is not, therefore, adapted to work upon a very large scale. Another disadvantage is that in such a barrel the anode area is usually very limited and hence the anode efficiency may be low.

By far the greater number of plating barrels consist of a perforated cylinder mounted on a horizontal axis and connected to the cathode, within which cylinder the articles are placed. This cylinder is rotated in a tank containing the plating solution and the anodes, which latter are sometimes curved so as to be approximately parallel to the circumference of the cylinder. The latter is in fact usually not a cylinder, but a hexagonal or octagonal prism, one of the long sides of which can be opened to introduce or remove the articles.

One of the most difficult problems in the construction of a plating barrel is the material for the perforated diaphragm. Plastics and rubber are now employed, and their greater service makes up for increased cost.

Although the barrel plating is the most practicable way of plating small objects on a large scale, it is not electrically efficient. In those types using a diaphragm, the resistance is relatively high, and even with solutions of low resistivity, barrel plating is usually done with 9 to 12 volts. The actual current density secured is difficult to measure, owing to the uncertainty as to the effective cathode area. At any given time only part of the objects are actually in the circuit, and of them only a small proportion of the surface is effective. Other conditions being equal, it is therefore desirable to use in a plating barrel a solution with high metal content, good conductivity, and good throwing power. The last property is useful in permitting deposition on parts of the surface that are relatively inaccessible. Usually, barrel-plating solutions have from one and one-half to twice the metal content of the regular solution.

CIRCULATION AND FILTRATION

It is necessary to filter plating solutions at intervals and at the same time remove any sludge accumulated upon the bottom of the tanks. For large installations and conveyor systems continuous filtration is essential. In order to do this efficiently, some means of pumping the liquids is desirable. For nearly neutral solutions, steel pumps can be used. For strongly acid solutions, however, it is necessary to use hard rubber, lead, or some acid-resisting iron, *e.g.*, the high-silicon irons, such as Duriron, Duralloy, Tantiron, Corrosiron, or stainless steel. Antimonial lead or lead alloyed with calcium or tellurium is also used for this purpose.

Owing to the practical difficulties in the operation of pumps with moving parts, there are certain advantages in the use of compressed air for pumping. This is accomplished by various devices, one of which, known as the *air-jet lift*, can be used very conveniently for acid copper solutions, provided compressed air at about 5 lb/in.^{2} is available. It can be constructed of brass or bronze for neutral solutions, but for strongly acid solutions lead is preferable. Solutions can also be conveyed by a steam injector pump, which, however, is less satisfactory because the steam heats and dilutes the solution. The air-jet lift type of pump is very compact and occupies only a small space, partly in the tank and partly outside. It is employed in a very compact pump and filter recently developed for continuous filtration of solutions. In certain cases filter presses have been applied successfully to plating solutions. Such a press, together with a suitable motor and pump, is now made portable by mounting it on a truck.

When a considerable number of tanks are used with the same solution and the same kind of work, it is often an advantage to circulate and mix the contents so that there is only one solution to be analyzed and adjusted. In large copper-refining plants this circulation is usually accomplished by having the tanks in cascade (*i.e.*, arranged on successive levels) or by allowing the solution to overflow from the tanks into a reservoir or sump, from which it is pumped to an elevated storage reservoir from which it flows back to the tanks. These methods are now being adapted to large electroplating and electrotyping plants. In such installations for nickel plating, care should be exercised to avoid aeration of the solutions, which may lead to pitting.

Filters for the nearly neutral solutions may consist of muslin, which should be previously thoroughly washed with soap and water and rinsed to remove any sizing such as dextrin, which in even small amounts may act as a harmful addition agent. For acid copper solutions, wool cloth should be used, and this should be washed out when not in use, or at least the solution should not be allowed to concentrate upon it by evaporation. For alkaline solutions, sand or asbestos filters can be used. Paper and many new synthetic fibers are now employed in filters.

LOCATION OF TANKS

The tanks should always be raised from the floor by resting upon insulating materials such as bricks or concrete. This permits frequent cleaning of the floor and also aids in the detection of leaks. The floor should, wherever possible, be made of concrete or of vitrified brick or tile with cement joints, laid with a slope of at least 1/8 in. to the foot toward a drain. A bituminous surface is especially advantageous where acid solutions are used. A false floor of wooden strips is usually placed where the workmen walk. The actual position of the plating and cleaning tanks will depend upon the type of work and the procedure used, but it should at least be arranged with a view toward saving steps; *i.e.*, the work should progress through or around a room. Those tanks using the highest currents should, wherever possible, be located nearest to the generator. Large stoneware tanks should rest upon several inches of sand to reduce strains that may come from settling of the floors.

CHAPTER XI

TYPES OF METALS AND SOLUTIONS

THE PERIODIC SYSTEM OF THE ELEMENTS

Much of the progress in chemistry has resulted from the discovery of a periodic relation of the elements and their properties by Lothar Meyer and Dimitri Mendeleeff in 1869. In the first published charts, certain vacant spaces existed, most of which have since been filled in by the discovery of new èlements. In 1913 Mosely, from studies of X-ray spectra, emphasized the importance of the *atomic numbers* of the elements in addition to their atomic weights. More recently the existence of *isotopes* was discovered, *i.e.*, different elements having the same atomic number and the same chemical properties but different atomic weights. Certain of these isotopes may disintegrate spontaneously into other elements and simultaneously emit radiations. Studies in this field resulted in the development of the atomic bomb and of other applications of atomic, or *nuclear*, energy. The net effect of such studies is greatly to expand the number and types of elements and their compounds that may enter into chemical or electrochemical reactions. At present there are very few direct applications of isotopes in electrodeposition.

Partly because the original forms of the periodic system did not conveniently associate the metals that may be involved in electrodeposition, little direct use of the periodic system has been made in this field. In recent years four papers have been published on the relation between plating and the periodic system.[1] In each of these papers, especially that of Dubpernell, emphasis is laid on the possibility of predicting from the periodic system the behavior and properties of plating baths of a specific metal.

Various forms of the periodic system have been devised to bring out certain relations. The form shown in Fig. 52 emphasizes the fact that, of all the known elements, about 30 metals can be

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[1] ELLINGHAM, H. J. T., *J. Electrodepositors' Tech. Soc.*, vol. 10, p. 109, 1935. BLUM, W., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 27, p. 923, 1940. DUBPERNELL, G., *Proc. Am. Electroplaters' Soc.*, p. 244, 1946. LOWENHEIM, F. A., *Proc. Am. Electroplaters' Soc.*, p. 187, 1948.

deposited in a nearly pure state from aqueous solutions. Of these, at least two, molybdenum and tungsten, are on the border line, but they can certainly be deposited as alloys with other metals. It should be emphasized that practically all the metals can be deposited from their fused salts and many of them from organic electrolytes.

In the arrangement shown in Fig. 52, which illustrates the relation of the elements to electrodeposition, the *group* designations used in the earlier forms of the table have been listed across the top. It will be noted that seven of the groups appear in two parts designated as A and B and that Group VIII (the iron and platinum metals group) and Group O (the rare gases) serve as transition groups. The metals will be considered in the succeeding chapters in the order of these historical groups, which serve to emphasize the valence relations of the elements.

Certain general facts regarding the periodic system are related to the deposition of the metals. Of the first seven groups, the metals in the B division are generally more noble, *i.e.*, more readily deposited from aqueous solutions than those in the A division. As we descend in each vertical column, the metals become more noble, *e.g.*, in the order copper, silver, and gold.

These relations are illustrated by the standard potentials shown in Fig. 52, for those elements whose potentials are fairly well established. When a standard potential of an element is more positive (or less negative) than that of another element, the former metal, in its active state, is the more noble. At present it is difficult to correlate the standard potentials in the horizontal rows.

These and other relations will be referred to in the treatment of each group of metals.

THE CONSTITUTION OF PLATING BATHS

With few exceptions (such as the chromic acid bath) the metal to be deposited from a plating bath is introduced as a salt of that metal and is replenished by anodic dissolving of that metal. Until recent years only two types of plating baths were in common use, *viz.*, those consisting of simple salts such as sulfates or chlorides and those containing double cyanides of the metals. To these must now be added baths in which the major constituents are fluoborates (which were first used in lead and lead-tin baths), pyrophosphates, sulfamates, sulfonates, acetates, and other complex salts, as well as those containing large additions of organic

			A					
I	II	III	IV	V	VI	VII	VIII	
1 H Hydrogen 0								
3 Li Lithium −2.96	4 Be Beryllium							
11 Na Sodium −2.71	12 Mg Magnesium −1.55							
19 K Potassium −2.92	20 Ca Calcium −2.76	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium −0.56	25 Mn Manganese −1.18	26 Fe Iron −0.44	27 Co Cobalt −0.28
37 Rb Rubidium −2.93	38 Sr Strontium −1.79	39 Yt Yttrium	40 Zr Zirconium	41 Cb Columbium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium +0.68
55 Cs Caesium	56 Ba Barium −1.57	57* La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium
87 Fa Francium	88 Ra Radium	89 Ac Actinium	90 Th† Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium

* The *rare-earth* metals consist of 14 elements (58 to 71), the best known of which is cerium. They have not been deposited from aqueous solutions.

† The elements from 90 to 96 are now also designated as a rare-earth group and do not properly fall in the vertical columns indicated.

FIG. 52. Periodic system of the elements. Those metals enclosed in the heavy lines have been deposited in nearly pure form from aqueous solutions. Those enclosed in dotted lines are doubtful. The circles enclose nonmetals that can be

B

	I	II	III	IV	V	VI	VII	0
								2 He Helium
			5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen +0.41	9 F Fluorine +1.9	10 Ne Neon
			13 Al Aluminum −1.33	14 Si Silicon	15 P Phosphorus	16 S Sulphur	17 Cl Chlorine +1.36	18 A Argon
28 Ni Nickel −0.23	29 Cu Copper +0.34	30 Zn Zinc −0.76	31 Ga Gallium −0.52	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine +1.06	36 Kr Krypton
46 Pd Palladium +0.82	47 Ag Silver +0.80	48 Cd Cadmium −0.40	49 In Indium −0.34	50 Sn Tin −0.14	51 Sb Antimony +0.10	52 Te Tellurium	53 I Iodine +0.53	54 Xe Xenon
78 Pt Platinum +0.90	79 Au Gold +1.36	80 Hg Mercury +0.80	81 Tl Thallium +0.72	82 Pb Lead −0.12	83 Bi Bismuth +0.20	84 Po Polonium	85 At Astatine	86 Rn Radon
96 Cm Curium								

liberated by electrolysis of aqueous solutions. The first number in each space is the *atomic number* of that element. The numerical value where given under the name of an element represents the approximate standard potential of that element (see also Table 10, p. 423).

salts such as acetates, tartrates, and citrates to modify the properties or behavior of a given type of bath. Because many of these developments are too new to have yielded extensive experience, and because their exact compositions have not all been fully disclosed, it is not now possible to discuss their behavior in detail. An effort will be made in this chapter to indicate the types and behaviors of the compounds present in such baths.

For convenience, the major constituents of plating baths may be classified in the following groups.

1. Simple inorganic salts.
2. Complex inorganic salts.
3. Simple organic salts.
4. Complex organic salts.

Typical examples of each class will be discussed in the following sections.

Simple Inorganic Salts. The three most common salts of this group are the chlorides, sulfates, and nitrates, derived, respectively, from hydrochloric acid, HCl; sulfuric acid, H_2SO_4; and nitric acid, HNO_3. Nitrates are rarely used in plating baths because they may be reduced to ammonia at the cathode. Chlorides of most metals have higher conductivities than the sulfates but are more corrosive to equipment. In practice, sulfates are most extensively used, *e.g.*, for copper, zinc, tin, and nickel plating, although chloride baths of iron, nickel and gold are also employed.

The most important characteristics of all of these salts are (1) high solubilities, (2) good conductivities, and (3) high metal-ion concentrations, as a result of a large degree of dissociation into metallic cations and nonmetallic anions, *e.g.*,

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

Complex Inorganic Salts. Common examples are the fluosilicates, fluoborates, and pyrophosphates.

Fluosilicates. These are derived from fluosilicic acid, H_2SiF_6, which is made by the action of hydrofluoric acid, HF, upon silica, SiO_2. This first forms silicon fluoride, SiF_4, which when volatilized and passed into water forms fluosilicic acid and insoluble silicic acid.

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$
$$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3$$

Fluosilicic acid is often obtained as a by-product in the manufacture of superphosphate by treating phosphate rock (which contains calcium fluoride and silica as impurities) with sulfuric acid. The principal use in electrolysis of fluosilicic acid is for lead refining and to a small extent for lead plating (page 330).

Fluoborates. These are derived from fluoboric acid, HBF_4, which, in turn, is produced by combining hydrofluoric acid, HF, with boric acid, H_3BO_3.

$$H_3BO_3 + 4HF = HBF_4 + 3H_2O$$

Fluoboric acid is relatively stable, as shown by the fact that it does not etch glass as it would do if HF were liberated. As a safeguard against its decomposition, it is customary to add about 10 per cent more boric acid than is needed by the above equation. It is a strong acid, *i.e.*, is highly dissociated; thus

$$HBF_4 \leftrightharpoons H^+ + BF_4^-$$

and the pH of solutions containing much free acid is below 2.

It was long used as the basis for lead plating (page 331), later of tin plating, and more recently of copper (page 293), zinc (page 310), nickel (page 362), and indium plating baths, in all of which free fluoboric acid is present, together with the appropriate metal salt, *e.g.*, $Pb(BF_4)_2$, etc. In many respects the fluoborate baths behave like sulfate baths (except with lead, of which the sulfate is insoluble). Any advantages of a particular bath, *e.g.*, of copper, over a corresponding sulfate bath must be found in a greater solubility or higher conductivity of the fluoborate. Strictly speaking, fluoborates should not be referred to as complex salts, since they are highly ionized with the production of metal ions.

Pyrophosphates. These salts are derived from pyrophosphoric acid, $H_4P_2O_7$, which is produced by heating phosphoric acid, H_3PO_4, thus:

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

Similarly

$$\underset{\text{disodium hydrogen phosphate}}{2\,Na_2HPO_4} \rightarrow \underset{\text{sodium pyrophosphate}}{Na_4P_2O_7} + H_2O$$

The heavy metal salts, such as copper pyrophosphate, $Cu_2P_2O_7$, and zinc pyrophosphate, $Zn_2P_2O_7$, are nearly insoluble in water but dissolve in an excess of potassium pyrophosphate, probably with the formation of complexes. Probably because complex ions are formed, the deposits are finer grained. The resulting solutions are slightly alkaline (pH of 8 to 9) and hence are less corrosive than acid baths.

Sulfamates. These salts are derived from sulfamic acid or amido-sulfonic acid, $HOSO_2NH_2$. This acid is sulfuric acid in which one OH group has been replaced by an amido group, NH_2. Salts of this acid are formed by replacing the H in the OH group with a metal. Thus, sodium sulfamate is $NaOSO_2NH_2$, and lead sulfamate is $Pb(OSO_2NH_2)_2$. Both the acid and its salts are quite stable. The lead salt is used in the sulfamate lead bath (page 331).

The addition of certain inorganic salts to simple heavy metal salts may form complex ions to a limited extent and thereby decrease the metal-ion concentration. There is some evidence that ammonium salts form complex ions with nickel sulfate, but certainly not to the same degree as does ammonium hydroxide, an excess of which forms the deep blue nickel solution of the type sometimes used for plating on zinc.

Simple Organic Salts. A good example of a simple organic salt bath is the acetate, derived from acetic acid, $HC_2H_3O_2$ (or CH_3COOH). Most metal acetates are soluble, but few have been used as the basis of plating baths. Early attempts to plate from lead acetate yielded coarsely crystalline deposits that were not entirely eliminated by addition agents. More recently a bath consisting largely of nickel acetate has been developed (page 381) especially for plating stereotypes and building up worn parts, and zinc acetate baths have also been proposed.

Acetic acid is a relatively weak acid, and together with its salts it has excellent buffer action in the range from pH 3 to 5, *i.e.*, at a lower pH than boric acid is effective. While its salts are usually well dissociated, their resistivities are not so low as those of sulfates or chlorides. There is little evidence of complex ion formation in acetate baths.

Complex Organic Salts. Most organic acids, especially hydroxy acids, such as hydroxyacetic, $CH_2OH{\cdot}COOH$; tartaric $(CHOH)_2(COOH)_2$; and citric, $(CH_2)_2COH(COOH)_3$, form complex salts with heavy metals, chiefly in alkaline solutions. Evidences of such complex formation are the dissolving of the hydroxides, *e.g.*, of nickel and iron, in alkaline solutions, in which they are normally insoluble, and the change in color of the solutions, *e.g.*, of nickel from green to blue. Plating baths are seldom prepared principally from these organic salts, but they are often added to modify the composition and behavior of baths. Good examples are the Rochelle salt copper bath (page 296) and the acetate nickel bath (page 381).

A very recent application of organic salts in plating is the use of *alkane sulfonates.*[1] These are salts of a sulfonic acid, derived from sulfuric acid in which one hydroxyl group has been substituted by a methyl group, CH_3; ethyl, C_2H_5; or propyl, C_3H_7. Thus we have methanesulfonic acid, CH_3HSO_3, which forms soluble salts with many metals. The cupric copper salt is $Cu(CH_3SO_3)_2$. The acid used in plating is a mixture of the methane, ethane, and propane sulfonic acids.

Organic amines. C. J. Brockman has described plating baths[2] that contain organic "amines," *i.e.*, compounds in which one or more of the hydrogen atoms in ammonia have been replaced by an organic radical. A copper bath containing diethylene triamine, $(NH_2C_2H_4)_2NH$, described by L. Greenspan,[3] is in commercial use.

Cyanides. The most important complex salts used in plating are the cyanides, which are sometimes considered as inorganic carbon compounds but for convenience will here be treated as organic. All the cyanide plating baths contain a metal cyanide dissolved in an excess of sodium or potassium cyanide to form complex cyanides. In those cases where some other metal compound such as copper carbonate, cadmium oxide, or silver chloride is dissolved in an alkali cyanide, the same double cyanides are formed together with, respectively, sodium carbonate, sodium hydroxide, or sodium chloride. Whether or not these auxiliary compounds are beneficial in a given plating process must be determined by experience.

In the study of any cyanide plating bath the following terms may be employed.[4]

1. The *total cyanide* is the content of the active cyanide ion, CN, in whatever form. It usually excludes any cyanide present in very stable compounds such as ferrocyanides.
2. The *total alkali cyanide* is the CN combined with sodium or potassium.
3. The *total combined cyanide* is that present in active complex compounds or ions.

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[1] Faust, C. L., Agruss, B., Combs, E. L., and Proell, Wayne A., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 34, pp. 541, 709, 1947.

[2] *Trans. Electrochem. Soc.*, vol. 71, p. 255, 1937.

[3] *Trans. Electrochem. Soc.*, vol. 78, p. 303, 1940.

[4] Thompson, M. R., *Trans. Electrochem. Soc.*, vol. 79, p. 417, 1941.

4. The *total combined alkali cyanide* is the alkali cyanide that is combined with heavy metal cyanides.

5. The *free cyanide* is the alkali cyanide that is not combined in complexes. This may often be determined by a suitable titration (page 191) but sometimes is computed from the other constituents. (It has also been suggested[1] that the free cyanide be defined as the excess of alkali cyanide above that required to maintain a clear solution, regardless of the assumed formulas of the complexes.)

6. The *metal cyanide* is that combined with and computed from the heavy metals present.

7. The *cyanide ratio* is the mol ratio of the total alkali cyanide to the metal cyanide. In an example given by M. R. Thompson, a solution containing

$$1M\ Na_2Zn(CN)_4 + 1M\ NaCN$$

would yield the following numerical values for the above quantities:

Total cyanide	5M
Total alkali cyanide	3M
Total combined cyanide	4M
Total combined alkali cyanide	2M
Free cyanide	1M
Metal cyanide	1M
Cyanide ratio	3

All the complex metal cyanides dissociate to a slight extent into metal ions and cyanide ions. The extent of this dissociation is expressed as the *instability constant*, usually a very small number such as 10^{-18}.

It is difficult to define with certainty the complexes present in the various metal cyanide solutions. The simplest method, *i.e.*, analysis of a solution of alkali cyanide saturated with the metal cyanide, does not always yield consistent results with methods in which, for example, the metal potential (and hence the metal-ion concentration or activity) is plotted against the ratio of metal cyanide to alkali cyanide. It is evident that two or more complexes may be present in the same cyanide solution and that the composition of the complexes may change with the cyanide ratio. Available evidence indicates that in cyanide baths the following ions are present:

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[1] BLUM, W., *Trans. Electrochem. Soc.*, vol. 60, p. 143, 1931.

METAL PRESENT	PRINCIPAL IONS PRESENT
Silver	$Ag(CN)_2^-$
Gold	$Au(CN)_2^-$
Zinc	$Zn(CN)_4^{--}$
Cadmium	$Cd(CN)_3^-$
	$Cd(CN)_4^{--}$
Nickel	$Ni(CN)_4^{--}$
Copper	$Cu(CN)_3^{--}$
	$Cu(CN)_2^-$

In computing results of analyses, the above ions (or the corresponding salts) are commonly assumed to be present. The first formula for the copper complex is generally used, even though solutions with very little free cyanide may also contain the second complex.

All cyanide solutions are alkaline, *i.e.*, have a pH above 7, because the alkali cyanide (and to a less extent the complex cyanide) hydrolyzes to liberate sodium hydroxide, NaOH, and hydrocyanic acid, HCN. The measurement ~~of pH (page 76) is~~ often used in the control of cyanide baths.

All cyanide baths, especially when heated, contain carbonates of sodium or potassium. These may result from direct absorption of carbon dioxide from the air and the liberation of hydrocyanic acid, HCN, which accounts for the characteristic almondlike odor of cyanide solutions. The reaction is accelerated by the spraying of solution into the air during electrolysis.

$2NaCN +$	CO_2	$+ H_2O$	$= Na_2CO_3$	$+ 2HCN$
sodium cyanide	carbon dioxide	water	sodium carbonate	hydrocyanic acid

This reaction is retarded by adding free sodium hydroxide.

Another source of carbonate is the oxidation of cyanide, which occurs especially if insoluble anodes are used. As an intermediate product a cyanate, *e.g.*, NaCNO, may be formed, but the ultimate products are sodium carbonate and ammonia.

$$2NaCN + 2H_2O + 2NaOH + O = 2Na_2CO_3 + 2NH_3$$

Cyanide may also be decomposed by a form of hydrolysis that occurs especially at high temperatures in acid or nearly neutral solutions (hence is retarded by addition of alkali.) The formic acid or sodium formate may also be oxidized to carbonate.

HCN	$+ 2H_2O$	$= HCOOH$	$+ NH_3$
hydrocyanic acid	water	formic acid	ammonia

Since all cyanide baths accumulate carbonate in use, there is seldom need to add carbonate after the bath is prepared. For certain baths, initial addition of carbonate is beneficial.

In baths containing sodium cyanide, the content of carbonate may become objectionably high, *e.g.*, over 60 g/l or 8 oz/gal of Na_2CO_3, and must be reduced. Three methods have been used for its removal.

1. Lowering the temperature of the bath to about −3°C (26°F) when the hydrated salt, $Na_2CO_3 \cdot 10\ H_2O$, crystallizes out. This usually requires artificial refrigeration and is the best method, since no new compounds are formed.

2. Adding a barium salt to precipitate barium carbonate, $BaCO_3$. If barium cyanide, $Ba(CN)_2$, were available, it would be preferable, because it would leave in the solution only sodium cyanide, an excess of which may, however, be objectionable. If barium chloride, $BaCl_2$, or barium hydroxide, $Ba(OH)_2$, is used, equivalent amounts of sodium chloride or hydroxide are formed and may be objectionable. The precipitated barium carbonate does not readily settle out and requires filtration.

3. Addition of hydrated calcium sulfate (gypsum), $CaSO_4 \cdot 2H_2O$. This produces an equivalent amount of sodium sulfate, which is assumed to be less objectionable than the sodium carbonate.

One of the problems in cyanide baths is the choice of sodium or potassium salts. Potassium cyanide, KCN, was first used, but with the availability of cheaper sodium cyanide, NaCN, it almost completely displaced the potassium. In more recent years potassium cyanide has been used in all gold and silver plating and in much of the copper plating. In comparing the effects of these two cyanides they should be used in equivalent proportions: *i.e.*, 65 parts by weight of KCN are equivalent to 49 of NaCN.

While certain advantages, *e.g.*, in permitting higher current densities, have been demonstrated for potassium cyanide baths, the reasons have not been fully established. Among the factors that may favor the use of potassium cyanide, *e.g.*, in copper and silver baths, are the following:

1. The equivalent resistivity of potassium salts is less than that of sodium salts.

2. The solubility of the potassium copper cyanide complex is greater than that of the sodium complex. This not only permits the use of higher metal concentrations but also reduces the need

for addition of free cyanide, since more is formed by dissociation of the stronger solution.

3. The solubility of potassium carbonate is greater than that of sodium carbonate, and hence higher concentrations of carbonate may be tolerated in potassium baths.

4. The potassium complex may be more stable than the sodium and hence be less rapidly decomposed when heated.

Potassium cyanide is not suitable for use in zinc or brass baths because of a lower solubility of potassium zinc cyanide.

The toxicity of all cyanide solutions makes it important to observe certain precautions in their use. The most important is to avoid the contact or addition of acid to any cyanide solution unless special ventilation is provided. The evolved gas, hydrocyanic acid, HCN, is very toxic if inhaled. Because some HCN is given off from cyanide baths, especially when heated, good ventilation should be provided, particularly for large installations or those operated at high current densities.

CHAPTER XII

GROUP 1B METALS: COPPER, SILVER, AND GOLD

GENERAL

The three metals copper, silver, and gold are all relatively noble; *i.e.*, their normal potentials are positive with respect to a hydrogen electrode. They become more noble as we descend from copper to gold. They are all easily deposited from solutions of their simple salts, such as the sulfates, or chlorides, but the deposits (except those of copper) are very coarsely crystalline and are usually not suitable for electroplating. Hence cyanide solutions are more commonly used. Chloride baths are sometimes used for very heavy gold deposits.

Each of these three metals has a valence of I in certain salts, in addition to which copper has a valence of II in cupric compounds, and gold has a valence of III in auric compounds. These valences are illustrated in the following table, in which the formulas of some of their compounds are listed. Crystals of many of these compounds contain *water of crystallization.*

COMMON COMPOUNDS OF COPPER, SILVER, AND GOLD

Compound	Copper		Silver, argentous, Ag^{I}	Gold	
	Cuprous, Cu^{I}	Cupric, Cu^{II}		Aurous, Au^{I}	Auric, Au^{III}
Oxide..........	Cu_2O	CuO	Ag_2O	Au_2O	Au_2O_3
Chloride........	$CuCl$	$CuCl_2$	$AgCl$	$AuCl$	$AuCl_3$
Sulfate.........	Cu_2SO_4	$CuSO_4$	Ag_2SO_4	Au_2SO_4	$Au_2(SO_4)_3$
Cyanide........	$CuCN$	$Cu(CN)_2$	$AgCN$	$AuCN$	$Au(CN)_3$
Double cyanide.	$K_2Cu(CN)_3$	....	$KAg(CN)_2$	$KAu(CN)_2$	

The complex cyanide solutions of the three metals all contain the metal with a valence of I. Cupric cyanide and auric cyanide are unstable, and when dissolved in excess of cyanide, they give off cyanogen and form the double cyanides listed above. The copper compounds $K_2Cu(CN)_3$ and $Na_2Cu(CN)_3$ are the most stable, but other copper compounds with more or less combined cyanide also exist under some conditions.

Copper is readily deposited from solutions of cupric sulfate, $CuSO_4$; cupric fluoborate, $Cu(BF_4)_2$; cupric pyrophosphate, $Cu_2P_2O_7$; and cupric alkane sulfonate, *e.g.*, $Cu(SO_3R)_2$, in all of which the valence of copper is II. Silver is deposited from silver nitrate for refining, and gold from auric chloride for refining and occasionally for plating thick deposits. Practically all the silver and gold plating and most of the copper plating are done in cyanide baths.

COPPER DEPOSITION

Applications and Choice of Baths. The most logical division of copper-plating baths is into the cupric (Cu^{II}) and cuprous (Cu^{I}) types, since the valence determines the electrochemical equivalent of the copper. As seen in Table 9 (Appendix), at 100 per cent cathode efficiency, 1 amp hr deposits 2.372 g of copper from cuprous baths and 1.186 g from cupric baths. It might therefore appear that the cuprous baths, *e.g.*, the cuprous cyanide, would always be more economical. However, many other factors such as the following must be considered.

In all the cupric salt baths, notably the copper sulfate bath, the cathode efficiency is practically 100 per cent, while in many cyanide copper baths the efficiency is not over 70 per cent and may be as low as 50 per cent. By the use of more concentrated cyanide baths, prepared with potassium salts, with low free cyanide and high alkalinity, efficiencies of nearly 100 per cent are obtained.

The cupric baths, especially the copper sulfate, are cheaper than the cyanide baths. The cupric salt baths are more stable than the cyanide baths; hence they require less time and attention for their control. Cyanide baths may be kept in plain steel tanks, but acid baths require a lead, rubber, or plastic lining.

Most of the cupric baths cannot be used to plate directly on steel or zinc, because they tend to deposit copper by immersion, usually in a nonadherent form. Hence, cyanide baths are generally employed to deposit at least an initial layer of copper. (The more concentrated cyanide copper baths also require an initial strike deposit on steel from a dilute copper cyanide bath.)

It is too early to evaluate the different types of cupric baths. To replace the very cheap, stable, copper sulfate bath, another bath must have its greater expense compensated for by specific advantages, such as higher permissible current densities, finer grained deposits, or greater ease of operation. The principal uses of the acid copper baths are in electrotyping and other applications of electroforming, *e.g.*, of phonograph matrices, and for relatively thick copper deposits, in many cases over an initial cyanide coating on steel.

Cyanide copper deposits are generally used to protect selected areas of steel against *casehardening*, though for thick deposits acid copper is sometimes applied over the cyanide copper. The thickness of copper required to prevent casehardening of steel depends upon the time and temperature of the hardening process. For most purposes coatings from 0.0005 to 0.001 in. (0.013 to 0.025 mm) are adequate. An important factor is the porosity, which is normally decreased by an increase in thickness. Copper coatings are also used to protect steel against scaling during heat-treatment and to facilitate deep-drawing operations.

Acid Copper Sulfate Bath. The two essential constituents are copper sulfate and sulfuric acid. The salt furnishes the metal ions, and the acid serves to reduce the resistivity, decrease the metal-ion concentration, increase the anode corrosion, and prevent precipitation of basic cuprous or cupric salts. The permissible concentrations and proportions of the copper sulfate and sulfuric acid are limited by the fact that addition of sulfuric acid decreases the solubility of copper sulfate, as shown in Table 20 (Appendix). The effect of acid upon the resistivity is shown in Table 21 (Appendix).

A typical formula for an air-agitated acid copper bath is as follows. The proportions are not critical, and frequently a lower concentration of sulfuric acid is employed.

ACID COPPER BATH

	N	g/l	avoir oz/gal	fl oz/gal
Copper sulfate, $CuSO_4 \cdot 5H_2O$	2	250	33	
Sulfuric acid, H_2SO_4	1.5	75	10	6

Temperature, 20 to 50°C (68 to 122°F)
Current density, 2 to 10 amp/dm^2 (20 to 100 amp/ft^2)

The exact purity of the copper sulfate is not important, since small amounts of nickel, zinc, or arsenic have practically no effect on the deposition or the properties of copper from acid sulfate solutions. On general principles it is desirable to use fairly pure copper sulfate, but no decided increase in cost is warranted.

Because additions of sulfuric acid are made more frequently than those of copper sulfate, relatively pure sulfuric acid, but not necessarily a C.P. grade, is desirable.

In continued operation, especially when air agitation is employed, as in electrotyping, the concentration of copper sulfate tends to increase and that of sulfuric acid to decrease. This change results from the fact that the anode efficiency is somewhat higher than the cathode efficiency. Since the latter is practically 100 per cent in the working range, it is evident that the apparent anode efficiency is over 100 per cent. This anomaly is explained by the fact that in copper sulfate solutions, copper may exist as both cupric sulfate, $CuSO_4$, and cuprous sulfate, Cu_2SO_4. Under normal conditions the concentration of cuprous salt is very low, and especially in the presence of oxygen from the air, it oxidizes to cupric sulfate. It is possible for copper to dissolve from the anode to form either cupric or cuprous salts or ions. At 100 per cent anode efficiency for solution of copper to form cuprous sulfate, twice as much copper is dissolved per ampere-hour as for cupric copper. The formation of even a small amount of cuprous salt at the anode therefore represents an excess of copper passing into solution above that deposited at the cathode. The cuprous salt then oxidizes in the solution to form cupric sulfate, from which the copper is principally deposited.

Some copper also dissolves in the bath when it is not in operation. This action depends upon the fact that cupric sulfate tends to react with copper to form cuprous sulfate.

$$Cu + CuSO_4 \leftrightarrows Cu_2SO_4$$

In contact with air this cuprous sulfate is oxidized to cupric, which permits the solution of the copper to continue.

$$2Cu_2SO_4 + O_2 + 2H_2SO_4 = 4CuSO_4 + 2H_2O$$

To correct this increase in copper content of the baths, it has been customary in electrotyping to discard a portion of the bath in order to remove part of the copper sulfate and then to add sulfuric acid and water to bring the solution to the normal composition. This wasteful practice can be avoided by using in part insoluble lead anodes to deposit part of the copper, whereby the copper content is reduced and sulfuric acid is regenerated. One practical objection to this procedure is that at insoluble anodes oxygen is evolved and carries into the air an irritating spray of the acid solution. Good ventilation must therefore be provided if insoluble anodes are used. A higher voltage is required, and cathodes opposite the lead anodes may receive less current than those opposite the copper.

Because the deposits of copper from acid sulfate baths are rather coarse grained and show a strong tendency toward treeing, addition agents are often employed. More addition agents have probably been proposed for acid copper baths than for any other. The most effective are the proteins, such as glue, which is universally employed in copper refining, usually in conjunction with *gulac*, an organic residue from the sulfite process for making paper pulp from wood. One serious objection to glue in copper-plating or electrotyping baths is that its effects are so pronounced that only a few parts per million are required or permitted and there is no satisfactory method of analysis for this small content of glue.

Another common type of addition agent for copper includes sugars, often added as molasses or as commercial dextrose. There is some evidence that the sugars, such as sucrose or the dextrose and levulose produced by its inversion in the acid solution, are less effective as addition agents than are the small amounts of impurities present, some of which, such as dextrin, are colloidal. In some cases starch has been added, because in the acid solution it forms dextrin.

Among the specific addition agents employed is phenol or carbolic acid, C_6H_5OH, which produces smoother and harder deposits in electrotyping.[1] It is usually added as phenolsulfonic acid, formed by combining the phenol with sulfuric acid. A concentration equivalent to 1 g/l (0.13 oz/gal) of phenol is adequate and is not critical. There is evidence that secondary products of the slow oxidation of the phenol, such as quinhydrone, may be more effective than the original phenol.

Increased use of copper plating in recent years has led to efforts to produce bright-copper deposits from acid baths. Among the proposed additions[2] is thiourea, N_2H_4CS, which produces semibright deposits that are relatively soft and can easily be buffed bright. A wetting agent, such as Triton 720, which is a salt of a sulfonated ether, can be used to increase the range of current

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[1] HULL, R. O., and BLUM, W., *J. Research Natl. Bur. Standards*, vol. 5, p. 767, 1930.

[2] CLIFTON, F. L., and PHILLIPS, W. M., *Proc. Am. Electroplaters' Soc.* p. 92, 1942.

density for good deposits. Molasses serves to reduce the tendency for striations at points of low current density. A typical formula for such a bath is as follows:

	g/l	oz/gal
Copper sulfate, $CuSO_4{\cdot}5H_2O$	250	33
Sulfuric acid, H_2SO_4	10–30	1.3–4
Thiourea, N_2H_4CS	0.01	0.0013
Molasses	0.8	0.1
Triton 720	0.2	0.03

This solution yields best results at or below 70°F (22°C) and a current density of 50 to 75 amp/ft^2 (5 to 8 amp/dm^2), provided good mechanical or air agitation is used.

Fluoborate Copper Bath. The fluoborate copper bath[1] is similar in many respects to the acid sulfate bath. The essential constituents and conditions are

	N	g/l	oz/gal
Copper fluoborate, $Cu(BF_4)_2$	2–4	224–448	30–60
(Copper, Cu)	2–4	60–120	8–16
Fluoboric acid, HBF_4	0.02	2	0.3

pH, 1.2–0.6

Temperature, 80–170°F (26–76°C)

Current density, without agitation, 150 amp/ft^2 (15 amp/dm^2)

Current density, with agitation, 300 amp/ft^2 (32 amp/dm^2)

Tests made by the authors mentioned showed that for equal copper concentrations, the fluoborate solution has a higher limiting current density than the sulfate copper bath. In addition the solubility of copper fluoborate (equivalent to about 120 g/l of copper or nearly 4*N*) is greater than that of copper sulfate in the presence of sulfuric acid (about 75 g/l of copper or 2.5*N*). Hence, especially in the more concentrated fluoborate bath, about twice as high a current density can be used as in the sulfate bath. To obtain the same current densities, however, it is necessary to use a higher voltage in the fluoborate bath, the resistivity of which is higher than that of the acid sulfate bath. This difference is largely the result of the much higher acidity of the sulfate bath. If much more than 2 g/l of free fluoboric acid is present in the fluoborate bath, its limiting current density is reduced.

There is no simple, adequate explanation for the higher limiting current density in the copper fluoborate bath with a given copper

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[1] Struyk, Clifford, and Carlson, A. E., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 33, p. 923, 1946.

concentration. It may be associated with the ability of fluoborates to prevent precipitation of basic copper compounds in the cathode film until a higher pH is reached than in the sulfate bath.

Alkane Sulfonate Copper Bath. This bath is also characterized by a high solubility of the copper salt and a relatively high limiting current density. Typical baths suggested by C. L. Faust[1] and associates have the following range of compositions and operating conditions.

	N	g/l	oz/gal
Basic copper carbonate....	0.8–3.2	45–180	6–24
Copper (metal)...........	0.8–3.2	25–100	3.3–13.3
Free alkane sulfonic acid...	0.04–0.08	5–10	0.7–1.3

Temperature, 120–150°F (50–65°C)

Current density, with moderate agitation, 100–600 amp/ft^2 (10–60 amp/dm^2)

From experiments with a bent cathode it was concluded that the fluoborate and alkane sulfonate copper baths, like the acid sulfate bath, have very poor throwing power compared with a cyanide bath. This behavior is to be expected in acid copper baths, in which there is little polarization and the cathode current efficiencies are uniformly high.

Pyrophosphate Copper Bath. This is an alkaline cupric bath that contains cupric pyrophosphate, an excess of potassium pyrophosphate, and free ammonia. The *Unichrome* bath is stated to have approximately the following composition and operating conditions:

	N	g/l	oz/gal
Metallic copper, Cu...............	1.0	30	4
Total pyrophosphate, P_2O_7.........	5	210	28
Ammonia, NH_3..................	0.2	3	0.4

Weight ratio, P_2O_7:Cu = 7

pH, 8.2–8.8

Temperature, 110–140°F (44–60°C)

Cathode current density, 10–70 amp/ft^2 (1–8 amp/dm^2)

Anode current density, 20–100 amp/ft^2 (2–11 amp/dm^2)

When this bath is agitated with air, especially at the higher temperature, ammonia is lost by evaporation and must be replaced by additions of ammonium hydroxide. Otherwise, the pH is adjusted by addition of potassium hydroxide.

It is necessary first to plate ferrous metals with copper from a cyanide bath before applying a deposit from the pyrophosphate

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[1] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 34, pp. 541, 709, 1947.

bath. Introduction of any cyanide into the pyrophosphate bath is deleterious. It can be removed by treatment with hydrogen peroxide. Deposits from this bath are relatively smooth and bright.

Amine Copper Bath. An amine bright copper bath has the following composition.[1]

	N	g/l	oz/gal
Copper sulfate, $CuSO_4{\cdot}5H_2O$.....	0.8	100	13.4
Ammonium sulfate, $(NH_4)_2SO_4$...	0.3	20	2.7
Diethylene triamine.............		80 (ml)	10 (fl oz)
pH (with ammonium hydroxide), 9.0			
Wetting agent			
Temperature, 25°C (77°F)			
Current density, 4 amp/dm² (40 amp/ft²)			

Cyanide Copper Baths. *Low-copper Baths.* A typical formula for a low-copper bath is as follows:

	N	g/l	oz/gal
Cuprous cyanide, CuCN.........	0.25	22.5	3
(Total copper, Cu)...............	0.25	16	2.1
Sodium cyanide, NaCN..........	0.65	34	4.5
(Free cyanide, NaCN)...........	0.15	7.5	1
Sodium carbonate, Na_2CO_3.......	0.30	15	2
pH, 11.5 to 12.5			

In former years it was customary to prepare a similar bath by dissolving basic cupric carbonate, $Cu(OH)_2{\cdot}CuCO_3$, in sodium cyanide. Sufficient of the latter must then be used to (1) reduce the cupric to cuprous compounds (with evolution of cyanogen, C_2N_2, which is poisonous), (2) form cuprous cyanide, (3) dissolve the cuprous cyanide, and (4) leave an excess, *i.e.*, free cyanide. The following formula will produce a bath essentially like the previous formula, except that it will contain a small amount of free sodium hydroxide, which will soon be converted to carbonate.

	N	g/l	oz/gal
Basic cupric carbonate, $Cu(OH)_2{\cdot}CuCO_3$	0.5	27.6	3.7
Sodium cyanide, NaCN..............	1.15	57	7.8
Sodium carbonate, Na_2CO_3...........	0.05	2.6	0.3

In the dilute copper bath it is customary (for bright deposits) to add as a brightener about 2 g/l or 0.25 oz/gal of sodium thiosulfate (*hypo*), $Na_2S_2O_3{\cdot}5H_2O$.

A temperature of about 40°C (104°F) is advantageous. Higher temperatures cause more rapid decomposition of the cyanide. At room temperature a current density of only about 5 amp/ft²

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[1] GREENSPAN, L., *Trans. Electrochem. Soc.*, vol. 78, p. 303, 1940.

(0.5 amp/dm²) is used, and at 40°C (104°F) about 15 amp/ft² (1.6 amp/dm²).

High-copper Baths. The so-called "high-speed" copper baths contain a high content of copper, usually combined as the potassium salt, a low content of free cyanide, a high content of potassium hydroxide, and a suitable wetting agent to prevent pitting. A typical formula for the Dupont bath is as follows:

	N	g/l	oz/gal
Cuprous cyanide, CuCN	0.66	53	7
(Equivalent to metallic copper, Cu)	0.66	42	5.6
Total potassium cyanide, KCN	1.44	98	13
(Free potassium cyanide, KCN)	0.12	7.5	1.0
Potassium hydroxide, KOH	0.75	42	5.6
Addition agent ("RH774")			0.25

Baths with about 50 per cent higher concentrations can be used.

The above bath is operated at 85°C (185°F) with cathode current densities from 30 to 60 amp/ft² (3 to 6 amp/dm²) and anode current densities from 10 to 30 amp/ft² (1 to 3 amp/dm²) in agitated baths. The anode and cathode efficiencies are close to 100 per cent.

The high current densities and high cathode efficiencies of this type of bath are largely the result of the high metal content. In addition, the resultant high concentration of combined cyanide reduces the required content of free cyanide, because the copper salt, $K_2Cu(CN)_3$, dissociates and acts as a reservoir for free cyanide. Especially at high temperatures it tends to decompose to form free cyanide ions, thus:

$$K_2Cu(CN)_3 \rightleftharpoons KCu(CN)_2 + KCN$$

or

$$Cu(CN)_3^{--} \leftrightarrows Cu(CN)_2^{-} + CN^{-}$$

The net result is to furnish enough cyanide ions to provide good anode corrosion and to keep the copper compounds in solution, without the rapid decomposition of free cyanide that normally occurs in hot solutions.

One limitation of this bath is that the effective cuprous ion concentration is sufficiently high to permit deposition of copper on steel or zinc by displacement. Hence it is usually necessary to give these metals an initial strike in a more dilute cyanide copper bath.

Rochelle Salt Copper Baths. In efforts to increase the cathode current density and efficiency of the regular cyanide copper bath, it was found that addition of *Rochelle salt*, sodium potassium tartrate, $NaKC_4H_4O_6 \cdot 4H_2O$, was advantageous. A typical formula for this bath is as follows:

	N	g/l	oz/gal
Cuprous cyanide, CuCN	0.3	26	3.5
(Copper, Cu)	0.3	19	2.5
Total sodium cyanide, NaCN	0.7	35	4.6
(Free cyanide, NaCN)	0.11	5.6	0.75
Sodium carbonate, Na_2CO_3	0.6	30	4.0
Rochelle salt, $NaKC_4H_4O_6 \cdot 4H_2O$	0.3	45	6.0
pH, 12.6			

This bath is operated at about 70°C (158°F), a cathode current density up to about 60 amp/ft^2 (7 amp/dm^2), and an anode current density of about 30 amp/ft^2 (3 amp/dm^2). Under these conditions the cathode efficiency is about 50 per cent.

The performance of the Rochelle salt bath is summarized by A. K. Graham and H. J. Read.[1] They attribute the beneficial effect of the tartrate to the formation of copper complexes that permit good anode corrosion with a lower content of free cyanide and yield higher cathode efficiencies at relatively high current densities. The successful use of this type of bath, in spite of the meager knowledge regarding the functions and mechanism of the tartrate, illustrates the need for basic studies on the constitution of plating baths.

Copper Anodes. There are three principal types of copper anodes, known as (1) *electrolytic cathodes*, (2) *cast copper*, and (3) *rolled copper*. All these are usually made from *electrolytic* copper, *i.e.*, copper that has been refined by electrolysis and is very nearly pure. The cathode sheets, sheared to convenient size, are the purest and cheapest and have found extensive use in electrotyping. They are usually rather thin (about 0.5 in. or 1.25 cm) and therefore may yield considerable scrap. If, as frequently occurs, there are laminations in the sheets, these may give rise to lacy residues that detach and cause roughness.

The cast-copper anodes may be made of any convenient size and shape, including bars and balls. In early years they often contained small amounts of oxide, probably cuprous oxide, which segregated at the grain boundaries and caused metallic particles to drop out during dissolution of the anodes. By greater care in melting and casting to yield a fine grain structure, this difficulty

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[1] *Trans. Electrochem. Soc.*, vol. 80, p. 341, 1941.

has been reduced. The use in cyanide baths of steel baskets, *e.g.*, to hold ball copper anodes, will introduce ferrocyanide into the baths.

Rolled copper anodes are made by rolling or extruding cast copper to the desired shape and thickness. This process reduces the grain size and promotes uniform corrosion. Rolled anodes are largely used in all copper baths.

SILVER PLATING

In spite of numerous researches on other types of silver baths, practically all silver plating is conducted in cyanide solutions. The latter are simple to prepare, are relatively stable, and have high anode and cathode efficiencies and good throwing power. Their chief drawback is the toxicity of the cyanide, which, however, is even less serious than with other cyanide baths used on much larger scales and at higher temperatures. Discussion will therefore be confined to the cyanide silver baths.[1]

The principal constituent is the double potassium silver cyanide, $KAg(CN)_2$, which is the only silver salt existing in significant amounts in a silver bath. For some years silver baths made with sodium cyanide were used, but it is now generally accepted that the potassium salts are superior because of (1) higher conductivity, (2) higher solubility of the resultant potassium carbonate, and (3) finer grained deposits.

All the cyanide in excess of $KAg(CN)_2$ is designated as free cyanide. As shown by R. M. Wick,[2] the end point of the titration of free cyanide with silver nitrate in the presence of potassium iodide corresponds very accurately to the compound $KAg(CN)_2$. Hence the *free cyanide* in a silver bath has a very definite meaning.

The simplest way to prepare such a bath is to dissolve silver cyanide, $AgCN$, in a solution of potassium cyanide. The use in early years of silver chloride, $AgCl$, resulted in the formation of an equivalent amount of potassium chloride, which does not seriously affect the bath operation, although it may lead to attack of steel tanks and hangers, with resultant contamination by ferrocyanide. If, as proposed by D. Wood,[3] large amounts of potassium nitrate are employed in silver baths, silver nitrate can logically be em-

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[1] For the potentials in silver deposition, *cf.* FINK, C. G., and HOGABOOM, G. B., JR., *Trans. Am. Electrochem. Soc.*, vol. 57, p. 99, 1930.

[2] *J. Research Natl. Bur. Standards*, vol. 7, p. 913, 1931, RP 384.

[3] *Proc. Am. Electroplaters' Soc.*, p. 150, 1937.

ployed as the source of silver, since it forms potassium nitrate when dissolved in potassium cyanide.

As in all cyanide baths, carbonate forms during the use of a silver cyanide bath and is added to a new bath. A summary of silver plating[1] concluded that the concentration of sodium carbonate should be kept below 45 g/l (6 oz/gal) while that of potassium carbonate may be permitted to reach 113 g/l (15 oz/gal). Moderate amounts of carbonate are beneficial in decreasing the resistivity, but an excess, especially of sodium carbonate, may cause coarse deposits and poor anode corrosion.

As mentioned above, Wood has recommended the addition of as much as 150 g/l or 20 oz/gal of potassium nitrate. This decreases the resistivity and permits good operation with a lower content of silver and of free cyanide. Its use is especially advantageous when, as is customary, carbon bisulfide is used as a brightener.

Partly because of the relatively high price of silver, the silver content of plating baths was formerly kept fairly low, *e.g.*, about 3 troy oz/gal (24 g/l). This practice limited the current density in former years to about 0.5 amp/dm^2 or 5 amp/ft^2 in still tanks. In conveyor tanks with mild agitation and at temperatures up to 27°C (80°F) current densities of 1.5 amp/dm^2 or 15 amp/ft^2 or more may be used.

The demand during the war for thick coatings of silver on airplane bearings led to efforts to increase the current density. It was early shown[2] that by use of more concentrated solutions, higher temperatures, and rapid agitation, current densities up to 200 amp/ft^2 (22 amp/dm^3) could be used. Later[3] it was reported that addition of potassium hydroxide is beneficial. In practice,[4] current densities up to 150 amp/ft^2 (16 amp/dm^2) were regularly used. The success in these unusual plating operations illustrates the fact that by the intelligent application of existing knowledge and principles, the range of plating conditions can be greatly broadened provided the results warrant the added care and expense. A general summary of methods and possible uses of

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[1] Promisel, N., and Wood, D., *Trans. Electrochem. Soc.*, vol. 80, p. 459, 1941.

[2] Simon, A. C., and Lumley, J. T., *Proc. Am. Electroplaters' Soc.*, p. 91, 1940.

[3] Schaefer, R. A., and Mohler, J. B., *Proc. Am. Electroplaters' Soc.*, p. 29, 1943.

[4] Hart, John S., and Heussner, C. E., *Monthly Rev. Am. Electroplaters' Soc.*, Mesle, F. C., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 33, p. 937, 1946.

silver plating will be found in the book "Silver in Industry," compiled by Lawrence Addicks.[1]

In almost all silver plating a brightener is used. The one most extensively employed is carbon bisulfide, CS_2. This is added in very minute amounts, *e.g.*, by first saturating a portion of the bath or preferably a separate solution of potassium cyanide with carbon disulfide and adding small portions of this solution to the bath at intervals. As carbon disulfide gradually evaporates, especially from warm solutions, it probably does not form any very stable compounds. It was early reported by Haring that, unlike most effective addition agents, it reduces the cathode polarization. In general, the effort is made to produce a semibright silver deposit that requires only light color buffing. Numerous other brighteners have been tried in silver baths, including many compounds of sulfur. Ammonium thiosulfate, $(NH_4)_2S_2O_3$, has been successfully used in the rapid silver plating of bearings. It can be more conveniently added than the carbon disulfide but may give rise to harmful secondary compounds.

Because most metals that are to be plated with silver will precipitate silver by immersion from the regular silver-plating baths and thus lead to poorly adherent deposits, it is customary to apply so-called silver "strike" solutions preparatory to the regular plating. With steel, two strike solutions, known as the *first* and *second strike*, are used, while for nickel and nickel alloys, brass, and copper a single strike is employed.

These strike solutions are simply silver-plating solutions in which the silver content is low and the free cyanide high. This combination produces so low a concentration of silver ions in the solution that the tendency for deposition of silver by replacement is reduced or eliminated. A relatively high current density is used, which counteracts any tendency for the basis metal to pass into solution. It is the practice to add a copper salt to the first silver strike. No copper is usually deposited with the silver from such a solution, and it is difficult to explain the benefit of the copper commonly used in this strike.

Another way to retard silver deposition by cementation is to coat the basis metal with another metal that is less reactive toward a silver bath. The oldest method, applied to copper and brass, involves immersion in a solution of a mercury salt, from which mercury is deposited by replacement. Because mercury amalgamates with the basis metal, a fairly good bond is obtained. One

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[1] Reinhold Publishing Corporation, New York, 1940.

objection is that the mercury may cause season cracking of cold-worked brass. The so-called "blue dip" contains about 1 oz/gal (7.5 g/l) of mercuric chloride, $HgCl_2$, and 0.5 oz/gal (4 g/l) of ammonium chloride. Another dip solution contains 1 oz/gal (7.5 g/l) of yellow mercuric oxide, HgO, and 8 oz/gal (60 g/l) of sodium cyanide, NaCN.

In plating steel, copper, brass, and nickel-brass it is customary first to coat with nickel, *e.g.*, from a nickel chloride strike solution (page 129), and then to use the silver strike on the nickel before silver-plating.

The following bath formulas are typical for these various applications of silver plating:

1. First Silver Strike on Steel

	N	g/l	oz/gal
Silver cyanide, AgCN	0.01	1.7	0.23
(Silver, Ag)	0.01	1.2	0.15 (troy)
Potassium cyanide, KCN	1.5	75	10
Copper cyanide, CuCN	0.16	15	2

2. Second Strike for Steel or First Strike for Brass, Nickel, Silver, and Britannia Metal

	N	g/l	oz/gal
Silver cyanide, AgCN	0.05	6.6	0.9
(Silver, Ag)	0.05	5.0	0.6 (troy)
Potassium cyanide, KCN	1.5	75	10
Potassium carbonate, K_2CO_3	0.2	15	2

3. Regular Silver Bath

	N	g/l	oz/gal
Silver cyanide, AgCN	0.27	36	4.8
(Silver, Ag)	0.27	29	3.5 (troy)
Potassium cyanide, KCN	0.92	60	8
(Free potassium cyanide, KCN)	0.65	42	5.6
Potassium carbonate, K_2CO_3	0.65	45	6.0
Carbon disulfide, CS_2		0.001	0.0001

Current density, 5–15 amp/ft² (0.5–1.5 amp/dm²)

Temperature, 27°C (80°F)

4. Nitrate-cyanide Silver Bath

	N	g/l	oz/gal
Silver cyanide, AgCN	0.17	23	3.0
(Silver, Ag)	0.17	18	2.2 (troy)
Sodium cyanide, NaCN	0.67	33	4.4
(Free cyanide, NaCN)	0.40	19	2.5
Sodium carbonate, Na_2CO_3	0.43	23	3.0
Potassium nitrate, KNO_3	1.5	150	20.0
Carbon disulfide		0.001	0.0001

Current density, still, 5–15 amp/ft² (0.5–1.5 amp/dm²)

Temperature, 27°C (80°F)

5. CONCENTRATED SILVER BATH

	N	g/l	oz/gal
Silver cyanide, AgCN	0.31	41	5.5
(Silver, Ag)	0.31	33	4.0 (troy)
Potassium cyanide, KCN	0.93	60	8.0
(Free cyanide, KCN)	0.62	40	5.3
Potassium carbonate, K_2CO_3	0.90	60	8.0
Potassium hydroxide, KOH	0.20	11	1.5

Current density (with rapid circulation), 100 amp/ft^2 (11 amp/dm^2)
Temperature, 45°C (113°F)

GOLD PLATING

Practically all gold plating is conducted from cyanide baths, usually containing potassium cyanide. In spite of the very extensive use of gold plating, comparatively little research has been conducted upon it. Hence there is not much quantitative information regarding such factors as polarization and cathode efficiency. As a result, most gold plating and especially gold *coloring* are done empirically, with little chemical control, although in recent years several large plants have been operated on a more scientific basis.[1]

One factor that has retarded the application of science in gold plating has been the frequent use of extremely thin gold coatings for purely ornamental purposes. Many such items as costume jewelry have gold coatings less than two-millionths of an inch (or 0.05 micron) thick. This is equivalent (at $35 per troy ounce of gold) to about 10 cents worth of gold per square foot. Such thin coatings furnish practically no protection against corrosion or abrasion. As they are commonly lacquered, however, they may have a fairly useful life.

There is a demand for and frequent application of somewhat thicker gold-plated coatings, of the order of 0.00001 in. (0.00025 mm), on articles such as tie clasps, cuff studs, and expensive safety razors, where good wear resistance is desired. Lacquer is also applied to increase their life.

There are relatively few applications of much thicker plated-gold coatings, partly because such coatings are likely to be dull and to require burnishing and partly because pure gold is relatively soft. An important war development was the application of as much as 0.001 in. of gold on radar equipment. For many purposes, *e.g.*, on watch cases, "rolled-gold" or "gold-filled" coatings are used, in

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[1] A comprehensive survey of methods of gold plating was published by J. B. Kushner in *Products Finishing*, vol. 5, 1940, and vol. 6, 1941.

which a gold alloy of a desired composition is rolled down with the basis metal, usually brass ("gilding metal"). Articles made of these composite sheets or wires are commonly gold-plated to protect cut edges and to yield a desired color to the surface.

In a method known as the *Bek* process,[1] gold (or a high-gold alloy) is plated onto brass articles and the assembly is then heated in an inert atmosphere to bring about alloying of the gold with the basis metal. The final result is a gold-alloy layer, varying in fineness from the outer surface, which is nearly pure gold, to the inner surface of more nearly pure brass. The final surface is usually gold-plated for color and finish.

In order to electrodeposit gold coatings having the color of specific gold alloys, such as rose gold (gold and copper), green gold (gold and silver), and white gold (gold and nickel), the appropriate metal is added to the gold-plating solution. The resultant plated alloys usually have a higher gold content than rolled alloys having the same color. For example, a plated 18 K gold-copper coating may resemble a rolled 14 K alloy or even a lower K alloy. [The fineness of gold alloys is expressed in terms of karats (K), *i.e.*, in twenty-fourths by weight. Pure gold is 24 K, and an 18 K alloy has 18/24, or 75 per cent, by weight of pure gold.] Often very small amounts of other metals are added to gold-plating baths to modify the exact color of the deposits, which, however, can also be governed by the conditions of plating. Unless a "colored" gold is specified, most plated-gold coatings have a fineness of at least 20 K. The use of karat marks, *e.g.*, 24 K, to define electroplated gold coatings is not generally approved, because it is difficult to control and to check the composition of very thin gold coatings.

Bath Composition. The essential constituents of a gold-plating bath are potassium aurocyanide, $KAu(CN)_2$, and free cyanide, KCN. Largely because of the high cost of gold, relatively weak gold solutions are commonly employed in order to reduce the investment and the loss by drag out. In general, the first rinse water from gold-plated articles is saved and used for replenishing the baths or is evaporated for gold recovery.

The concentration of gold is usually between 2 and 10 dwt/gal or 1 to 5 g/l, and the free cyanide is relatively high, *e.g.*, 3 to 15 g/l or 0.4 to 2 oz/gal of KCN. Carbonate or phosphate can be added to increase the conductivity and to serve as pH buffers. Typical formulas are as follows:

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[1] WEISBERG, L., *Metal Ind.* (*N.Y.*), vol. 34, p. 295, 1936.

	N	g/l	oz/gal
1. Metallic gold (as cyanide)	0.01	2.1	0.25 (troy)
Potassium cyanide, KCN	0.20	15	2.0
Sodium phosphate, $Na_2HPO_4 \cdot 12H_2O$	0.03	4	0.5
2. (For heavy deposits)			
Metallic gold (as cyanide)	0.04	8.4	1.0 (troy)
Potassium cyanide, KCN	0.16	11	1.4
(Free cyanide, KCN)	0.12	8	1.0

The gold may be introduced as the cyanide, AuCN, or as the double cyanide, $KAu(CN)_2$ or $NaAu(CN)_2$, which sometimes also contains some free cyanide. These compounds should be bought and used on the basis of their stated gold content, *e.g.*, 41 per cent gold. The gold cyanide is more stable and easily weighed. In early years it was customary to dissolve in potassium cyanide a precipitate of gold "fulminate," produced by adding ammonium hydroxide to a solution of gold chloride. The resultant compound of gold, hydrogen, nitrogen, and oxygen is very explosive and must be kept wet. It is now seldom used.

Another method that is sometimes used for preparing gold-plating solutions involves the anodic solution of gold in a cell with a porous cup. An insoluble cathode, *e.g.*, of steel, is put inside the porous cup, in which is placed a strong solution of potassium cyanide. Outside the cup is a solution of the desired strength of potassium cyanide, *e.g.*, 22.5 g/l (3 oz/gal). Anodes of pure gold or of certain alloys of gold are then placed in the outer compartment, and current is passed until the desired weight of gold is dissolved as determined by the loss in weight of the anode. Under these conditions none of the dissolved gold passes through the porous pot into the cathode compartment.

Gold-plating baths are commonly heated, *e.g.*, to about 70°C (158°F), and current densities of 0.1 to 0.5 amp/dm^2 (1 to 5 amp/ft^2) are used. In general, the permissible current density depends upon the concentration of gold. With higher gold content, such as 1 troy oz/gal (8.2 g/l) of gold, current densities of 1 amp/dm^2 (10 amp/ft^2) can be used, with a cathode efficiency close to 100 per cent.

Additions of formate or benzoate have been suggested for plating gold directly on steel. By the use of a *gold strike*, low in gold and high in cyanide, followed by a more concentrated gold bath, adherent deposits can be applied directly to steel.

The anodes usually consist of pure gold unless colored deposits are desired, in which case suitable gold alloys are employed. Because gold tends to dissolve with a higher anode than cathode efficiency, the gold content of the baths may increase. To avoid this condition, part of the gold anodes may be replaced with steel or carbon anodes. In some cases it is advantageous to employ entirely insoluble anodes, *e.g.*, of steel, Duriron, or carbon, and to replenish the gold content by the addition of the double gold cyanide. Insoluble chromium-iron anodes can be used if no chloride or free alkali is present in the bath. In principle this method would increase the content of free cyanide, but in practice it is likely about to compensate for the conversion of cyanide to carbonate.

Occasional use is made of a gold chloride bath for producing thick gold deposits, which, however, are more coarse-grained than from cyanide baths. Such a solution may contain from 16 to 32 g/l (2 to 4 troy oz/gal) of gold, introduced as gold chloride or "chlorauric acid" $AuCl_3 \cdot HCl \cdot 4H_2O$, which, when pure, contains 48 per cent of gold together with about 5 per cent of hydrochloric acid. (The commercial salt contains about 50 per cent of gold.) As in this bath the gold is in the trivalent state, Au^{III}, only one-third as much gold is deposited per ampere-minute as from a cyanide bath at 100 per cent efficiency.

Salt-water Gold. In another method of gold plating, known as the *salt-water gold-plating process,* the current is furnished by the solution of a piece of zinc that acts as anode in a cell with a porous cup.[1] Around the porous cup a sheet of zinc is immersed in a 20 per cent solution of sodium chloride, NaCl. The gold-plating solution is placed within the cup. When an object is hung on the copper cathode bar, the circuit is closed, zinc dissolves in the outer compartment, and gold is deposited on the article in the cup. A typical solution for the salt-water process is as follows:

	N	g/l	oz/gal
Metallic gold, Au, as cyanide	0.006	1.2	0.15 (troy)
Sodium ferrocyanide, $Na_4Fe(CN)_6 \cdot 10H_2O$	0.12	15	2
Sodium phosphate, $Na_2HPO_4 \cdot 12H_2O$	0.06	7.5	1
Sodium carbonate, Na_2CO_3	0.08	4	0.5
Sodium sulfite, Na_2SO_3	0.002	0.15	0.02

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[1] More details of this method are contained in the second edition of this book, p. 368.

This solution is usually boiled and filtered before use and is operated at about 70°C (158°F). Deposits made by this method are relatively thin but uniform in thickness and color.

Dip Gold. In the dip-gold process the coating is produced by immersing the articles, usually of brass, into a suitable gold solution for a short period. The zinc and copper of the brass pass into solution and are replaced by gold, similar to the action that takes place when steel is introduced into copper sulfate and is coated with copper. Because the process stops when the basis metal is completely covered, the coatings are always thin, *e.g.*, they may be only 0.000001 in. (0.000025 mm) thick. For such thin coatings they are relatively free from pores, possibly because the volume of gold deposited by zinc or copper is about twice that of the metal displaced. As the dip coatings are cheaply made, they serve a useful purpose when very thin coatings are applicable, *e.g.*, on cheap, perishable articles. The luster and color of the gold coatings depend largely upon the finish of the brass to which they are applied, and on the bath content of zinc and copper derived from the dipping.

Many complicated solutions have been employed for dip gold, some of which contain ferrocyanide. Satisfactory results can be obtained from a simple solution such as the following:

DIP GOLD

	N	g/l	oz/gal
Metallic gold, Au, as cyanide	0.01	2.1	0.25 (troy)
Potassium cyanide, KCN	0.18	12	1.6
Free cyanide, KCN	0.17	11	1.5

This solution is first heated in a stone crock or enameled vessel for a few hours, and is operated at about 80°C (176°F).

CHAPTER XIII

GROUP 2B METALS: ZINC, CADMIUM, AND MERCURY

GENERAL CONSIDERATIONS

Even though there is almost no industrial application of mercury deposition, its inclusion in this chapter may serve to illustrate and emphasize differences in the deposition of zinc and cadmium. For example, the metals become more noble in the order zinc, cadmium, and mercury. It is therefore easier to deposit cadmium than zinc, and mercury is the most easily deposited. Zinc will displace cadmium from its solutions, and practically all common metals will displace mercury from its salts. For this reason the coating of metals with mercury is usually accomplished by their immersion in a solution of a mercury salt. The fact that mercury is a liquid at ordinary temperature assists it to alloy, *i.e.*, to *amalgamate* with metals on which it is deposited.

Both zinc and cadmium exist in salts almost entirely with a valence of two; hence their simple salts have the formulas shown in the following table. Mercury has two series of salts: mercurous with a valence of I and mercuric with a valence of II.

TYPICAL COMPOUNDS OF ZINC, CADMIUM, AND MERCURY

Compound	Zinc, Zn^{II}	Cadmium, Cd^{II}	Mercury	
			Mercurous, Hg^{I}	Mercuric Hg^{II}
Oxide	ZnO	CdO	Hg_2O	HgO
Chloride	$ZnCl_2$	$CdCl_2$	$HgCl$	$HgCl_2$
Sulfate	$ZnSO_4$	$CdSO_4$	Hg_2SO_4	$HgSO_4$
Cyanide	$Zn(CN)_2$	$Cd(CN)_2$	$HgCN$	$Hg(CN)_2$
Double cyanide	$Na_2Zn(CN)_4$	$Na_2Cd(CN)_4$		$NaHg(CN)_3$

Zinc is *amphoteric*, *i.e.*, it may act as a base or an acid. As a base it forms salts such as zinc chloride or sulfate, $ZnCl_2$ or $ZnSO_4$. As an acid it combines with a strong base to form a *zincate*, such as Na_2ZnO_2, sodium zincate, produced by dissolving zinc oxide in sodium hydroxide. Neither cadmium nor mercury is amphoteric.

Among the minor applications of mercury in electroplating are the following: It is sometimes introduced into zinc anodes to promote their uniform dissolving and to decrease the solution of zinc anodes when no current is passing. It can also be introduced into zinc cyanide solutions to produce bright-zinc deposits that contain a small amount of mercury. Mercury salts are used in dips before silver-plating.

ZINC DEPOSITION

General. Zinc can be deposited from both acid and alkaline baths. The acid baths consist of sulfate, chloride, or fluoborate, and the alkaline baths usually contain both cyanide and zincate. Pyrophosphate baths are also alkaline. The alkaline baths have better throwing power and are therefore most commonly used to plate irregularly shaped articles. The acid baths are used to plate wire and sheet metal, where good throwing power is not required. Cyanide baths cannot be used to deposit zinc directly on malleable or cast iron unless special steps are taken in the preparation of the basis metals.

Acid Zinc Baths. A summary and extensive bibliography of the composition and use of acid zinc baths was published[1] in 1942.

Consideration of the electrochemical series (page 423) shows that the normal potential of zinc is over 0.7 volt more negative than that of hydrogen, *i.e.*, that hydrogen is much more easily discharged than zinc. It might therefore be predicted that it would be impossible to deposit zinc, at least with any good cathode efficiency, from acid solutions. The fact that it is possible to do so depends upon the high overvoltage (page 53) of hydrogen on zinc. Actually, as in the Tainton process (page 309), zinc can be deposited with high cathode efficiencies from strongly acid solutions provided they are pure. The presence of very small amounts of certain metals, such as cobalt and nickel, lowers the overvoltage of hydrogen on zinc and greatly decreases the cathode efficiency.

The principal salt used in acid zinc baths is zinc sulfate, the crystals of which have the formula $ZnSO_4 \cdot 7H_2O$. It is customary to employ high concentrations of zinc sulfate, *e.g.*, up to 400 g/l

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[1] LYONS, ERNEST H., JR., *Trans. Electrochem. Soc.*, vol. 80, p. 387, 1941.

(53 oz/gal) of $ZnSO_4 \cdot 7H_2O$. This high concentration facilitates deposition of zinc by increasing the ratio of zinc to hydrogen ions and also of zinc to any impurities that may be introduced, *e.g.*, from the anode. The other essential constituent is sulfuric acid. Its concentration may be very small, *i.e.*, just sufficient to maintain a desired pH of 3 to 4, but in certain methods the acid content may be very high.

One special application of acid zinc plating is the *Tainton process*,[1] in which insoluble lead-silver anodes are used, principally for plating on steel wire. The solution of zinc sulfate is prepared by dissolving zinc ore or impure zinc in sulfuric acid and rigidly purifying the resultant solution. It contains a relatively high concentration of sulfuric acid, *e.g.*, as high as 75 g/l (10 oz/gal), which is still further increased by the liberation of acid during the plating. The spent liquid is removed and is used to dissolve more zinc ore. Because the plating bath is highly acid and very pure, and because the wires to be plated are moved through the bath very rapidly, current densities as high as 1,500/amp/ft^2 (160 amp/dm^2) can be used.

Additions of large amounts of a chloride such as sodium or ammonium chloride to a zinc sulfate bath greatly reduce its resistivity[2] and hence decrease treeing and slightly increase throwing power. One objection to the high-chloride zinc bath is the added corrosion of bus bars and coils and consequent contamination of the bath. Addition of chlorides to the bath to increase corrosion of zinc anodes is unnecessary.

In ordinary acid zinc baths, where it is not feasible to maintain the high purity of the Tainton baths, it is desirable to maintain a pH between 3 and 4. The usual high anode efficiency and the solution of the zinc anodes when not in use tend to maintain or slightly exceed the desired pH, so that it is necessary to add small amounts of sulfuric acid daily or more frequently. These additions of acid may make the bath "self-sustaining"; *i.e.*, they may form enough zinc sulfate to make up for losses by drag out. The use of buffer salts, such as sodium acetate, may stabilize the pH. Addition of aluminum chloride also furnishes a buffer in this range, because aluminum hydroxide tends to precipitate at a pH of about 4, and the appearance of the white flocculent $Al_2(OH)_6$ indicates the need for more acid.

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[1] TAINTON, C., *Steel*, vol. 98, p. 40, May 18, 1936.

[2] THOMPSON, M. R., *Trans. Am. Electrochem. Soc.*, vol. 50, p. 193, 1926.

Especially at low current densities, acid zinc baths tend to produce coarse-grained deposits, which may even consist of isolated crystals. Organic addition agents, such as licorice, dextrin, glycerin, and beta-naphthol, produce finer grained deposits and slightly improve the throwing power. They are not used primarily as brighteners, because acid zinc deposits are usually whiter and brighter than the cyanide deposits produced without addition agents.

While zinc fluoborate solutions have been proposed, they have not come into use sufficiently to demonstrate their advantages and limitations. Their constitution and behavior are probably similar to those of copper fluoborate baths.

TYPICAL FORMULAS AND OPERATING CONDITIONS FOR ACID ZINC BATHS

		N	g/l	oz/gal
1.	Zinc sulfate, $ZnSO_4 \cdot 7H_2O$	1.7	240	32
	Ammonium chloride, NH_4Cl	0.3	15	2
	Aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$	0.25	30	4
	Licorice		1	0.13
2.	Zinc sulfate, $ZnSO_4 \cdot 7H_2O$	2.5	360	48
	Ammonium chloride, NH_4Cl	0.6	30	4
	Sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$	0.1	15	2
	Glucose, $C_6H_{12}O_6$		120	16
3.	Zinc sulfate, $ZnSO_4 \cdot 7HO$	3.0	410	54
	Aluminum chloride, $AlCl_3 \cdot 6HO$	0.25	20	3
	Sodium sulfate, Na_2SO_4	1.0	75	10

pH, 3–4.5

Temperature, 20–30°C (72–85°F)

Current density

In still baths, 2–3 amp/dm^2 (20–30 amp/ft^2)

In agitated baths, 2–10 amp/dm^2 (20–100 amp/ft^2)

Alkaline Zinc Baths. Cyanide Baths. For a summary and bibliography of cyanide zinc plating baths, consult R. O. Hull and C. J. Wernlund.[1] The principal constituent of alkaline zinc baths is the double cyanide $Na_2Zn(CN)_4$. In addition the baths always contain sodium zincate, Na_2ZnO_2, and free sodium cyanide or sodium hydroxide or both. In principle it is immaterial whether the bath is prepared from zinc cyanide and sodium hydroxide or from zinc oxide and sodium cyanide, with necessary additions to yield the final desired composition. The above relations may be

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[1] *Trans. Electrochem. Soc.*, vol. 80, p. 407, 1941.

most conveniently explained for a simple bath by reference to the normalities.

The same composition of bath results from either of the following formulas:

	N	g/l	oz/gal
1. Zinc cyanide, $Zn(CN)_2$	1.0	60	8
Sodium cyanide, NaCN	0.5	23	3
Sodium hydroxide, NaOH	1.3	53	7
2. Zinc oxide, ZnO	1.0	45	6
Sodium cyanide, NaCN	1.5	75	10
Sodium hydroxide, NaOH	0.3	15	2

Such a solution has a zinc content of $1.0N$, a total cyanide content of $1.5N$, and a total alkali content of $1.3N$. It is not possible to state what compounds or concentrations are actually present in such a bath. If we arbitrarily assume that the zinc first combines with the cyanide to form the double cyanide $Na_2Zn(CN)_4$ and that any excess of zinc combines with the sodium hydroxide to form sodium zincate, Na_2ZnO_2, the above solution would contain $0.75N$ $Na_2Zn(CN)_4$, $0.25N$ Na_2ZnO_2, and $0.8N$ free NaOH.

A. K. Graham[1] proposes to control this bath by maintaining a definite zinc content and a desired value of R, defined thus:

$$R = \frac{\text{NaCN normality} + \text{NaOH normality}}{\text{Zn normality}}$$

In the above case

$$R = \frac{0.5 + 1.3}{1.0} = 1.8$$

In other words, the sum of alkali cyanide and hydroxide is equivalent to 1.8 times that required to keep the zinc in solution; hence there is an excess in the ratio of 0.8 (in this case $0.8N$) of sodium hydroxide plus cyanide.

Hull and Wernlund base their control of this bath on the zinc content and the weight ratio M of total cyanide (expressed as NaCN) to zinc, with independent definition of the total alkali.

$$M = \frac{\text{total cyanide (as g/l NaCN)}}{\text{g/l zinc}}$$

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[1] *Trans. Electrochem. Soc.*, vol. 63, p. 129, 1933.

In the above example

$$M = \frac{1.5\,N \times 49 \text{ g/l}}{1.0 \text{ N} \times 32.7 \text{ g/l}} = \frac{74}{32.7} = 2.36$$

This value of M is within the range of 2.0 to 2.5 recommended by Hull and Wernlund for plain baths. (The same result might be expressed more simply as the ratio of normalities of total cyanide and zinc, in this case 1.5.)

Fortunately it is possible (page 192) to determine by analysis the total cyanide, alkali, and zinc in this bath and thus to control its operation. Determination of the free cyanide is not possible, and its value would be meaningless.

Three types of zinc cyanide baths are in use, *viz.*, (1) plain baths for dull deposits; (2) baths containing small amounts of mercury or other metals such as cobalt, nickel, or molybdenum and producing relatively white deposits; and (3) those with organic additions that produce bright deposits. Extensive tests have shown that a given thickness of zinc produced by any of these processes yields about the same protective value in the atmosphere. Hence when protection of steel against corrosion is the only consideration, there is no advantage in using bright deposits, which may even be objectionable, *e.g.*, on military supplies where light reflection is undesirable. One advantage of bright zinc is a reduced tendency to staining. Zinc deposits from different baths may differ in hardness and ductility and in their behavior in subsequent forming operations.[1]

The bath used above for illustration (page 311) represents a typical plain cyanide zinc bath, which can be operated at 40 to 50°C (104 to 140°F) with current densities up to 2 amp/dm^2 (19 amp/ft^2). By increasing the concentrations, current densities up to 12 amp/dm^2 (110 amp/ft^2) can be used at 70°C (158°F), although high temperatures are not commonly used. The following formula is then recommended:

	N	g/l	oz/gal
Zinc cyanide, $Zn(CN)_2$	1.5	9.0	12
Sodium cyanide, NaCN	0.75	37.5	5
Sodium hydroxide, NaOH	2.25	90	12

Zinc deposits from plain cyanide baths are often brightened by *dipping* in solutions of nitric or chromic acid, such as are also used for cadmium (page 317).

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[1] HOGABOOM, G. B., *Proc. Am. Electroplaters' Soc.*, p. 255, 1936.

A typical bath containing mercury has the following composition:

	N	g/l	oz/gal
Zinc cyanide, $Zn(CN)_2$	0.63	37.5	5
Sodium cyanide, NaCN	0.45	22.5	3
Sodium hydroxide, NaOH	0.75	30	4
Mercuric oxide, HgO	0.02	0.25	0.03

Temperature, 40°C (104°F)
Cathode current density, up to 4 amp/dm^2 (37 amp/ft^2)
Anode current density, 1–1.5 amp/dm^2 (10–15 amp/ft^2)

Such baths are not now used extensively, because mercury in the deposits may be objectionable for some purposes, *e.g.*, in contact with brass.

For bright plating from cyanide zinc baths, the most important factor is the elimination of metallic impurities such as copper and lead. It is therefore customary to purify such baths at intervals by addition of sodium sulfide, which precipitates lead but not copper, or of zinc dust, which precipitates both of these impurities.

The ratio of total cyanide to zinc, expressed by Hull and Wernlund as *M* (page 311), is more critical in bright baths and is usually kept between 2.5 and 2.7 (or, in terms of the ratio of normalities, between 1.6 and 1.7). The higher the value of *M* the greater must be the current density to secure bright plating.

A large number of brighteners, summarized by Hull and Wernlund, have been proposed for zinc plating baths. Most of these are complex organic compounds, the exact functions of which have not been defined. Some of them serve to counteract the effects of small amounts of harmful metallic impurities, *e.g.*, by forming complex compounds with them. Molybdenum, also used as a brightener, is believed to act in this way.

Typical formulas for bright-zinc baths (to which brighteners are also added) have been summarized as follows:

	N	g/l	oz/gal
Zinc cyanide, $Zn(CN)_2$	1.0–1.4	60–82	8–11
Sodium cyanide, NaCN	0.4–1.3	19–64	2.5–8.5
Sodium hydroxide, NaOH	1.9–2.8	75–112	10–15

Temperature, 28–38°C (82–100°F)
Current density, 1–5 amp/dm^2 (10–50 amp/ft^2)

Because of the usual high content of sodium hydroxide, the pH of all the cyanide zinc baths is relatively high and is probably not so critical as with some other cyanide baths. A. G. Gray[1] concluded that a pH of about 13 to 13.5 yielded the best deposits from both plain and bright baths. This is about the range reported by G. B. Hogaboom.[2] It is probable that this extremely alkaline condition can be better controlled by titrations of the free alkali than by pH measurements.

Pyrophosphate Zinc Baths. The pyrophosphate zinc bath consists essentially of zinc pyrophosphate dissolved in an excess of potassium pyrophosphate, together with a brightener and a wetting agent. The *Unichrome bath* is stated to have about the following composition and operating conditions:

	N	g/l	oz/gal
Zinc pyrophosphate, $Zn_2P_2O_7 \cdot 3H_2O$	0.7	65	9
Potassium pyrophosphate, $K_4P_2O_7$	4.3	360	48
(Zinc, Zn)	0.7	25	3.3
(Total pyrophosphate), P_2O_7	5.0	225	30
Brightener		0.5	0.07
Wetting agent		0.5	0.07

pH, 11.0–11.6
Temperature, 38–50°C (100–122°F)
Current density, 1.5–5 amp/dm^2 (15–50 amp/ft^2)

Zinc Anodes. There are three principal grades of zinc that might be used as anodes, known as (1) prime Western spelter, with up to 98.5 per cent of zinc; (2) intermediate grade, 99.5 to 99.8 per cent of zinc; and (3) high purity, with 99.95 to 99.98 per cent of zinc. The prices increase with the purity. On general principles it is especially desirable to produce deposits of nearly pure zinc, because the presence of very small amounts of impurities such as copper and lead in the deposits may accelerate corrosion of the zinc and thus reduce the life of the coatings. Undoubtedly the usual high purity of electrodeposited zinc coatings accounts for the fact that, especially under mild conditions of exposure, they last longer than hot-dipped coatings of the same thickness.

It is in general more important to use high-purity zinc anodes in cyanide baths than in acid baths. In the latter, most of the impurities in the anodes are insoluble and remain in the anode sludge. They may then detach and cause rough zinc deposits, or they may accelerate secondary corrosion of the zinc when no current is passing, but they are unlikely to be deposited with the

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[1] *Proc. Am. Electroplaters' Soc.*, p. 36, 1941.

[2] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 24, p. 713, 1937.

zinc. On the other hand, in cyanide baths these impurities may dissolve and be deposited with the zinc to cause dark deposits that cannot be bright-dipped and may have less protective value. For this reason it is preferable to use the highest purity zinc anodes in cyanide baths.

To overcome the effects of small amounts of impurities in zinc anodes for cyanide baths, various additions are made to the zinc anodes.[1] Addition of a small amount of aluminum has been used to promote uniform corrosion and reduce the chemical attack when not in use. Small additions of magnesium or of calcium to zinc anodes have been recommended as a means of reducing the anode efficiency to approximately the cathode efficiency, *e.g.*, 90 per cent.

In the absence of any additions, zinc anodes always tend to dissolve, either chemically or electrochemically, so as to increase the zinc content of the bath. The introduction of some steel anodes in the alkaline baths or of lead anodes in the acid baths counteracts a too high anode efficiency but may accelerate corrosion of the zinc when not in use.

CADMIUM PLATING

While it is possible to deposit cadmium from acid baths such as the sulfate or fluoborate, such deposits are usually coarsely crystalline unless very effective addition agents are used. Moreover, the acid baths have very poor throwing power. Cadmium plating is therefore done almost entirely from the cyanide baths. The literature and practice on these baths have been summarized by G. Soderberg and L. R. Westbrook.[2]

It is difficult to decide whether in cadmium baths the principal compound is $NaCd(CN)_3$ or $Na_2Cd(CN)_4$. M. R. Thompson[3] and also N. Hall[4] concluded that both compounds are probably present. The titration of free cyanide (page 192) in cadmium baths gives erratic results and it is preferable to determine the total cyanide, in which case no assumptions regarding the constitution of the complex cyanides are directly involved. For convenience, in

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[1] Graham, A. K., and Hogaboom, G. B., *Trans. Electrochem. Soc.*, vol. 62, p. 49, 1932.

[2] *Trans. Electrochem. Soc.*, vol. 80, p. 429, 1941.

[3] *Trans. Electrochem. Soc.* vol. 79, p. 417, 1941.

[4] *Metal Finishing*, vol. 37, p. 404, 1939.

computing the formulas of cadmium baths the presence of $NaCd(CN)_3$ will be arbitrarily assumed.

It is possible to prepare the cadmium baths either from cadmium cyanide, sodium cyanide, and sodium hydroxide or from cadmium oxide and sodium cyanide. The latter is more commonly used because cadmium oxide of the requisite purity is more readily available than the cyanide. When cadmium oxide is dissolved in sodium cyanide, sodium hydroxide is produced; thus

$$CdO + 3NaCN + H_2O = NaCd(CN)_3 + 2NaOH$$

Unlike zinc, cadmium is not amphoteric and does not form a compound similar to the zincate. The sodium hydroxide produced in the reaction is therefore present in the bath and increases its conductivity but it is not otherwise important or critical.

These principles may be illustrated by the following two formulas, which produce baths with identical compositions:

		N	g/l	oz/gal
1.	Cadmium oxide, CdO	0.5	32	4.2
	Sodium cyanide, $NaCN$	1.5	75	19
2.	Cadmium cyanide, $Cd(CN)_2$	0.5	41	5.5
	Sodium cyanide, $NaCN$	1.0	49	6.5
	Sodium hydroxide, $NaOH$	0.5	20	2.7

(On the above assumption, such a solution is $0.5N$ in $NaCd(CN)_3$, $0.75N$ in free $NaCN$, and $0.5N$ in free $NaOH$.)

Commercial baths may vary in cadmium concentration by about 50 per cent above and below this formula. Higher concentrations of cadmium permit higher current densities but involve greater investment and loss by drag out. Soderberg and Westbrook advise a weight ratio $R = \frac{\text{total NaCN (g/l)}}{\text{Cd (g/l)}}$ of about 3.75, which is equivalent to a normality ratio, *i.e.*, $\frac{\text{total NaCN}(N)}{\text{Cd }(N)}$ of 4.3. In the above example the weight ratio is $75/28 = 2.7$ and the normality ratio is $1.5/0.5 = 3.0$. To bring the above formula to their recommended value of R would require the addition in formula 1 of $0.7N$, *i.e.*, 35 g/l or 4.7 oz/gal, of $NaCN$.

It is a universal practice to employ brighteners in cadmium baths. These are usually organic substances, which may be definite compounds, such as certain sulfonic acids, or furfural compounds or complex mixtures, such as wool extract, condensed milk, instant postum or gulac (from the sulfite pulp process). In concentrated baths for use at high current densities, small amounts of nickel or cobalt are sometimes added. A trace of nickel may deposit with the cadmium, but apparently no cobalt. Cadmium deposits containing these metals cannot be readily bright-dipped. A typical formula for such a bath is as follows:

	N	g/l	oz/gal
Cadmium oxide, CdO	0.7	45	6
Sodium cyanide, NaCN	2.5	120	16
Addition agents			

This bath is used at room temperature at 2 amp/dm^2 (20 amp/ft^2).

Cadmium plating is generally conducted at room temperature, *e.g.*, from 70 to 95°F (20 to 35°C). The cathode current density may vary from 5 to 50 amp/ft^2 (0.5 to 5 amp/dm^2), but the anode current density should usually not exceed 20 amp/ft^2 (2 amp/dm^2) to secure a high anode efficiency. The carbonate content should not be allowed to exceed from 6 to 10 oz/gal (45 to 75 g/l) of Na_2CO_3.

Anodes and chemicals for cadmium plating should be nearly free from impurities. One government specification for anodes requires a minimum of 99.9 per cent of cadmium, with not more than 0.05 per cent of silver plus lead plus tin or 0.005 per cent of arsenic plus antimony plus thallium. These impurities, particularly lead, are especially objectionable if bright-cadmium deposits are desired or if deposits are to be bright dipped.

It is customary to *dip* cadmium coatings (and also zinc coatings) into oxidizing solutions, which brighten the deposits and also render the surfaces passive, so that they resist tarnish and are not so easily finger-marked in handling.

The three most commonly used oxidizing agents for cadmium dips are (1) nitric acid, (2) chromic acid, and (3) hydrogen peroxide. Typical formulas for these dips are

1. 1 per cent by volume of nitric acid, sp gr 1.42.
2. 100 g/l (13.3 oz/gal) of CrO_3 and 2 g/l (0.27 oz/gal) of H_2SO_4.
3. 70 g/l (9 oz/gal) of 30 per cent H_2O_2 and 5 g/l (0.7 oz/gal) H_2SO_4.

The time of dipping is usually from 2 to 30 sec. It should be made as short as practicable; otherwise sufficient cadmium will be dissolved to reduce the thickness and protective value materially.

MERCURY DEPOSITION

While there are almost no commercial applications of the electrodeposition of mercury, it will be briefly discussed for completeness. Because it is so noble a metal, mercury can be readily deposited from practically any of its soluble salts. Because it is liquid at room temperatures, the deposits have no definite crystal structure. On most metal cathodes, any deposited mercury tends to alloy with the basis metal to form amalgams, many of which are solids.

CHAPTER XIV

GROUP 3B METALS: ALUMINUM, GALLIUM, INDIUM, AND THALLIUM

GENERAL CONSIDERATIONS

These four metals all have a valence of III, and thallium also has a valence of I in its most stable compounds. As in other vertical groups, the metals become more noble as we descend; *i.e.*, it is easier to deposit thallium than gallium. Each of these metals resembles in its properties those of the adjacent metals in the horizontal periods. Thus gallium is somewhat similar to zinc, indium is similar to cadmium, and thallium is much like lead.

There is no conclusive evidence that aluminum has ever been deposited from an aqueous solution. In at least one case in which deposition of aluminum from an aqueous solution was reported,[1] it is highly probable that the deposit was obtained from a bath containing salts of both zinc and aluminum and that the deposit consisted of zinc. Aluminum is regularly produced by electrolysis of its fused salts, principally from fused cryolite, Na_3AlF_6, in which Al_2O_3 is dissolved. Because of the high temperatures required in this process, it is not used to coat metals with aluminum. This metal can be deposited from organic electrolytes, which will be briefly described in this chapter.

The remaining three metals illustrate the fact that, if a metal is readily available, some use is generally found for it and, conversely, if the metal is useful, new sources of supply are generally found. Gallium, which is a liquid at ordinary temperature (mp 30°C or 86°F), is the most scarce of these three metals, and few uses have been suggested for it or coatings of it. Indium was also considered rare but is now quite available. It has found some special uses, the most notable of which is in airplane bearings. The latter are first coated with silver, usually at high current densities (page 299). They are then plated with a thin coating of lead followed by just sufficient indium to produce a lead-indium alloy

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[1] *Sci. American*, Oct. 22, 1892, reprinted in *Metal Finishing*, vol. 45, No. 5, p. 66, 1947. See comment in *Metal Finishing*, vol. 45, No. 8, p. 97, 1947.

of the desired composition, *e.g.*, with 4 per cent of indium. The bearing is then heated in oil for 2 hr to about 350°F (177°C), and the lead and indium form an alloy layer that is very resistant to corrosion by engine oils or the products of their oxidation.

Thallium is the cheapest of these three metals, but no important uses have been found for thallium coatings. It is possible that thallium-alloy deposits, *e.g.*, with lead, may find use on anodes for copper refining.

ALUMINUM DEPOSITION (FROM ORGANIC BATHS)

Various authors have shown that, when an aluminum salt, *e.g.*, aluminum bromide, $AlBr_3$, is dissolved in an organic solvent such as ethyl bromide, C_2H_5Br, the resultant solution is a fairly good conductor, from which aluminum may be deposited. The most detailed description of this process is that of R. D. Blue and F. C. Mathers.[1] Their baths were made by treating aluminum foil with a few drops of bromine and then with ethyl bromide. Benzene, C_6H_6, was then added. Part of the latter combined with the other constituents, and part remained as a surface layer, which retarded but did not entirely prevent absorption of moisture from the atmosphere. Aluminum was then deposited in a bright crystalline form at room temperature and a current density from 1 to 2 amp/dm^2 (10 to 20 amp/ft^2). The deposits were adherent to copper, steel, and platinum but not to aluminum. Absorption of even a small amount of water caused the bath to decompose and become inoperative. By adding salts of other metals such as copper or by using a copper anode, corresponding alloys with aluminum can be deposited.[2]

While these results are of scientific interest, it is unlikely that a process of this type will be applied in practical plating, owing to the difficulty of excluding moisture.

GALLIUM DEPOSITION

In a review of gallium deposition, H. C. Fogg[3] advises the use of an alkaline bath, prepared by dissolving gallium hydroxide, $Ga(OH)_3$, in sodium or potassium hydroxide. The temperature and current density are apparently not critical. It is interesting

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[1] *Trans. Electrochem. Soc.*, vol. 65, 339, 1934, and vol. 69, p. 519, 1936.

[2] Blue, R. D., and Mathers, F. C., *Trans. Electrochem. Soc.*, vol. 69, p. 529, 1936.

[3] *Trans. Electrochem. Soc.*, vol. 66, p. 107, 1934.

to note that, especially if the deposited gallium is liquid (*i.e.*, if the temperature is above 30°C or 86°F), some sodium or potassium is deposited with the gallium (just as they may be deposited in a liquid mercury cathode). Gallium can also be deposited from acidified sulfate or perchlorate baths.

INDIUM DEPOSITION

Indium can be deposited from sulfate, fluoborate, or cyanide baths. The last are more extensively used because of their better throwing power. The sulfate baths are, however, more stable and hence more easily controlled.

Deposition of indium from sulfate baths was investigated by C. G. Fink and R. H. Lester.[1] They recommend the following bath composition and conditions for use with insoluble anodes:

	N	g/l	oz/gal
Indium oxide, In_2O_3	0.6	28	3.7
[Equivalent to indium sulfate, $In_2(SO_4)_3$]	0.6	51	6.8
(Equivalent to indium, In)	0.6	23	3.1
Sulfuric acid, H_2SO_4	0.6	30	4.0
Aluminum sulfate, $Al_2(SO_4)_3$	0.1	5.7	0.8
Gelatin		0.01	0.0013

Temperature, 25°C (77°F)
Current density, 3.3 amp/dm² (30 amp/ft²)

Subsequently, H. B. Linford[2] recommended the use of fairly concentrated solutions, such as the following:

	N	g/l	oz/gal
Indium sulfate, $In_2(SO_4)_3$	0.52	45	6
(Equivalent to indium, In)	0.52	20	2.7
Sodium sulfate, Na_2SO_4	0.14	10	1.3

pH, 2.0–2.7
Temperature, 20–60°C (68–140°F)
Current density, 0.5–5 amp/dm² (5–50 amp/ft²)

A mixture of soluble indium anodes and of insoluble anodes, *e.g.*, platinum, can be used to maintain the desired pH. The cathode efficiency is from 50 to 80 per cent, while the anode efficiency of indium anodes is close to 100 per cent. Hence the pH tends to rise and to cause precipitation of indium hydroxide, $In(OH)_3$.

It is possible to dissolve indium hydroxide, $In(OH)_3$, in sodium cyanide to form a double cyanide, probably $NaIn(CN)_4$ and

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[1] *Trans. Electrochem. Soc.*, vol. 78, p. 349, 1940.

[2] *Trans. Electrochem. Soc.*, vol. 79, p. 443, 1941.

sodium hydroxide, but the resultant solution is unstable, and soon a white precipitate of indium appears, followed by darkening. D. Gray[1] found that the addition of a very weak organic acid such as dextrose (glucose) made the solution more stable. He recommended preparation of the solution by dissolving freshly precipitated indium hydroxide (made by adding ammonium hydroxide to a solution of indium chloride) in a solution containing 600 g/l (80 oz/gal) of sodium cyanide and glucose equivalent to half the weight of indium to be dissolved.

Typical cyanide indium baths are as follows:[2]

	N	g/l	oz/gal
Indium chloride, $InCl_3$	0.9	63	8.4
Dextrose, $C_6H_{12}O_6$		15	2
Sodium cyanide, NaCN	1.8	90	12

This bath is operated at 35 amp/ft² (3.5 amp/dm²) at room temperature, with insoluble anodes of platinum, stainless steel, or graphite.

J. B. Mohler[3] recommends a *high pH* indium bath with the following composition:

	N	g/l	oz/gal
Indium chloride, $InCl_3$	0.8	58	7.7
Potassium cyanide, KCN	2.5	160	21
Potassium hydroxide, KOH	0.7	40	5.3
Dextrose, $C_6H_{12}O_6$		30	4

This bath is operated at room temperature at 30 amp/ft² (3.0 amp/dm²) with steel anodes. It is reported that the additional alkali stabilizes the bath.

THALLIUM DEPOSITION

O. W. Brown and A. McGlynn[4] concluded that the best deposits of thallium were obtained from perchlorate solutions. Like lead, thallium tends to form coarse, treed deposits and also to produce a peroxide on the anode. These authors recommended use of cresylic acid and peptone as addition agents. Their bath had the following composition:

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[1] *Trans. Electrochem. Soc.*, vol. 65, p. 377, 1934.

[2] From Whitehead, M. A., *Metal Finishing*, vol. 42, p. 405, 1944.

[3] *Metal Finishing*, vol. 43, p. 60, 1945.

[4] *Trans. Am. Electrochem. Soc.*, vol. 53, p. 351, 1928.

	N	g/l	oz/gal
Thallium perchlorate, $TlClO_4$	0.5	160	21
Perchloric acid, $HClO_4$	0.6	60	8
Cresylic acid (cresol)		10	1.5
Peptone		10	1.5

Temperature, 50°C (122°F)
Current density, 1–2 amp/dm^2 (10–20 amp/ft^2)

Subsequently C. G. Fink and C. K. Conard, Jr.,[1] described the deposition of alloys containing about 70 per cent lead and 30 per cent thallium from a perchlorate bath containing

	N	g/l	oz/gal
Lead perchlorate	0.05	12	1.6
Thallium perchlorate	0.15	71	9.5
Perchloric acid, $HClO_4$	0.30	30	4

Temperature, 25°C (77°F)
Current density, 5 amp/ft^2 (0.5 amp/dm^2)

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[1] *Trans. Am. Electrochem. Soc.*, vol. 58, p. 457, 1930.

CHAPTER XV

GROUP 4B METALS: GERMANIUM, TIN, AND LEAD

GENERAL CONSIDERATIONS

The metals of this group have principal valences of II or IV. They are all amphoteric, *i.e.*, their oxides may act as either acids or bases. Hence we have such compounds as the following:

	Valence, II	Valence, IV
Oxide..........	Germanous, GeO Stannous, SnO Plumbous, PbO	Germanic, GeO_2 Stannic, SnO_2 Plumbic, PbO_2
Salts from oxides as bases, *e.g.*, chlorides.....	Germanous, $GeCl_2$ Stannous, $SnCl_2$ Plumbous, $PbCl_2$	Germanic, $GeCl_4$ Stannic, $SnCl_4$ Plumbic, $(PbCl_4)$*
Salts from oxides as acids, *e.g.*, with NaOH...	Sodium germanite, Na_2GeO_2 Sodium stannite, Na_2SnO_2 Sodium plumbite, Na_2PbO_2	Sodium germanate, Na_2GeO_3 Sodium stannate, Na_2SnO_3 Sodium plumbate, Na_2PbO_3

* $PbCl_4$ is very unstable.

Germanium is a very rare element, and few uses have been developed for it or its compounds. Tin coatings are extensively applied, either by dipping or plating, especially for food containers and utensils, because tin is not readily attacked by foods and is nontoxic. Lead is poisonous and hence is used in coatings principally to protect against specific agents, such as sulfuric acid in storage batteries, or against atmospheric corrosion, especially in industrial atmospheres.

GERMANIUM DEPOSITION

It was reported by J. I. Hall and A. E. Koenig[1] that germanium can be deposited from a solution containing

	N	g/l	oz/gal
Germanium dioxide, GeO_2........	0.1	2.6	0.3
Potassium hydroxide, KOH.......	3.0	168	23

Temperature, 80–90°C (176–194°F)
Current density, 0.2 amp/dm^2 (2 amp/ft^2)

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[1] *Trans. Electrochem. Soc.*, vol. 65, p. 215, 1934.

In this solution the metal is present as potassium germanate, K_2GeO_4 (similar to the stannate in alkaline tin baths). It was found that, after the copper cathode was covered with germanium, it was difficult to continue deposition.

More recently, C. G. Fink and V. M. Dokras[1] also reported that it is possible to deposit only very thin coatings of germanium from either acid or alkaline solutions. Alloys of germanium with copper were deposited from alkaline cyanide baths. They obtained deposits of germanium from an organic bath containing ethylene glycol and also from a fused tetraborate bath.

The chief interest in germanium deposition is the fact, reported by U. C. Tainton and E. T. Clayton,[2] that the merest trace of germanium in an acid zinc electrowinning bath greatly reduces the efficiency of zinc deposition. This and the preceding observation indicate that the hydrogen overvoltage on germanium is very low.

TIN DEPOSITION

General. Methods of tin deposition are summarized in two articles.[3] In the acid baths the tin is present as stannous salt, *e.g.*, $SnSO_4$, while in the alkaline baths it is present as stannic, *e.g.*, Na_2SnO_3, sodium stannate. The most important difference in these baths is the greater throwing power of the alkaline stannate baths. The acid bath has the advantage that the valence of tin in it is II, compared with IV in the stannate bath; hence twice as much tin is deposited, at 100 per cent efficiency, per ampere-hour in the acid as in the alkaline bath. As the cathode efficiency is usually above 95 per cent in the acid bath and may be only 75 per cent in the alkaline, and as the conductivity of the acid bath is usually higher than that of the alkaline, the power cost for depositing a given weight or thickness of tin is less in the acid than in the alkaline bath. The latter has the advantage that it can be used in plain steel tanks, whereas the acid bath requires a rubber or other acid-resistant lining.

The substitution of tin plating for hot dipping of sheet steel for use in the canning industry[4] came about through the wartime

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[1] *Trans. Electrochem. Soc.*, vol. 95, p. 80, 1949.

[2] *Trans. Am. Electrochem. Soc.*, vol. 57, p. 279, 1930.

[3] Alkaline baths: Oplinger, F. F., and Bauch, Fred, *Trans. Electrochem. Soc.*, vol. 80, p. 617, 1941.

Acid baths: Pine, Paul R., *Trans. Electrochem. Soc.*, vol. 80, p. 631, 1941.

[4] Timby, T. G., *Proc. Am. Electroplaters' Soc.*, p. 90, 1946. Johnston, S. S., and Jenison, G. C., *Proc. Am. Electroplaters' Soc.*, p. 102, 1946 (includes bibliography).

scarcity of tin and the fact that thinner coatings can be applied by plating than by hot dipping. Both the acid and alkaline baths are used successfully for electrolytic tin plate, where throwing power is a minor consideration. For irregular shapes, such as refrigerator coils and trays, the alkaline bath is usually employed.

The electrolytic tin plate is usually much thinner than the hot-dipped, *e.g.*, about 0.00003 in. (0.000075 mm) equivalent to about 0.5 lb per base box (with a surface of 31,360 in.^{2} or 2,023 dm^3) as compared with from 0.00007 to 0.00009 in. (0.0018 to 0.0023 mm), or 1.25 to 1.5 lb per base box in the usual hot-dip plate. As deposited, the very thin electrolytic tin is more porous than the thicker hot-dipped tin. By heating the electrotinned sheets either in hot oil or by electrical induction, the tin coatings are brightened and made less porous. Intermediate weight coatings, *e.g.*, 3/4 lb per base box, *i.e.*, about 0.00005 in. (0.0013 mm), have found extensive postwar use.

Acid Tin Baths. It is possible to deposit tin from a large variety of acid stannous baths, including chloride, fluoride, sulfate, fluosilicate, fluoborate, perchlorate, and sulfamate. Of these, the sulfate has been most extensively employed, although in strip tinning, a fluoride bath has also been used commercially. It is characteristic of all the acid tin baths that the deposits are coarsely crystalline unless a suitable addition agent is present. In fact, the development of commercial acid tin baths has depended largely upon the selection of addition agents.

Colloids such as glue are beneficial but not wholly adequate. Aromatic compounds such as phenol or cresol are hence usually employed along with a colloid. These compounds are generally combined with sulfuric acid to form *sulfonic* acids. For example, when phenol, C_6H_5OH, is mixed with concentrated sulfuric acid and heated or allowed to stand, the following reaction occurs:

$$\underset{\text{phenol}}{C_6H_5OH} + H_2SO_4 = \underset{\text{phenolsulfonic acid}}{C_6H_4OH{\cdot}SO_3H} + H_2O$$

Cresol compounds are similar. Cresol is $CH_3C_6H_4OH$, which exists in three forms, ortho, meta, and para cresol, all of which are usually present in commercial cresol.

Because the stannous sulfate bath is most extensively used, its composition and operation will be described. Stannous sulfate, $SnSO_4$, tends to oxidize to stannic sulfate, $Sn(SO_4)_2$, which, in turn, is more likely to hydrolyze, *i.e.*, to react with water, to form insoluble stannic hydroxide, thus

$$Sn(SO_4)_2 + 2H_2O = Sn(OH)_4 + 2H_2SO_4$$

It is therefore necessary to have the tin bath rather strongly acid to prevent precipitation of the stannic hydroxide (or the corresponding metastannic acid, H_2SnO_3). The free acid also increases the conductivity and, by its commonion effect, reduces the stannous-ion concentration. Sodium sulfate is also added for the latter purpose.

A typical formula for an acid tin bath is as follows:

	N	g/l	oz/gal
Stannous sulfate, $SnSO_4$	0.5	54	7.3
Sulfuric acid, H_2SO_4	2.0	100	13.4
Cresol sulfonic acid, $C_7H_6OH \cdot HSO_3$		100	13.4
Beta naphthol, $C_{10}H_7OH$		1	0.13
Gelatin		2	0.27

Room temperature, 77°F (25°C).

Current density:

Still baths, 2.5 amp/dm^2 (25 amp/ft^2) With very high agitation, up to 50 amp/dm^2 (500 amp/ft^2)

A large number of other addition agents have been used in stannous sulfate baths. In general, they produce finer grained deposits and improve the throwing power.

Alkaline Tin Baths. In the early development of the sodium stannate plating bath, difficulty was often experienced with gray or spongy deposits. It was subsequently concluded that this difficulty was caused by the presence in the bath of stannous salts, in this case sodium stannite, Na_2SnO_2. At first it was found necessary to add an oxidizing agent such as hydrogen peroxide, H_2O_2, or sodium perborate, $NaBO_3$, to reoxidize the stannite to stannate. Subsequently it was learned that, by careful control of the free alkali content and the anode current density, it is possible to obtain practically complete solution of the tin anodes to form stannate and thus avoid the introduction of stannite. This condition is defined by the maintenance on the anodes of a greenish yellow film, which probably contains both stannous and stannic compounds but imparts to the solution only stannic (stannate) compounds. If the anode current density is too low, the surface becomes gray and stannite is formed. As the current density is increased to the critical value, there is a sudden rise in potential, at which point the surface becomes greenish yellow and only stannate is formed. At a still higher current density the anode surface becomes brown or black and oxygen is evolved, with a corresponding decrease in anode efficiency. The anode current density should normally be kept slightly below the critical value, which, in turn, depends on temperature, concentration, and free alkalinity. The last should be relatively low but high enough to prevent hydrolysis and precipitation. Under favorable conditions little or no hydrogen peroxide is required.

In all stannate baths it is necessary to have some excess of free alkali, because otherwise the stannate hydrolyzes, especially if carbon dioxide is absorbed, and precipitates stannic hydroxide (metastannic acid).

In the sodium stannate bath, sodium acetate is sometimes added and acetic acid is added to decompose carbonates and to lower the pH. It is doubtful if in the alkaline bath, acetate serves as a buffer. It may, however, influence the anode corrosion. Sodium rosinate is sometimes added to form a foam that reduces spray.

A typical sodium stannate bath has the following composition and operating conditions:

	N	g/l	oz/gal
Sodium stannate, $Na_2SnO_3 \cdot 3H_2O$	1.3	90	12
Sodium hydroxide, NaOH	0.2	7.5	1
Sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$	0.1	15	2
Hydrogen peroxide (if needed) H_2O_2 (100 vol)		0.5	0.07

Temperature, 60–80°C (140–180°F)
Cathode current density, 1–2.5 amp/dm^2 (10–25 amp/ft^2)
Anode current density, at least equal to the cathode current density (and adjusted to form green film on anodes)

More recently, the use of potassium stannate has been recommended,[1] because the potassium salt has a higher solubility and conductivity than the sodium stannate. The following conditions were employed for plating strip steel.

	N	g/l	oz/gal
Potassium stannate, $K_2SnO_3 \cdot 3H_2O$	1.1	80	10.6
Free potassium hydroxide, KOH	0.5	30	4

Temperature, 85°C (185°F)
Cathode current density, 40 amp/ft^2 (4 amp/dm^2)
Anode current density, 35 amp/ft^2 (3.5 amp/dm^2)

Pure tin anodes are used, in bars or balls in wire cages.

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[1] STERNFELS, M. M., and LOWENHEIM, F. A., *Trans. Electrochem. Soc.*, vol. 82, p. 77, 1942. LOWENHEIM, F. A., *Trans. Electrochem. Soc.*, vol. 84, p. 195, 1943.

Contact and Immersion Processes for Tin. Large quantities of small articles, such as pins, safety pins, thimbles, and buttons are coated with tin by the contact or immersion processes, which are, strictly speaking, electrolytic, although the current is furnished within the tank instead of from an outside source. On all such work the coatings are very thin, but very fine grained and bright, and unlike most deposits produced by immersion they are very adherent. This is partly due to the fact that in all the solutions used the tin-ion concentration is very low and hence the rate of deposition is slow and treeing is prevented. The production of dense impervious deposits is aided by the relatively high overvoltage of hydrogen on tin. In those immersion processes which depend upon the electrolytic action of the base metal, deposition necessarily stops as soon as the basis metal is entirely covered; hence only very thin deposits are secured.

In one of the simplest methods the brass articles to be tinned are rotated for 2 to 4 hr at a temperature of 80°C (176°F) in a barrel containing the solution and small pieces of zinc. The solution consists of

	N	g/l	oz/gal
Tin (stannous) chloride, $SnCl_2 \cdot 2H_2O$	0.20	25	3.5
Cream of tartar (potassium acid tartrate, $KHC_4H_4O_6$)	0.12	10	1.3

If pieces of brass and of zinc are in contact in such a solution, a cell is produced in which the zinc becomes the anode, *i.e.*, passes into solution, and the brass becomes the cathode, *i.e.*, is coated with the tin. One function of the acid tartrate is to form, to some extent at least, complex ions, which produce a small concentration of stannous ions and which do not readily hydrolyze or precipitate stannous hydroxide.

In a somewhat similar method known as the *cream of tartar immersion process* the solution consists of

	N	g/l	oz/gal
Cream of tartar (potassium acid tartrate, $KHC_4H_4O_6$)	0.015	1.5	0.2
Sodium chloride, NaCl	0.05	3.0	0.4

The brass objects are placed in thin layers on iron wire trays covered with perforated sheets of pure tin in the solution, which is heated by steam coils in a copper tank to a temperature of at least 90°C (194°F) for 3 to 5 hr. In this case the tin gradually passes into solution but at no time reaches a high concentration, as it is soon deposited upon the brass, the potential of which is similar to that of copper, *i.e.*, is below tin in the electromotive series. A fresh solution is used for each batch of work, which is removed quickly in order to permit rapid rinsing and drying of the parts.

For coating brass with tin by immersion, alkaline solutions are also employed. Such a solution, for example, may contain

	N	g/l	oz/gal
Stannous chloride, $SnCl_2 \cdot 2H_2O$........	0.25	30	4
Sodium hydroxide, NaOH............	1.50	60	8

The brass articles to be coated are placed in an iron tank on iron-wire trays covered with perforated sheets of tin in the solution, which is heated to 90°C (194°F) for 2 to 3 hr. In this process the tin becomes the anode and passes into solution and is deposited upon the brass. For some articles more dilute solutions are used.

Iron and steel articles are tinned by being placed in thin layers on iron-wire trays covered with perforated zinc sheets in a galvanized iron vessel. The articles are kept for about 45 min in a solution that has been heated nearly to boiling but is not subsequently heated. The solution is discarded each time, and the articles are quickly rinsed and dried. A typical solution is as follows:

	N	g/l	oz/gal
Stannous chloride, $SnCl_2 \cdot 2H_2O$........	0.13	15	2
Sodium sulfate, $Na_2SO_4 \cdot 10H_2O$.........	1.0	160	21

In preparing this solution it is customary to dissolve the required amounts of the above salts in about one-third of the final volume of hot water and to add this solution to the remaining two-thirds of the hot water, which has been placed in the iron tank containing the articles to be plated. A little hydrochloric acid is then added, *e.g.*, about 1 ml to each gallon of solution. The probable function of the sodium sulfate is to increase the conductivity.

LEAD DEPOSITION

General. While some quadrivalent lead compounds, such as PbO_2, are very stable, most of the soluble lead compounds contain the metal with a valence of II, *i.e.*, divalent. Many salts of lead are fairly soluble, but the sulfate is practically insoluble, and the chloride is appreciably soluble only in hot water. The chief salts from which lead has been deposited are the fluoborate, $Pb(BF_4)_2$; fluosilicate, $PbSiF_6$; perchlorate, $Pb(ClO_4)_2$; and sulfamate, $Pb(SO_3NH_2)_2$. The fluosilicate solution is difficult to prepare and is somewhat unstable, but as it is the cheapest, it is used in large-scale refining of lead. The perchlorate introduces some explosion hazard if wood or paper become saturated with it. The sulfamate bath is too new to evalute fully, but it yields deposits with about the same properties, such as porosity, as the fluoborate. It is possible to deposit lead from alkaline solutions, such as sodium plumbite, Na_2PbO_2, formed by dissolving litharge, PbO, in sodium hydroxide, but no commercial use has been made of such baths. While lead forms soluble complex cyanides, no use has been made of them in plating.

The various acid lead solutions all tend to yield coarsely crystalline or treed deposits unless suitable addition agents are used. Glue is the most common addition in the fluosilicate baths for refining lead and in the fluoborate plating baths. The operation of these two types of lead bath was summarized by A. G. Gray and W. Blum.[1]

Fluoborate Bath. The fluoborate bath is most extensively used. A typical formula is as follows:

	g/l	oz/gal
Basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$	150	20
Hydrofluoric acid, HF (50 per cent solution)	240	32
Boric Acid, H_3BO_3	106	14
Glue	0.2	0.025

The resultant solution has approximately the following composition:

	N	g/l	oz/gal
Lead fluoborate, $Pb(BF_4)_2$	1.25	232	31
Free fluoboric acid, HBF_4	0.25	22	3
Free boric acid, H_3BO_3	0.2 (*M*)	12	1.6
Glue		0.2	0.025

Temperature, 25°C (77°F)
Current density, 2 amp/dm^2 (20 amp/ft^2)

The solution can be prepared by carefully mixing the hydrofluoric and boric acid, which form fluoboric acid. The lead carbonate (white lead) is mixed with water to form a paste that is slowly poured into the acid. Carbon dioxide is evolved and causes the solution to foam. When the reaction is complete, the glue, dissolved in warm water, is added. Any insoluble white

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[1] *Trans. Electrochem. Soc.*, vol. 80, p. 645, 1941.

precipitate remaining is probably lead sulfate, derived from the small amount of sulfuric acid commonly present in commercial hydrofluoric acid. It can be disregarded, or the clear solution can be decanted from it.

It is now possible to purchase prepared concentrated solutions of lead fluoborate and of fluoboric acid, use of which avoids their troublesome preparation. An excess of boric acid is always used, as it decreases any tendency of the fluoborate to decompose and to permit precipitation of lead fluoride. The excess of boric acid also retards attack of glass containers. The free fluoboric acid increases the conductivity of the bath and reduces the lead-ion concentration and thereby decreases the tendency for lead to be plated out on steel by immersion, with decreased adhesion.

While lead can be deposited directly on steel, exposure tests have shown that a thin flash of copper on the steel increases the protective value of thin lead coatings.

CHAPTER XVI

GROUP 5B METALS: ARSENIC, ANTIMONY, AND BISMUTH

GENERAL CONSIDERATIONS

Although it is well known that these metals can be electrodeposited from their solutions, very few applications of them have been made in electroplating. All three of these metals are brittle and not especially suitable for protective coatings. However, antimony and bismuth both remain fairly bright in the atmosphere and may warrant certain applications. During the Second World War, scarcity of nickel led to the suggestion that antimony be substituted for nickel in protective and decorative coatings on steel, followed by the usual thin layer of chromium. As far as is known, no extensive applications of antimony plating have been made. In former years a deposit of "arsenic black" was commonly used to produce dark "oxidized" finishes, which are now more commonly made by means of sulfides or by black-nickel plating. One serious objection to the use of arsenic compounds is their poisonous character, especially of arsine, AsH_3, a gas that may be evolved during electrolysis. Certain forms of deposited antimony are explosive and therefore inapplicable. As, therefore, there is no present large field for electroplated coatings of these three metals only brief descriptions will be given.

ARSENIC DEPOSITION

This element can be deposited from a solution containing 7.5 g/l (1 oz/gal) of arsenic trioxide, As_2O_3, and 60 g/l (8 oz/gal) of sodium cyanide, NaCN. (In this solution the arsenic is present as sodium arsenite, Na_3AsO_3, and not as a double cyanide.) At room temperature a current density of 0.5 to 1.0 amp/dm^2 (5 to 10 amp/ft^2) is used. It is also possible to deposit arsenic from solutions of sulfarsenite, Na_3AsS_3, made by dissolving arsenic trisulfide, As_2S_3, in sodium sulfide, Na_2S.

ANTIMONY DEPOSITION

It is possible to deposit "explosive antimony" from a solution of antimony trichloride, $SbCl_3$, containing free hydrochloric acid. When such a deposit is struck or scratched, it explodes and changes to the ordinary gray antimony.

The latter can be deposited from various baths, including antimony fluoride. F. C. Mathers, K. S. Means, and B. F. Richards[1] obtained from such baths coarsely crystalline deposits unless addition agents were used. A large number of these additions were beneficial, but best results were obtained with aloin. A typical solution contained

	N	g/l	oz/gal
Antimony trioxide, Sb_2O_3	1.25	60	8
Total hydrofluoric acid, HF (48 per cent)	2.75	114	15
Equivalent to			
Antimony fluoride, SbF_3	1.25	72	10
Free hydrofluoric acid, HF	1.5	30	4
Aloin	.....	0.25	0.03

BISMUTH DEPOSITION

M. Harbaugh and F. C. Mathers[2] concluded that the best bismuth deposits were obtained from a perchlorate bath. The deposits were fairly smooth, and no addition agent is necessary, although additions of 0.3/g/l of glue and 0.8 g/l of cresol are advantageous. The following solution and conditions were recommended:

	N	g/l	oz/gal
Bismuth oxide, Bi_2O_3	0.5	40	5.3
Total perchloric acid, $HClO_4$	1.0	104	13.9
Equivalent to			
Bismuth perchlorate, $Bi(ClO_4)_3$*	0.5	85	11.5
Free perchloric acid, $HClO_4$	0.5	52	7

Temperature, 45°C (113°F)
Current density, 3 amp/dm^2 (28 amp/ft^2)

* The bismuth may be present as a soluble oxyperchlorate, $BiOH(ClO_4)_2$.

C. G. Fink and O. H. Gray[3] described conditions for depositing alloys of lead and bismuth from perchlorate solutions with clove oil as an addition agent. Alloys of copper and bismuth were deposited from perchlorate solutions by A. Brenner.[4]

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[1] *Trans. Am. Electrochem. Soc.*, vol. 31, p. 293, 1917.

[2] *Trans. Electrochem. Soc.*, vol. 64, p. 293, 1933.

[3] *Trans. Electrochem. Soc.*, vol. 62, p. 123, 1932.

[4] Doctoral dissertation, University of Maryland, 1938.

CHAPTER XVII

GROUP 6A METALS: CHROMIUM, MOLYBDENUM, AND TUNGSTEN

GENERAL CONSIDERATIONS

These three metals all have valences of VI in their acidic compounds, such as the oxides, CrO_3, MoO_3, and WO_3, which form chromic, molybdic, and tungstic acids and the corresponding salts. In their lower valences, usually of II or III, these metals form salts, of which those with the lowest valence are strong reducing agents. Typical compounds have the following compositions:

Valence	Chromium	Molybdenum	Tungsten
VI	Chromic anhydride, CrO_3	Molybdic anhydride, MoO_3	Tungstic anhydride, WO_3
	Chromic acid, H_2CrO_4	Molybdic acid, H_2MoO_4	Tungstic acid, H_2WO_4
	Sodium chromate, Na_2CrO_4	Sodium Molybdate, Na_2MoO_4	Sodium tungstate, Na_2WO_4
III	Chromic oxide, Cr_2O_3	Molybdic oxide, Mo_2O_3	Tungstic oxide, W_2O_3
	Chromic chloride, $CrCl_3$	Molybdic chloride, $MoCl_3$	Tungstic chloride, WCl_3
	Chromic sulfate, $Cr_2(SO_4)_3$	Molybdic sulfate, $Mo_2(SO_4)_3$	Tungstic sulfate, $W_2(SO_4)_3$
II	Chromous chloride, $CrCl_2$	Molybdous chloride, $MoCl_2$	Tungstous chloride, WCl_2

The above list represents the simplest formulas of these compounds, some of which are not stable. The acid anhydrides, which when dissolved in water form the acids, are commonly referred to as the *acids*. For example, CrO_3 is called *chromic acid*, although it is really *chromic acid anhydride*. Chromic acid is H_2CrO_4, but in solution it tends to form *dichromic* acid, $H_2Cr_2O_7$, which forms salts such as sodium dichromate, $Na_2Cr_2O_7$, and potassium dichromate, $K_2Cr_2O_7$. Molybdenum and tungsten form various more complex acids. The most common tungstate is the metatungstate, $Na_2W_4O_{13}$.

As noted on page 277, these metals are on the border of those elements in the periodic system which can be deposited from aqueous solutions. Although chromium can be deposited from many types of bath, the cathode efficiency is always relatively low, usually not over 15 per cent in the regular chromic acid bath.

It is very doubtful if nearly pure molybdenum or tungsten can be deposited from aqueous solutions, but it is possible to deposit alloys of each of these metals with a metal of the iron group, *i.e.*, iron, nickel, or cobalt.

Uranium is sometimes placed in Group 6A of the periodic system and sometimes with the rare earths. It has been deposited from fused salts and from certain organic solutions, but no record has been found of its deposition from aqueous solutions. No further reference will be made to it.

One factor that makes it difficult to deposit these metals from aqueous solutions is the relatively high negative value of their standard potentials. That of chromium is −0.56 volt, *i.e.*, nearly as negative as zinc. No exact values for molybdenum and tungsten are known, but they are certainly quite negative. In other words, in the active state they tend to react and pass into solution. Accordingly we would expect these metals to tarnish or corrode readily. Actually, as is well known, chromium surfaces remain bright in the atmosphere as do also molybdenum and tungsten, because they become "passive" (page 50), probably by formation of a thin transparent film of oxide or adsorbed oxygen.

Another obstacle to the deposition of these metals is the low overvoltage of hydrogen upon them. It will be recalled (page 53) that zinc can be deposited from acidic aqueous solutions only because the hydrogen overvoltage on zinc is relatively high. The greater ease of depositing alloys of molybdenum or tungsten than the pure metals may be associated with a higher hydrogen overvoltage on the alloy surface than on the pure metal, or on a lower solution pressure of the alloys.

These three metals are all characterized by high melting points and high hardness, which properties determine many of their present or proposed uses. Their approximate melting points are as follows:

Metal	°C	°F
Chromium.	1900	3450
Molybdenum.	2550	4620
Tungsten.	3400	6150

The hardness of each varies with the method of preparation. The hardness of electrodeposited chromium ranges from 200 to 1000 Brinell and can be controlled according to the conditions of deposition (page 347).

DEPOSITION OF CHROMIUM

The widespread use of deposited chromium for industrial and ornamental coatings since about 1925 represents a veritable revolution in the plating industry, because it involves the deposition of a metal from an entirely new type of bath, in which much closer control of operating conditions is required than in most of the plating baths previously used. The knowledge and equipment needed to meet these requirements of chromium plating have undoubtedly advanced the state of plating of all kinds.

Chromium Salt Baths. While it is possible to deposit chromium from its salts such as the chloride or sulfate, no such baths have come into commercial use. Many unsuccessful efforts have been made to develop a workable chromium salt bath. If this were accomplished, the effective cathode efficiency might be greatly increased. In the chromic acid bath the chromium has a valence of VI and the cathode efficiency does not usually exceed 15 per cent. Under these conditions only 0.048 g of chromium is deposited per ampere-hour. If, as has been reported from certain experiments, a cathode efficiency of 45 per cent can be obtained from chromic chloride, $CrCl_3$, in which the valence of chromium is III, the yield of chromium will be 0.29 g/amp-hr, *i.e.*, six times that from the chromic acid bath. If chromous chloride, $CrCl_2$, were used and gave an efficiency of 45 per cent, this would deposit nine times as much chromium per ampere-hour as the chromic acid bath.

The only practical chromic salt bath reported is that developed by the U.S. Bureau of Mines[1] for the electrowinning of chromium from its ores. In this process the bath consists of a mixture of chromic sulfate, $Cr_2(SO_4)_3$; chromous sulfate, $CrSO_4$; and sodium sulfate, Na_2SO_4. The insoluble anodes are surrounded by a diaphragm, *e.g.*, of impregnated asbestos, in order to prevent oxidation of the chromous salt. The cathode efficiency approaches 50 per cent (computed for trivalent chromium). The deposits are gray and may contain as much as 4 per cent of Cr_2O_3. While they may serve as a source of metallic chromium, they are not suitable for either decorative or industrial chromium plating.

When a chromic salt is electrolyzed, some reduction takes place to chromous salt, *e.g.*, from $CrCl_3$ to $CrCl_2$. This chromous salt

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[1] LLOYD, R. R., RAWLES, W. T., and FEENEY, R. G., *Trans. Electrochem. Soc.*, vol. 89, p. 443, 1946.

is very readily reoxidized by the air. It is possible that an entirely chromous salt bath would be more efficient, but it is not practicable to exclude air completely. In efforts to operate a mixture of chromic and chromous salts it is very difficult to keep their ratio constant because of oxidation by the air and by the insoluble anodes. It is difficult to get chromium anodes to dissolve uniformly in a chromic salt bath. If the anode becomes passive, the chromium compounds are oxidized to chromic salt or chromic acid. If the chromium dissolves with too high an anode efficiency, the pH increases and causes precipitation of basic chromium compounds.

Chromium salt baths are sensitive to changes in pH and to the presence of very small amounts of impurities, which may change the hydrogen overvoltage and lower the cathode efficiency. While such baths warrant further study, they are not now in practical use.

Chromic Acid Baths. *Composition.* Because of the limitations of the chromium salt baths, all commercial chromium plating is conducted from the chromic acid bath. The operation of the chromic acid bath is summarized by G. Dubpernell.[1] The essential constituent is chromic acid, introduced as the anhydride, CrO_3. In aqueous solution this forms dichromic acid, $H_2Cr_2O_7$, or still more complex acids. It is important to note that in such compounds the chromium is in the anion, *e.g.*, $Cr_2O_7^{--}$, and does not directly form any positively charged chromium ions.

Early attempts to deposit chromium from solutions of chromic acid yielded erratic results. In the light of present knowledge it is not feasible to deposit chromium from pure chromic acid. When chromium deposits were obtained in early studies, it is probable that the chromic acid contained an impurity such as sulfuric acid.

A number of acids can be added in very small amounts to chromic acid to permit chromium deposition, including sulfuric acid; hydrofluoric acid, HF; and fluosilicic acid, H_2SiF_6; or their salts. While baths with the last two acids have been successfully used, practically all chromium plating is now conducted from baths containing chromic acid and sulfuric acid. It is immaterial whether the sulfuric acid is added as such or in the form of a soluble sulfate. Since the chromic acid is a strong acid, it probably liberates sulfuric acid from any soluble sulfate.

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[1] *Trans. Electrochem. Soc.*, vol. 80, p. 589, 1941.

In operating with insoluble anodes, the chromic acid is consumed (1) by its reduction to metallic chromium or (2) to trivalent chromium (until an equilibrium with its reoxidation is reached) and (3) by loss through drag out and spray. It must therefore be replenished at intervals in accordance with periodic analyses. It is now possible to purchase commercial chromic acid containing at least 99 per cent of CrO_3 and not over 0.2 per cent of SO_4. Where the drag out and spray loss are relatively large, this small content of sulfate is not objectionable but should be taken into account in adjusting the baths.

Any additional sulfate required can then be added as sulfuric acid. If, by error, an excess of sulfuric acid enters the bath, the sulfate can be partly removed by adding a calculated amount of barium carbonate, $BaCO_3$. This reacts first to form barium chromate, $BaCrO_4$, which then more slowly forms the less soluble barium sulfate, $BaSO_4$. The bath should be well agitated for some time and allowed to settle, after which the liquid is decanted from the precipitate.

When a bath made from chromic and sulfuric acids is operated for some time, part of the hexavalent chromium present in the chromic acid is reduced to trivalent chromium, which may be present as chromic sulfate, $Cr_2(SO_4)_3$, or as chromic dichromate, $Cr_2(Cr_2O_7)_3$. All operated chromium baths contain both hexavalent and trivalent chromium and a sulfate, the concentrations of each of which must be controlled within appropriate limits.

Under given operating conditions the content of trivalent chromium tends to reach an equilibrium, because the chromic acid is partially reduced at the cathode and the resultant trivalent chromium is reoxidized at the anode. In order to keep the final concentration of trivalent chromium relatively low, it is desirable to have the anode surface as large as practicable and to use anodes made of or coated with lead, or an alloy of lead and antimony, of lead and tellurium or of lead and tin (page 343).

If the content of trivalent chromium becomes too high, it can be removed by electrolysis, using a large area of lead anodes and a cathode of small area, *i.e.*, a low anode current density and a high cathode current density.[1] If a porous pot is used, the solution in the pot acquires an increased content of trivalent chromium and should be discarded.

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[1] SEEGMILLER, R. and LAMB, V. A., *Proc. Am. Electroplaters' Soc.*, p. 125, 1948.

Chromium baths are likely to be contaminated with iron, derived from reverse current cleaning in the bath or from steel racks or hangers or from steel articles that have been pickled and not adequately rinsed. This dissolved iron is always in the ferric state and is probably present as ferric dichromate, $Fe_2(Cr_2O_7)_3$. Other metals such as copper and zinc can be introduced, *e.g.*, by solution of brass articles dropped into the bath or on which there are areas that are not cathodic. While each of these impurities, if present in large amount, may have harmful effects, *e.g.*, by reducing the bright range, the chromic acid bath is not so sensitive to the effects of metallic impurities as are many other plating baths. There is no practical method of removing iron, copper, or zinc from chromic acid baths; hence if they become excessive, part or all of the bath must be discarded.

In practice, relatively high concentrations of chromic acid are used, *e.g.*, from 250 to 400 g/l (33 to 53 oz/gal) of CrO_3. An increase in concentration increases the conductivity up to a maximum but decreases the cathode efficiency. In a given case these two factors may offset each other, so that the higher current density obtainable at a given voltage in a more concentrated chromic acid bath may not yield a greater weight of chromium. For certain purposes, where a high cathode efficiency is important, use of more dilute baths, *e.g.*, with 100 g/l of chromic acid, is advantageous, even though a higher voltage is then required to obtain a given current density. The final selection of concentration involves engineering considerations, such as the available current sources. In general, it is customary to employ about 250 g/l (33 oz/gal) of CrO_3 for industrial or hard chromium plating, because a higher rate of deposition can be used, and 400 g/l (53 oz/gal) for thin bright chromium coatings, because a lower voltage and current density are required.

The ratio of chromic acid to sulfate, CrO_3/SO_4, is more important than their actual concentrations. The most commonly used ratio of CrO_3/SO_4 (by weight) is 100, but under specified conditions other ratios may be superior. A higher ratio, *e.g.*, of 150, yields slightly better throwing power on copper or brass at 45°C (113°F). At higher temperatures, such as 70°C (158°F) a sulfate ratio as low as 50 may be advantageous.

Bright Plating Range. The wide use of decorative chromium coatings depends largely on the fact that under appropriate conditions it is possible to obtain bright deposits that require no buffing. This behavior is more important because chromium coatings are very hard and hence are difficult to buff. The conditions under which bright deposits are obtainable are often defined as the *plating range* for bright chromium.

In general, in a given chromic acid bath, the cathode efficiency and the appearance of the deposit depend upon both the temperature and the current density. At a given temperature an increase in current density increases the cathode efficiency and causes the appearance of the deposit to change from (1) milky to (2) bright to (3) frosty and finally to (4) burnt. These changes correspond to a progressive increase in cathode efficiency, which is usually from 10 to 15 per cent for bright deposits. For a given current density an increase in temperature causes a decrease in cathode efficiency and a variation in the character of deposit in the reverse order, *i.e.*, burnt, frosty, bright, and milky.

This dependence of the appearance on the conditions of deposition makes it necessary in chromium plating to hold the temperature nearly constant. For example, if a bath is operated at 45°C (113°F), this temperature should be kept, preferably by automatic control, between 44 and 46°C (111 and 115°F).

It is also desirable to keep the current density as nearly uniform as practicable. On flat sheets or nearly symmetrical articles there is no difficulty in obtaining a nearly uniform cathode current density, but on irregular shapes the ratio of the maximum to the minimum current density is usually at least 2 and may be 5 or larger. The bright range for chromium deposits seldom covers a current density ratio greater than about 3 to 1. Hence with more irregularly shaped articles, it is not possible to produce bright deposits or in some cases any deposit in the areas with low current densities without obtaining burnt deposits on the more exposed areas. In all such cases efforts must be made to make the primary current distribution more nearly uniform by such devices as (1) conforming anodes, (2) intermediate or bipolar anodes (page 248), (3) *thieves* to detract current from points or edges, or (4) shields to obstruct current to more exposed areas.[1] Much of the success in chromium plating has resulted from ingenious applications of these methods.

Throwing Power. The notoriously poor throwing power of chromic acid baths frequently refers to three different but related phenomena, *viz.*, (1) the actual *throwing power* (page 89), *i.e.*, the ratio of the thicknesses of deposit on different parts of a given

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[1] LOGOZZO, A., *Proc. Am. Electroplaters' Soc.*, p. 146, 1940.

object; (2) the *covering power* (page 90), *i.e.*, the ability to cover all parts of the object with chromium regardless of its thickness or appearance; and (3) the *bright range*, *i.e.*, the ability to yield bright deposits over the entire surface.

All these properties are related to each other and to the low cathode efficiency of chromium deposition, especially at low current densities. The other two factors in throwing power, *viz.*, cathode polarization and conductivity, have much less effect than the cathode efficiency. For a given temperature a definite current density is required to yield a chromium deposit; hence up to that point the cathode efficiency is zero. As the current density is increased, the cathode efficiency increases along a curve that flattens out. The flatter this curve, within the range of bright deposits, the better is the throwing power, as defined above in its broadest sense.

From a study of throwing power in chromium plating[1] the following conclusions may be reached:

1. The throwing power is decreased by an increase in temperature for a given current density.
2. The throwing power is increased by an increase in current density for a given temperature.
3. If the temperature is increased and the current density is also increased so as to yield bright deposits, the throwing power is improved.
4. For a given average current density the throwing power is better in more dilute baths, but for a given tank voltage (*e.g.*, 6 volts) the throwing power may be better in more concentrated baths.
5. A sulfate ratio up to 150 gives slightly better throwing power than a ratio of 100.
6. Small amounts of trivalent chromium or of iron have no appreciable effects on the throwing power with respect to thickness. High concentrations of either trivalent chromium or iron increase the "thickness" throwing power, but as they decrease the conductivity and the bright plating range, they are undesirable.
7. The throwing power is better on bright than on dull surfaces and is very poor on roughened surfaces where the hydrogen overvoltage is very low. Part of this effect is caused by the greater area of a rough surface and consequent lower current density.

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[1] Farber, H. L., and Blum, W., *J. Research Natl. Bur. Standards*, vol. 4, p. 27, 1930.

8. The covering power as measured by the bent cathode (page 95) is practically parallel to the throwing power as measured in the throwing power box (page 97).

9. Under the most favorable conditions the throwing power in chromium plating is always negative, *e.g.*, −15 per cent, and may be as low as −100 per cent.

Condition of the Basis Metal. Even when other conditions are favorable, it is sometimes difficult to obtain uniformly bright chromium deposits, especially upon some types of nickel. This problem has arisen with bright nickel deposited from solutions containing certain addition agents. It also arises when a plain nickel coating has been buffed and has thereby become hot enough to oxidize the nickel. It may also occur when buffed nickel deposits have stood a long time before being chromium-plated. In all such cases it is necessary to *activate* the nickel surface just before applying chromium.

The following steps or a combination of them can be employed to activate the nickel. Each of them probably depends upon the removal of a passive oxide film from the nickel.

1. Clean cathodically in an alkaline bath.
2. Dip momentarily in concentrated hydrochloric acid.
3. Apply a nickel film from a high-acid nickel chloride strike.
4. Pickle cathodically in dilute sulfuric acid.
5. Apply an abnormally high or low current density in the chromic acid bath for a few seconds before adjusting to the normal current density.

Anodes. While it is possible to employ chromium anodes in the chromic acid bath, there are two serious objections: (1) Chromium anodes are difficult to prepare and are more expensive than chromium purchased as chromic acid. (2) Chromium anodes dissolve with a much higher anode efficiency, *e.g.*, 80 to 100 per cent, than the prevailing low cathode efficiency, *e.g.*, 15 per cent. Hence the chromium will tend to build up in the solution, partly in the form of objectionable trivalent chromium.

It is therefore a universal practice to employ insoluble anodes. Many metals, such as steel, nickel, and lead, are nearly insoluble in chromic acid, but only lead or its alloys are used, because the reoxidation of trivalent chromium occurs more readily on lead than on other available metals. Pure lead is fairly satisfactory but is more rapidly attacked than are the 6 per cent alloys of antimony or tin with lead. Such alloys are hence used for both anodes and tank linings. The lead-tin alloy with 6 to 10 per cent of tin can be readily plated onto steel or copper anodes that may be required in special cases for strength or conductivity. Lead with a small content of tellurium is also used in anodes.

During operation, some brown lead peroxide, PbO_2, is formed on the anode surface and fosters reoxidation of trivalent chromium. If the anodes stand unused, this compound is converted to yellow lead chromate, $PbCrO_4$, which adheres to the surface. It is sometimes desirable to operate the bath with dummy cathodes, especially after a week end, in order to detach the lead chromate and re-form some lead peroxide. The resistance at the anode surface is thereby reduced. Where practicable, it is advantageous to remove the anodes when not in use for considerable periods.

Theory. Any adequate theory of the chromic acid bath must account for such facts as (1) the deposition of chromium from a strong acid (chromic acid) in which there are few if any positively charged chromium ions, (2) the necessity of having sulfate or some other foreign ion present to permit reduction to metal, (3) the low cathode efficiency, (4) the range of brightness and other physical properties and their dependence on the temperature and current density.

No adequate theory has yet been developed, and those proposed are largely outside the scope of this text.[1] They generally agree that the pH of the cathode film is much higher than in the bath (which has a very low pH) and that there exists at or near the cathode surface some sort of a semipermeable diaphragm, which may consist of a basic chromium chromate. The exact composition, constitution, and properties of this film have not been defined or the relation of the sulfate ion to its behavior.

Cloyd A. Snavely[2] has confirmed by X-ray studies the earlier observations that chromium may be deposited, especially at low temperatures, in the hexagonal crystal form, which on standing changes to the body-centered cubic form, in which normal chromium deposits exist. He suggests that the codeposition of hydrogen in the crystal lattice and its subsequent release may account for the contraction and cracking of the ordinary chromium deposits.

From a recent study of the physical properties of chromium[3] it

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[1] For a review of these theories, see C. KASPER, *J. Research Natl. Bur. Standards*, vol. 9, p. 353, 1932, RP 476; and vol. 14, p. 693, 1935, RP 797.

[2] *Trans. Electrochem. Soc.*, vol. 92, p. 537, 1947.

[3] BRENNER, A., BURKHEAD, P., and JENNINGS, C. W., *J. Research Natl. Bur. Standards*, vol. 40, p. 31, 1947.

was concluded that all chromium deposits contain oxygen as well as hydrogen and that the content of oxygen is closely parallel to many of the physical properties. As the oxygen content increases, the hardness, tensile strength, and electrical resistivity increase and the density decreases. The oxygen in chromium deposits is probably present as chromic oxide, Cr_2O_3, which forms in the cathode film and is occluded during deposition. Far more study is required to explain the mechanism of so complicated a process as the deposition of chromium from chromic acid. Until this is done, the operation of the bath must be largely empirical.

Types of Deposit. In practice a distinction is often made between *bright*, or *ornamental*, chromium plating and *hard*, or *industrial*, chromium plating. Actually the deposits of these two types are produced from very similar solutions and under almost the same conditions and have nearly the same composition and properties. The chief real distinction is that the ornamental deposits are very thin, usually less than 0.00003 in. (0.00075 mm) thick and are applied over a protective coating of nickel on steel, brass, or zinc (page 136) while the industrial chromium coatings are generally more than 0.001 in. (0.025 mm) thick and are applied directly to steel and seldom to other basis metals. The usual lack of brightness in the industrial coatings is caused by their greater thickness and by the practice of depositing them in the upper part of the current density range for a given temperature, where the deposits may be *frosty*. For example, for a bath with 250 g/l (33 oz/gal) of CrO_3 and a CrO_3/SO_4 ratio of 100, at 45°C (113°F), an average current density of about 150 amp/ft^2 (16 amp/dm^2) is used for thin bright deposits on nickel and about 200 amp/ft^2 (21 amp/dm^2) for thick, frosty, but slightly harder deposits on steel.

Recent studies[1] have shown that at relatively high temperatures, such as 85°C (185°F), and current densities from 400 to 1000 amp/ft^2 (43 to 107 amp/dm^2) much softer chromium deposits are produced. These deposits contain less oxide than the ordinary bright chromium, have fewer cracks, and contract less when heated. Because they are dull, they will not replace bright chromium, and because they are soft, *e.g.*, 400 Brinell as compared with 900 for the normal chromium deposits, they are not especially useful for severe wear resistance. However, because it is

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[1] GARDAM, G. E., *J. Electrodepositors' Tech. Soc.*, vol. 20, p. 69, 1945. BRENNER, A., BURKHEAD, P., and JENNINGS, C. W., *J. Research Natl. Bur. Standards*, vol. 40, p. 31, 1947.

machinable and relatively free from cracks, the soft chromium may find special applications.

Properties of Chromium Deposits. Many of the industrial uses of deposited chromium depend upon its specific physical properties, which may be varied over a wide range. The data in the following table are derived largely from the above research by A. Brenner and associates on the physical properties of electrodeposited chromium.

From these and other data in this report, the following conclusions may be drawn:

1. Hardness. The hardness of deposited chromium ranges from about 300 to 900 Brinell. In general, softer deposits are obtained at high temperatures such as 85°C (185°F) and at relatively low current densities, *e.g.*, 20 amp/dm^2 or 190 amp/ft^2. The soft chromium is always dull, as it is deposited in the *milky* range for the high temperatures used. When heated to about 1200°C (2200°F) all chromium deposits decrease in hardness to about 200 Brinell.

2. Tensile strength. The tensile strength of the high-temperature soft chromium is higher than that of ordinary hard chromium.

3. Ductility. All deposits of chromium are very brittle and have an elongation of much less than 1 per cent.

4. Oxygen content. The usual hard chromium deposits contain considerable oxygen, probably present at Cr_2O_3, while the soft deposits are nearly free of oxygen. The properties of chromium deposits are closely related to their contents of oxygen.

5. Density. The density of soft chromium is appreciably higher than that of hard chromium.

6. Electrical resistivity. The electrical resistivity of soft chromium is lower than that of hard chromium.

7. Stress and cracking. During deposition of the soft chromium there is a higher stress than with hard chromium. However, the hard chromium cracks more than the soft because its tensile strength is lower.

For bright decorative plating and also for wear resistance, the ordinary hard chromium, deposited at from 40 to 60°C (104 to 140°F), is generally most suitable. The soft, more nearly crack-free chromium, deposited at higher temperatures, may find applications where protection against corrosion is the principal requirement.

Comparison of Properties of Low-temperature (50°C), High-temperature (85 to 100°C), and Annealed Chromium

Deposit No.	Bath	Plating conditions			Density, g/cm^3	Hardness, Knoop	Tensile strength, lb/in.^{2} × 10^3	Young's modulus, lb/in.^{2} × 10^6	Resistivity, microhm-cm	Oxygen content, per cent
		Temperature, °C	Current density, amp/dm^2	Cathode efficiency, per cent						
8	Standard	50	20	15	7.05	920	15	15	47	0.40
42	Dilute	85	20	15	7.18	325	47	30	22	0.04
53	Fluoride	85	20	15	7.18	470	31	30	16	
32	Standard	85	80	11	7.17	550	70	33	15	0.05
45	Dilute	100	80	8	7.20	310	35	32	14	0.08
	Annealed, 1200°C				7.20	200	70	36	13	

Porous Chromium. Just before and during the Second World War, extensive use was made of so-called "porous" chromium deposits for applications where good lubrication was essential, *e.g.*, aircraft and Diesel engine cylinders and piston rings. These deposits consisted of chromium coatings that had been etched so as to produce or accentuate cracks or pores, in which lubricating oil could be retained. The details of preparation have been fully described in several articles.[1]

Two types of porous chromium have been used, designated as the *channel* type and the *pin-point* type. The former deposits contain cracks that form a network surrounding small, flat areas or *plateaus.* The average size of these plateaus and the width of the cracks may be used to define the channel porosity for specified purposes. The pin-point porosity consists, in effect, of a large number of relatively coarse pits in which oil may be retained.

In general, those conditions for *hard* plating are employed which yield approximately the desired crack pattern. The chromium deposit is then usually etched anodically in a chromic acid bath to deepen and widen the cracks. The surface is finally honed to produce the correct dimensions. The pin-point type has initially a larger number of fine cracks and is etched sufficiently that these cracks merge into each other, leaving small pits or projections.

MOLYBDENUM DEPOSITION

There is no conclusive evidence that pure molybdenum has been deposited consistently from aqueous solutions. In the light of our present knowledge of tungsten deposition, it is at least probable that the reported deposits of molybdenum contained appreciable amounts of other metals, such as iron, nickel, or cobalt.

W. P. Price and O. W. Brown[2] obtained steel-gray deposits on iron or copper cathodes at 50°C (122°F) and 36 amp/dm^2 from a solution prepared initially by dissolving 400 g of MoO_3 in 1 l of sulfuric acid (sp gr 1.45). This solution was first reduced electrolytically by passing 1,600 amp-hr through 1 l of solution between platinum electrodes. The resultant viscous, golden brown solution probably contained salts of the lower oxides of molybdenum. The rate of deposition decreased as soon as the cathode was completely covered by the gray deposit.

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[1] Van der Horst, H., *Metal Finishing*, vol. 40, p. 69, 1942. Coyle, T. G., *Proc. Am. Electroplaters' Soc.*, p. 20, 1944.

[2] *Trans. Electrochem. Soc.*, vol. 70, p. 425, 1936.

Recent success in depositing alloys of tungsten with iron, nickel, or cobalt (page 350) indicates that molybdenum alloys may be similarly deposited from appropriate solutions.

Black coatings, known as *Moly Black* have been produced[1] from baths containing nickel salts and a molybdate. These coatings contained about 45 per cent of molybdenum, apparently in the form of an oxide and not as metallic molybdenum (page 413).

TUNGSTEN DEPOSITION

It was reported[2] that silver-white tungsten deposits were obtained from solutions of sodium tungstate, prepared by dissolving tungstic acid (anhydride), WO_3, in sodium hydroxide or carbonate. The resultant solutions may have contained the normal, meta-, or para-tungstate, but for simplicity the normal tungstate, Na_2WO_4, may be assumed to be present. A typical solution contained 330 g/l (44 oz/gal) of Na_2CO_3 and 100 g/l (13 oz/gal) of WO_3 and had a pH of 12 to 13. At 100°C (212°F) and 100 to 400 amp/ft^2 (11 to 43 amp/dm^2) the cathode efficiency was about 1 per cent and decreased when the cathode was completely covered.

Similar deposits were reported from solutions of tungstate and citric acid[3] and from solutions of tungstate and phosphate.[4]

Subsequently it was concluded[5] that the deposits so obtained always contained appreciable amounts of iron or nickel, derived from (1) impurities in the bath, (2) the anodes, or (3) intentional additions. When the alloying element was exhausted, deposition ceased.

While it is doubtful if pure tungsten can be deposited from aqueous solutions, it is now certain that alloys of tungsten, especially with iron, nickel, or cobalt, can be so obtained. Such alloy deposition from fluoride baths has been reported[6] but not extensively applied.

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[1] HOFFMAN, R. A., and HULL, R. O., *Proc. Am. Electroplaters' Soc.*, p. 45, 1939.

[2] FINK, C. G., and JONES, F. L., *Trans. Am. Electrochem. Soc.*, vol. 59, p. 461, 1931.

[3] YNTEMA, L. F., *J. Am. Chem. Soc.*, vol. 54, p. 3775, 1932.

[4] HOLT, M. L., and KAHLENBERG, L., *Metal Ind.* (*N.Y.*), vol. 31, p. 94, 1933.

[5] HOLT, M. L., *Trans. Electrochem. Soc.*, vol. 66, p. 453, 1934, and vol. 71, p. 301, 1937.

[6] Tungsten Electrodeposit Corporation, *Automotive Ind.*, vol. 75, p. 353, 1936.

The most extensive studies on these alloys of tungsten[1] have shown that deposits containing up to 50 per cent of tungsten, with cobalt, iron, or nickel, can be obtained from alkaline baths containing a tungstate, the appropriate alloying metal, and a hydroxy acid, such as hydroxyacetic, citric, or tartaric acid. A typical bath and conditions for depositing a cobalt-tungsten alloy are as follows:

	N	g/l	oz/gal
Cobalt chloride, $CoCl_2 \cdot 6H_2O$	0.9	102	14
Sodium tungstate, $Na_2WO_4 \cdot 2H_2O$	0.8	45	6
Rochelle salt, $NaKC_4H_4O_6 \cdot 4H_2O$	1.4(*M*)	400	53
Ammonium chloride, NH_4Cl	1.0	50	7

pH, 8.5 (adjusted with NH_4OH)
Temperature, 90°C (194°F)
Current density, 2–5 amp/dm^2 (20–50 amp/ft^2)

Tungsten anodes are used. The tungsten content of the deposit, up to about 50 per cent by weight, increases if the ratio of tungsten to cobalt in the solution is increased or if the current density is increased. The deposits as produced are relatively hard, *e.g.*, 400 to 600 Vickers, and when they are heated to 600°C (1110°F), they become harder (by precipitation hardening). They are most likely to find applications where considerable hardness and wear resistance are required at high temperatures.

[1] Brenner, A., Burkhead, P., and Seegmiller, E., *Proc. Third International Deposition Conf.*, *Electrodepositors' Tech. Soc.*, p. 131, 1947, and *J. Research Natl. Bur. Standards*, vol. 39, p. 351, 1947, RP 1834. Also Clark, W. E., and Holt, M. L., *Trans. Electrochem. Soc.*, vol. 94, p. 224, 1948, and Lietzke, M. H., and Holt, M. L., *Trans. Electrochem. Soc.*, vol. 94, p. 252, 1948.

CHAPTER XVIII

GROUP 6B METALS: SELENIUM, TELLURIUM, AND POLONIUM

SELENIUM DEPOSITION

This element is often called a *metalloid* because it is on the border line between metals and nonmetals. It occurs in two forms, one that is red and nonmetallic and one that is gray and metallic. It was shown by E. Müller[1] that, when $2N$ sulfuric acid, 98 g/l (13 oz/gal), containing selenous acid, H_2SeO_3, is electrolyzed, a deposit of selenium is first obtained but after a short time deposition stops. If, however, a larger quantity of another metal, *e.g.*, copper, is present in the bath, all the selenium deposits with the copper. It is not known whether the copper in the deposit changes the hydrogen overvoltage or merely makes the deposit a better conductor than pure selenium. In former years coatings of selenium (usually produced by melting the selenium upon the metal to be coated) were used in photoelectric cells, which have now been superseded by other types. There is no present obvious application for electrodeposited selenium coatings, and it is at least doubtful if they can be produced with an appreciable thickness.

TELLURIUM DEPOSITION

Tellurium is a brittle metal that has not thus far found many applications in electroplating. F. C. Mathers and H. L. Turner[2] found that smooth deposits were obtained from the following solutions:

	N	g/l	oz/gal
Tellurium dioxide, TeO_2	9	360	48
Hydrofluoric acid, HF (48 per cent)	12	500	67
Sulfuric acid, H_2SO_4	4	200	27

Temperature, 20–30°C (68–86°F)
Current density, 1.6 amp/dm^2 (15 amp/ft^2)

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[1] *Z. physik. Chem.*, vol. 100, p. 346, 1922.

[2] *Trans. Am. Electrochem. Soc.*, vol. 54, p. 293, 1928.

In this solution the tellurium may be present as the fluoride, TeF_4 or as H_2TeF_6. This bath is somewhat objectionable because it evolves vapors of hydrofluoric acid. Like all baths containing hydrofluoric acid, it must be kept in lead, hard rubber, plastic, or wax-lined containers.

POLONIUM DEPOSITION

Polonium is one of the rare radioactive elements that is associated with radium. It is readily electrodeposited from its solutions; in fact, it deposits by immersion upon a strip of silver or copper. Its electrodeposition is sometimes used as a means of separating or purifying it. No specific uses have been suggested for coatings of polonium.

CHAPTER XIX

GROUP 7A METALS: MANGANESE, TECHNETIUM, AND RHENIUM

GENERAL

Of these metals, manganese is very cheap and available. Technetium (formerly known as *masurium*) is very rare, and rhenium is relatively scarce. No data have been found on the electrodeposition of technetium.

Manganese and rhenium are characterized by compounds having valences from II to VII. Typical compounds of manganese are as follows:

Manganous chloride, $Mn^{II}Cl_2$.
Manganic chloride, $Mn^{IV}Cl_4$ (unstable).
Manganese dioxide, $Mn^{IV}O_2$.
Sodium manganate, $Na_2Mn^{VI}O_4$.
Sodium permanganate, $NaMn^{VII}O_4$.

Of these, the manganous salts are the most stable. All the others are oxidizing agents, which on reduction form manganous salts.

MANGANESE DEPOSITION

During recent years it has been shown in numerous studies that manganese can be deposited from aqueous solutions under conditions similar to those used for depositing zinc from acid baths. The principal purpose of these studies was to define conditions for the *electrowinning* of manganese, *i.e.*, its deposition (with insoluble anodes) from solutions prepared by leaching manganese ores.[1] Manganese is relatively cheap and is an essential constituent of most steels. Electrolytic recovery of manganese would permit the substitution of domestic low-grade ores for part of the imported ores. In many respects manganese resembles zinc but is much harder and more brittle. It is readily attacked by moist air unless it has been rendered passive by dipping into chromic acid (250 g/l). It then stays bright for long periods. Like zinc,

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[1] MANTELL, C. L., *Trans. Electrochem. Soc.*, vol. 94, p. 232, 1948.

it protects exposed steel against corrosion and may find uses where both protection and hardness are required.

The metal manganese may exist in three or four *allotropic* forms, which differ in crystal structure and properties. The best known forms are the *alpha* and the *gamma* modifications. Under most conditions of deposition, the alpha form, which is hard and brittle, is obtained. Under carefully controlled conditions from especially purified electrolytes,[1] the soft, ductile gamma manganese can be deposited. It is, however, unstable, and in a few weeks at room temperature it reverts to the brittle gamma manganese.

H. H. Oaks and W. E. Bradt[2] obtained smooth silver-white deposits of pure manganese from the following bath:

	N	g/l	oz/gal
Manganous chloride, $MnCl_2$..........	5.5	350	47
Ammonium chloride, NH_4Cl.........	0.6	30	4
Temperature, 26°C (79°F)			
Current density, 20 amp/dm^2 (186 amp/ft^2)			

The cathode efficiency was about 75 per cent. Manganese anodes or insoluble anodes were used.

W. E. Bradt and H. H. Oaks[3] obtained equally good deposits from the following solution:

	N	g/l	oz/gal
Manganous sulfate, $MnSO_4 \cdot 4H_2O$.....	0.9	100	13
Ammonium sulfate, $(NH_4)_2SO_4$	0.6	75	10
Ammonium thiocyanate, NH_4CNS....	0.8	60	8
pH, 4–5.5			
Temperature, 25°C (77°F)			
Current density, 25 amp/dm^2 (230 amp/ft^2)			

The cathode efficiency was about 65 per cent. Graphite anodes and manganese anodes were used in such a ratio (8 to 1) as to keep the pH constant.

Subsequently, W. E. Bradt and L. R. Taylor[4] showed that manganese can be deposited from almost any soluble manganese salt, including those of many organic acids.

From unpublished experiments at the National Bureau of Standards by A. Brenner and Thelma Steinberg, the following conditions were recommended:

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[1] Schlain, D., and Prather, J. D., *Trans. Electrochem. Soc.*, vol. 94, p. 58, 1948.

[2] *Trans. Electrochem. Soc.*, vol. 69, p. 567, 1936.

[3] *Trans. Electrochem. Soc.*, vol. 71, p. 279, 1937.

[4] *Trans. Electrochem. Soc.*, vol. 73, p. 327, 1938.

	N	g/l	oz/gal
Manganous chloride, $MnCl_4 \cdot 4H_2O$	3.3	325	43
Ammonium chloride, NH_4Cl	3.7	200	27
Ammonium sulfate, $(NH_4)_2SO_4$	1.5	100	13
Potassium thiocyanate, KCNS	0.02	2	0.3

pH, 6–6.5 (maintained with NH_4OH)
Temperature, 25°C (77°F)
Current density, 5–10 amp/dm² (50–100 amp/ft²)
Cathode efficiency, 80 per cent
Manganese anodes
Rinse, then dip deposits in solution of 250 g/l (33 oz/gal) of CrO_3 and rinse

Conditions for the electrowinning of manganese from sulfate solutions with insoluble anodes have been described by C. G. Fink and M. Kolodney[1] and by the U.S. Bureau of Mines.[2]

RHENIUM DEPOSITION

Rhenium is one of the most recently discovered elements and is still a scarce metal but not much more expensive than rhodium. The deposits are hard and bright. While rhenium is resistant to hydrochloric acid, it oxidizes rapidly in moist air.[3] No important uses have been suggested for the deposits.

C. G. Fink and P. Deren[4] showed that rhenium can be deposited from acid, neutral, or alkaline baths. They recommend baths made by acidifying the perrhenate with sulfuric acid. For example, a bath containing 11 g/l (1.5 oz/gal) of potassium perrhenate, $KReO_4$, and 3.3 g/l of sulfuric acid, H_2SO_4, is operated at a pH of 0.9, a temperature of 25 to 45°C (77 to 113°F), and a current density of 10 to 14 amp/dm² (93 to 130 amp/ft²).

Subsequently C. B. F. Young[5] recommended an increase from 3.3 to 9.3 g/l of sulfuric acid in the above formula. He also deposited an alloy of nickel and rhenium by adding 6 g/l of nickel sulfate, $NiSO_4 \cdot 6H_2O$, to this bath and using a current density of 5 to 6 amp/dm² (50 to 60 amp/ft²).

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[1] *Trans. Electrochem. Soc.*, vol. 71, p. 287, 1937.

[2] Shelton, S. M., and Royer, M. B., *Trans. Electrochem. Soc.*, vol. 74, p. 447, 1938. Schlain, D., Manganese investigations, electrodeposition of manganese, *U.S. Bur. Mines, Repts. Invest.* 3651, July, 1942.

[3] Lundell, G. E. F., and Knowles, H. B., *J. Research Natl. Bur. Standards*, vol. 18, p. 629, 1937, RP 999.

[4] *Trans. Electrochem. Soc.*, vol. 66, p. 471, 1934.

[5] *Metal Ind.* (*N.Y.*), vol. 34, p. 176, 1936.

CHAPTER XX

GROUP 8: IRON-GROUP METALS: IRON, COBALT, AND NICKEL

GENERAL CONSIDERATIONS

There are nine metals in Group 8 of the periodic system, which constitute a transition from the *A* to the *B* portions of Groups 1 to 7. It is convenient to discuss Group 8 metals in two sections: (1) the *iron-group* metals, iron, cobalt, and nickel, and (2) the six *platinum-group* metals. The iron metals will be treated in this chapter, and the platinum metals in Chap. XXI.

Iron, cobalt, and nickel are very similar in physical and chemical properties. They are all magnetic, iron the most and nickel the least. Iron is the most active chemically, as evidenced by its great tendency to oxidize, *i.e.*, to rust. Nickel is the least active and under most conditions tends to become passive and to resist tarnish or oxidation. Cobalt is intermediate in chemical properties. It turns blue or black when heated in air to 400°C (750°F), while nickel does not oxidize till a higher temperature is reached. (This behavior can be used to detect the presence of 10 per cent or more of cobalt in nickel deposits.) Under favorable conditions nickel is deposited on steel by immersion.[1] This process is used to apply very thin nickel coatings prior to enameling of steel.

Electrochemically these three metals are characterized by *chemical polarization* (page 46); *i.e.*, they are not deposited at an appreciable rate until potentials considerably more negative than their equilibrium potentials have been reached. This delay in deposition may be associated with the initial deposition of the metal in an unstable state, which slowly changes to the stable form.

Each of these three metals has compounds with valences of II and III, with higher valences in some unusual compounds. The divalent compounds of iron, *i.e.*, the ferrous compounds, are readily

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[1] Wesley, W. A., and Copson, H. R., *Trans. Electrochem. Soc.*, vol. 94, p. 20. 1948.

oxidized to the trivalent ferric compounds, which are the most stable. With nickel and cobalt, the divalent compounds are most stable. All deposition of these three metals is done from their divalent compounds. Typical formulas are as follows (some of these compounds are not stable):

	Ferrous	Ferric	Cobaltous	Cobaltic	Nickelous	Nickelic
Oxide......	FeO	Fe_2O_3	CoO	Co_2O_3	NiO	Ni_2O_3
Hydroxide..	$Fe(OH)_2$	$Fe_2(OH)_6$	$Co(OH)_2$	$Co_2(OH)_6$	$Ni(OH)_2$	$Ni_2(OH)_6$
Chloride....	$FeCl_2$	$FeCl_3$	$CoCl_2$	$CoCl_3$	$NiCl_2$	$NiCl_3$
Sulfate.....	$FeSO_4$	$Fe_2(SO_4)_3$	$CoSO_4$	$Co_2(SO_4)_3$	$NiSO_4$	$Ni_2(SO_4)_3$

IRON DEPOSITION

Because iron readily tarnishes and rusts in the atmosphere, it is not used as a protective coating. In fact, much of the deposition of other metals is done in order to cover and to protect iron or steel against corrosion.

The principal uses of iron deposition depend upon its desirable physical properties and its cheapness. It is employed in electroforming, *e.g.*, of printing plates, tubes, and sheets; in building up worn or underdimensioned steel parts; and in special instances because of its magnetic properties. Its ability to assist in the welding together of two metals such as stainless steel and low-carbon steel is sometimes used in the production of *stainless-clad* steel. It can also be used as a means of preparing pure iron in either a dense or a powdered form. One advantage of iron deposits, *e.g.*, for building up, is that they are soft enough to be machined or otherwise finished, after which they can be case-hardened.

The baths and conditions for iron deposition have been summarized by C. T. Thomas.[1] Practically all iron deposition is conducted from ferrous salts, usually the chloride or sulfate. Because ferrous salts tend to oxidize in the air to form ferric salts, it might appear desirable to use the more stable ferric compounds. However, the yield of iron for a given current at 100 per cent cathode efficiency would be only two-thirds as much from a ferric as from a ferrous salt. Moreover, the ferric salts tend to hydro-

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[1] *Trans. Electrochem. Soc.*, vol. 80, p. 499, 1941.

lyze in aqueous solutions and to precipitate ferric hydroxide, unless considerable free acid is present. The use of iron anodes in ferrous baths tends to reduce any ferric salt that is formed by oxidation, so that, when a bath is in nearly continuous operation, it remains almost completely ferrous, as indicated by a clear green color. If some ferric salt forms when the bath is unused, it can be readily reduced by adding a small amount of acid, which causes some chemical solution of the iron anodes (or suspended scrap iron) with simultaneous reduction of the ferric salt. The presence of ferric salts in ferrous baths tends to yield more brittle deposits. In certain proprietary processes, small concentrations of ferric salts have been recommended, with the claim that they increase the throwing power.

Satisfactory iron deposits can be produced from baths prepared from ferrous sulfate, $FeSO_4 \cdot 7H_2O$, or ferrous chloride, $FeCl_2 \cdot 4H_2O$. As the chloride is much more soluble and has a higher conductivity than the sulfate, it is more commonly used. Most ferrous salt baths are fairly concentrated, *e.g.*, at least $3N$ in ferrous sulfate and as high as $5N$ if chloride is used. The latter concentration corresponds to about 500 g/l (67 oz/gal) of ferrous chloride, $FeCl_2 \cdot 4H_2O$, or to 140 g/l (19 oz/gal) of dissolved iron.

Additions of other salts can be made to increase the conductivity and to decrease the ferrous ion concentration. In sulfate baths, ammonium sulfate is commonly added or the double salt, ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, is used. In ferrous chloride baths, calcium chloride, $CaCl_2$, is often added. Potassium chloride, KCl, can be used when harder deposits are desired. The concentrations of these added salts are not critical, as they have very little direct effect on the properties of the deposits.

Iron baths are generally used at a fairly low pH, *e.g.*, between 1 and 2. For certain purposes, especially when operating at very high temperatures and current densities, it is more convenient to determine the free acid by titration than to use pH control. At very high current densities in $5N$ ferrous chloride baths, free acid equivalent to $0.1N$ is desirable. The acidity of a hot iron bath tends to reach an equilibrium in continuous operation, and its control is usually not difficult. If slightly too much acid is added, the anode efficiency increases and the excess acid is soon neutralized. If the pH is too high, the anode efficiency decreases. In practice, small occasional additions of acid, *e.g.*, of H_2SO_4 to a sulfate bath or of HCl to a chloride bath, are required to maintain the desired pH or acidity.

The properties of the iron deposits are determined largely by the temperature of operation. Deposits produced at room temperature are relatively hard and brittle and have a high stress, as indicated by a tendency to crack and curl, especially on surfaces treated to permit separation. The full benefits of higher temperatures are not realized below about 90°C (194°F). For very high current densities, it is desirable to operate at 105°C (221°F) and to have a fairly high acidity, *e.g.*, $0.1N$ free acid.

Nearly pure iron or steel anodes dissolve readily, but there is some separation of solid particles that may cause rough deposits. From steel anodes this residue or sludge consists chiefly of carbon, while from ingot iron it may consist of iron oxide. In either case it is desirable to employ anode bags in order to prevent the sludge from becoming suspended in the bath. The most satisfactory diaphragm is cloth woven from African blue asbestos. Glass cloth and plastic cloth have proved less satisfactory. The iron baths are not very sensitive to metallic impurities. Most of the latter, such as copper and lead, are likely to be cemented out on the iron anodes. It was reported by W. B. Stoddard, Jr.,[1] that very small amounts of manganese chloride in the iron bath cause formation of finer grained and more ductile deposits.

Most organic impurities cause very hard, brittle deposits. Treatment with activated carbon and continuous filtration remove impurities and permit continuous operation. It is not customary to use organic additions in iron baths, but wetting agents can be employed to prevent pitting.

For various purposes the following baths and operating conditions have been recommended:

1. SULFATE BATH OF MACFADYEN[2]

	N	g/l	oz/gal
Ferrous ammonium sulfate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	1.8	360	48
Free sulfuric acid, H_2SO_4	0.005	0.25	0.03

Temperature, 25°C (77°F)
Current density, 20 amp/ft^2 (2 amp/dm^2)

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[1] *Trans. Electrochem. Soc.*, vol. 84, p. 305, 1943.

[2] *Trans. Faraday Soc.*, vol. 15, p. 98, 1915.

2. CHLORIDE BATH (LANGBEIN-PFANHAUSER) FOR THICK, FAIRLY SOFT DEPOSITS[1]

	N	g/l	oz/gal
Ferrous chloride, $FeCl_2 \cdot 4H_2O$	3	300	40
Calcium chloride, $CaCl_2$	6	335	45

pH, 1.0–1.5
Temperature, 90°C (194°F)
Current density, 60 amp/ft^2 (6.5 amp/dm^2)

3. CHLORIDE BATH FOR HARD DEPOSITS ON PRINTING PLATES[2]

	N	g/l	oz/gal
Ferrous chloride, $FeCl_2 \cdot 4H_2O$	2.4	240	32
Potassium chloride, KCl	2.4	180	24

pH, 5
Temperature, 35°C (95°F)
Current density, 35 amp/ft^2 (3.5 amp/dm^2)

4. SULFATE-CHLORIDE BATH FOR HARD DEPOSITS ON PRINTING PLATES[3]

	N	g/l	oz/gal
Ferrous sulfate, $FeSO_4 \cdot 7H_2O$	1.9	250	33
Ferrous chloride, $FeCl_2 \cdot 4H_2O$	0.4	42	5.6
Ammonium chloride, NH_4Cl	0.4	20	2.7

pH, 4.5–6
Temperature, 100°F (38°C)
Current density, 50–100 amp/ft^2 (5–10 amp/dm^2)

COBALT DEPOSITION

In many respects cobalt is very similar to nickel, so much so that there are few advantages of cobalt deposits to offset their higher cost. Early studies on cobalt deposition[4] showed that it was possible to employ high current densities and to obtain hard, fairly bright deposits of cobalt. Subsequent studies of nickel deposition, notably those by O. P. Watts, showed that high current densities can be used in nickel baths of similar composition. Hence the studies on cobalt plating led to great improvements in nickel plating.

No strictly comparable studies have been made to establish the reported ability to use higher current densities in cobalt than in nickel baths. If such a difference is confirmed, it may be explained

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[1] THOMAS, C. T., and BLUM, W., *Trans. Am. Electrochem. Soc.*, vol. 57, p. 59, 1930.

[2] LAMB, VERNON A., and BLUM, W., *Intern. Assoc. Electrotypers, Tech. Bull.* 7, Apr. 15, 1942.

[3] SCHAFFERT, R. M., and GONSER, B. W., *Trans. Electrochem. Soc.*, vol. 84, p. 319, 1943.

[4] KALMUS, H. T., HARPER, C. H., and SAVELL, W. L., *Trans. Am. Electrochem. Soc.*, vol. 27, p. 1, 1915.

by differences in the pH at which $Ni(OH)_2$ precipitates, as recently suggested in a review of cobalt plating.[1]

It has been found that nickel can be deposited with as great hardness as cobalt; in fact there is a wide range of hardness of each of these deposits. Cobalt is more active than nickel and hence is not so resistant to high temperatures (*e.g.*, on electric irons) or to corrosive inks on printing plates. While certain special applications of deposited cobalt may prove warranted, it is in no sense a substitute for nickel. Cobalt may be deposited with nickel in alloys that have specific desired properties. For example, the Weisberg bright-nickel deposits may contain up to 15 per cent of cobalt. All nickel anodes and deposits produced in America are likely to contain from 0.5 to 1 per cent of cobalt. However, nickel made by the Mond process in England is practically free from cobalt. Studies are in progress in the American Electroplaters' Society Research Project No. 9 that will define the effects of small amounts of cobalt on the properties of electrodeposited nickel.

Baths for cobalt deposition are very similar to those for nickel. The double cobalt ammonium sulfate, $CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, is much more soluble than the corresponding double nickel salt. The pH range for cobalt is about the same as for nickel, but the low pH bath has not been so extensively used as for nickel. The following formulas from the work of Kalmus and associates are typical. Addition of fluorides has also been suggested.

1. "I B," DOUBLE SALT BATH

	N	g/l	oz/gal
Cobalt ammonium sulfate, $CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	0.90	180	24

pH, about 5.8
Temperature, 25°C (77°F)
Current density, 4–40 amp/ft^2 (0.4–4 amp/dm^2)

2. "XIII B," SINGLE SALT BATH

	N	g/l	oz/gal
Cobalt sulfate, $CoSO_4$	3.6	278	37
or Cobalt sulfate, $CoSO_4 \cdot 7H_2O$	3.6	500	67
Sodium chloride, NaCl	0.3	17	2.3
Boric acid, H_3BO_3	0.75(*M*)	45	6

pH, about 5
Temperature, 25–45°C (77–113°F)
Current density, 33–160 amp/ft^2 (3.5–17 amp/dm^2)

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[1] SODERBERG, G., PINNER, W. L., and BAKER, E. M., *Trans. Electrochem. Soc.*, vol. 80, p. 579.

NICKEL DEPOSITION

General. Nickel is the most important metal applied by plating, in terms not only of the tonnage of metal consumed but also of the wide diversity of its uses, with respect both to the many basis metals covered and to the numerous types of articles plated. The development of tarnish-resistant chromium deposits led to the almost universal adoption of a final chromium finish on all electroplated surfaces where appearance is important. It is well known to the plating industry but not to the layman that the successful use of chromium plating for decoration depends upon the previous application of a metal coating which will protect the steel or other basis metal against corrosion, since chromium coatings are relatively porous and hence do not prevent corrosion. Experience has shown that nickel coatings are most suitable to furnish this type of protection against corrosion. This conclusion was confirmed by wartime experience, when other demands for nickel greatly restricted its use in plating except for special important military uses. Efforts to substitute copper for a large part of the nickel normally used in plated coatings yielded deposits with inferior protective value. While copper is still often used as an initial or intermediate layer on steel, the present tendency is to increase both the proportion of nickel and the thickness of the final nickel layer in such coatings.

Nickel deposition is also important because it illustrates and involves many of the important factors in electrodeposition, such as anode passivity, high cathode chemical polarization, stressed deposits, pH control, pitting, and the effects of addition agents. Intensive study of nickel plating is therefore useful not only directly but also because it throws light on many other problems of plating.

Types of Nickel Baths. In spite of the many formulas of nickel baths for specific purposes, practically all of them contain nickel sulfate; a chloride, usually nickel chloride; and a buffering agent, usually boric acid. Nickel fluoborate solutions have been proposed but are not in general use. Practically all nickel plating is conducted from acid solutions, which have, however, a wide range in pH for specific purposes, *e.g.*, from 1.5 to 6.0. One exception is the use of an alkaline ammonical nickel bath with a pH of about 9 (such as Zialite) and used to apply thin coatings of nickel directly on zinc base die castings.[1]

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[1] HIRSCH, A., *Trans. Electrochem. Soc.*, vol. 63, p. 135, 1935.

The principal inorganic additions to nickel baths are sulfates or chlorides, such as sodium, potassium, ammonium, or magnesium salts. These may be added to decrease the nickel-ion concentration or otherwise to influence the properties of the deposit. During the past decade there has been a rapid development of *bright-nickel* plating, temporarily suspended during the war but now again expanding to cover a very large part of the protective and decorative applications of nickel deposits.

Nickel baths may be usefully classified according to their applications. Deposits for protection against corrosion and for appearance and that are to be chromium-plated can be either plated *dull* and subsequently buffed, *semibright* requiring only light buffing, or *bright* with no buffing. For resistance to wear, *e.g.*, on printing plates, relatively hard, tough nickel is employed. For electroforming of various articles fairly hard but ductile deposits are preferred, especially if any further forming operations are necessary. To perhaps a greater degree than with other electrodeposits, the properties of nickel may be varied over wide ranges by proper selection of the bath composition and operating conditions. In many cases compromises are necessary; *e.g.*, certain bright-nickel deposits may be used even though they are relatively brittle.

Bath Composition. *Nickel Salts.* The principal nickel salts used in plating are the sulfate and the chloride. The sulfate may exist according to the temperature of crystallization as either $NiSO_4{\cdot}7H_2O$ or $NiSO_4{\cdot}6H_2O$, which, when pure, contain, respectively, 20.9 and 22.3 per cent of nickel. In many cases the salt purchased is a mixture of these two salts, but in recent years the salt with $6H_2O$ predominates. This uncertainty makes it impractical to specify the purity of nickel sulfate in terms of its nickel content.

Nickel chloride is supplied as $NiCl_2{\cdot}6H_2O$, which when pure contains 24.7 per cent of nickel.

Nickel ammonium sulfate, $NiSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$, the so-called "double nickel salt," was formerly used extensively in plating but now to only a limited extent, *e.g.*, in electrotyping. When pure it contains 14.9 per cent of nickel. It has a low solubility and hence is not suitable for modern plating baths.

In recent years nickel acetate, $Ni(C_2H_3O_2)_2$, and nickel formate, $Ni(HCO_2)_2{\cdot}2H_2O$, have been used in special baths to be referred to later. Nickel carbonate, $NiCO_3$ (or basic carbonate), is sometimes used for neutralizing nickel baths and is generally sold as a wet paste, which dissolves more rapidly in the bath than the dry powder.

The purity of nickel salts for plating is important. U.S. Federal Specification O S-61 (1930) includes the following requirements:

	Nickel sulfate, per cent	Nickel ammonium sulfate, per cent	Nickel chloride, per cent
Nickel (+ cobalt), min	21.4	14.6	24.3
Iron, max	0.08	0.08	0.08
Zinc, max	0.05	0.05	0.05
Copper, max	0.02	0.02	0.02
Free acid, max	0.10	0.10	0.10
Insoluble, max	0.10	0.10	0.10

The British Standards Institution Specification BSS 564 has slightly more rigid limitations on impurities and also a maximum of about 1 per cent on cobalt content. The latter restriction, which is equivalent to about 5 per cent of the content of metallic nickel, appears superfluous. The *Mond process* nickel and most of the nickel salts used in England contain very little cobalt, while *electrolytic* nickel used in the United States as the principal source of nickel anodes and of part of the nickel salts contains about 0.5 to 1 per cent of cobalt. Much of the nickel sulfate used in the United States is derived as a by-product of copper refining and also contains up to 1 per cent as much cobalt as nickel. With the high price of cobalt, it would never be added as an adulterant of salts. It has not been shown that small amounts of cobalt are detrimental in nickel anodes or salts. Hence in the United States all analyses report the sum of *nickel plus cobalt.*

Other Salts Used in Nickel Baths. All modern nickel baths contain some chloride, which is necessary to ensure corrosion with a high anode efficiency of the nearly pure nickel anodes now used. The earlier use of impure nickel anodes, to which carbon, silicon, manganese, iron, and tin were often added to decrease the melting point and to induce corrosion, was associated with the use of low-nickel baths containing little or no chloride, *e.g.*, the *double salt* bath. It is now known that very pure nickel will dissolve anodically if sufficient chloride is present in the bath.

As far as anode corrosion is concerned, it is immaterial what chloride is added. If, therefore, other metallic ions are not desired in the bath, it is logical to supply the chloride as nickel chloride. Adequate anode corrosion can usually be obtained with about 0.25*N* chloride, equivalent to 30 g/l (4 oz/gal) of $NiCl_2 \cdot 6H_2O$, but it is now customary to add as much as 0.5*N* nickel chloride, *i.e.*, twice the above concentration, especially when high-purity anodes are used.

The use of any other chloride must be justified by some advantage in having the other metallic ion present. The most commonly used chloride in earlier years was ammonium chloride, NH_4Cl, which is now sometimes used in baths to produce hard nickel deposits and also for barrel plating.

Sodium chloride, NaCl, and potassium chloride, KCl, have also been used in nickel baths. The exact functions of ammonium, sodium, or potassium ions in nickel baths have not been defined. Such effects as have been demonstrated are probably related to their concentrations in the cathode film, where they may influence the precipitation or inclusion of colloidal basic compounds in the deposits.

The three sulfates sometimes added are ammonium sulfate, $(NH_4)_2SO_4$ (in the double nickel salt); magnesium sulfate, $MgSO_4 \cdot 7H_2O$; and sodium sulfate, Na_2SO_4. The ammonium salt hardens the deposits. Magnesium sulfate has been reported to have various beneficial effects, not clearly demonstrated. Although codeposition of some magnesium with the nickel was early reported, it has not been confirmed in more critical tests. Sodium sulfate in high concentrations has been used in the high-sulfate bath for plating nickel directly on zinc. Its function is to furnish sulfate ions, which, by their *common-ion effect* reduce the nickel-ion concentration and thus retard deposition of nickel by immersion. It is doubtful if the sodium ions as such have significant effects.

Buffers. Although it is now known that good nickel deposits can be obtained from baths with pH values from 1.5 to 6.0, the optimum range for a specific bath or given operating conditions is usually fairly narrow, *e.g.*, ±0.5 pH. There are three roughly defined pH ranges in use in nickel plating. The so-called "low pH" baths are operated at a pH of from 1.5 to 3.0, at relatively high temperatures and current densities. Most of the bright-nickel baths are used in the pH range from 3.0 to 4.5. Baths used at low temperature and current density, for thin deposits or for hard coatings on printing plates, are generally used at pH values from 4.5 to 6.0.

If these baths contained only nickel salts or other sulfates and chlorides, they would be only slightly *buffered*; hence a small difference between the anode and cathode efficiencies would cause a relatively large change in pH and necessitate its frequent adjustment by addition of acid or alkali (page 79). The most commonly used buffer in nickel baths is boric acid, H_3BO_3, a very weak acid. Its concentration is not critical, and as it has a limited solubility, there is little chance of having too high a concentration unless it actually crystallizes out on the anode bags. Hence it is not necessary to determine it frequently, which is fortunate, as its determination is difficult. Boric acid exerts its maximum buffer effect at a pH from 5 to 6. It might therefore appear that use of boric acid in baths operated at a lower pH would be unwarranted. The fact that boric acid is considered beneficial in all nickel-plating baths indicates that its effect is exerted principally in the cathode film, the pH of which usually exceeds 5. The boric acid probably retards increase of pH in the cathode film to a value at which nickel hydroxide (or another basic compound) precipitates and thus increases the *limiting current density* above which *burnt* deposits are produced.

Acetic acid, $HC_2H_3O_2$, is relatively weak, though stronger than boric acid. It exerts its maximum buffer action in a somewhat lower pH range than boric acid, *e.g.*, from pH 3 to 5. In practice[1] the buffer action of acetic acid is obtained by adding nickel acetate, $Ni(C_2H_3O_2)_2$, to the bath in concentrations about equivalent to the nickel chloride.

Formic acid, HCOOH, is somewhat stronger than acetic acid. It exerts a buffer action when added as a formate, *e.g.*, in the nickel-cobalt bright bath (page 381).

Brighteners. The very extensive use of bright-nickel plating during the past decade represents a greater industrial than a scientific advance. Although it is now possible to classify the brighteners into a few fairly well-defined groups, no clear understanding of the functions or mechanism of the various organic compounds has been reached.

Most of the modern bright-nickel deposits are *laminated* into very thin layers that are parallel to the cathode surface. This

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[1] LALONDE, P. J., *Electrotypers' and Stereotypers' Bull.*, vol. 32, No. 12, p. 3, 1946.

behavior is a strong indication that the process of deposition is *cyclic*, or intermittent. During each cycle that leads to a discrete layer, there may be a building up of the concentration of the addition agent or of products derived from it, which retards metal deposition till a sufficient electrode potential has been developed to cause deposition and inclusion of the organic matter. Corresponding fluctuations in the cathode potential have been reported but not yet closely correlated with the thickness or composition of the successive layers.

In a review of nickel plating,[1] brighteners are divided into two classes, which include, respectively, (1) cobalt salts, aryl sulfonic acids, sulfanamides, and sulfanimides, and (2) cadmium or zinc salts, formates, aldehydes and ketones, and amino polyarylmethanes. Materials of the latter group yield bright but brittle deposits, and their concentrations are very critical. Substances of the first group are less effective brighteners, but they permit more of the first group to be tolerated and modify their properties.

When it is realized that a given bright-nickel bath may contain both an organic and an inorganic substance of each class plus a wetting agent in addition to the three normal constituents, *i.e.*, nickel sulfate, nickel chloride, and boric acid, one appreciates that the modern bright-nickel bath is a very complicated solution. The fact that such baths are so extensively used is a tribute to the ingenuity of their developers and users. On the other hand, the degree of control required is usually beyond the ability of a practical plater and often taxes the skill of a chemist. Any simplification of these baths that would preserve their advantages would be very welcome.

In practice the difficulties of producing *full-bright* nickel deposits have led to extensive adoption of *semibright* deposits, which require only light color buffing. Their control is more simple.

Certain nickel-plating baths, especially those that produce semibright deposits, have been found to possess a *smoothing action*.[2] If such a deposit is applied to a fairly rough surface, *e.g.*, one with a profilometer reading of 20 micro-inches, the surface becomes smoother as the coating thickness is increased. In con-

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[1] PINNER, W. L., SODERBERG, G., and BAKER, E. M., *Trans. Electrochem. Soc.*, vol. 80, p. 539, 1941.

[2] GARDAM, G. E., *J. Electrodepositors' Tech. Soc.*, vol. 22, p. 155, 1947. WILLSON, K. S., and DUROSE, A. H., *Plating*, vol. 36, p. 246, 1949.

trast, most plating baths, *e.g.*, the Watts nickel bath and the acid copper bath, yield rougher deposits as the thickness is increased. No adequate explanation of this smoothing action has been proposed, *e.g.*, any correlation with measurable properties such as polarization and throwing power. When applicable, the use of such baths may reduce polishing costs.

The basic formula for most of the present bright-nickel baths is the *Watts bath*, with relatively high concentrations of nickel sulfate, nickel chloride, and boric acid. The bright baths are even more susceptible to certain impurities than the dull baths. It is significant that cadmium and zinc, sometimes used as brighteners, are detrimental impurities in the dull baths and must be carefully controlled in the bright baths. Cobalt may be present in fairly large concentrations, *e.g.*, 10 to 15 per cent of the nickel content, in the bright nickel-cobalt baths, which contain also formates and formaldehydes. Lower cobalt contents such as 1 per cent of the nickel are used in similar baths to yield semibright deposits. One of the chief functions of cobalt is to offset the detrimental effects of impurities such as copper and zinc. Hence baths with at least 1 per cent as much cobalt as nickel are claimed to be more tolerant of certain impurities.

The most serious limitations of bright-nickel deposits are their brittleness and stress and their tendency to become passive (page 50). While these properties are not necessarily parallel in a given deposit, stress is more harmful with a brittle deposit and vice versa. Certain addition agents, such as saccharin, have been reported to reduce the stress in bright-nickel deposits.

The multiplicity of bright-nickel formulas and the absence of published information regarding the exact composition and control of each bath make it impracticable to discuss details. To a large degree, the operation of each bath is still specific.

Antipitting Agents. One of the most common and unpredictable defects of nickel baths is their tendency to yield pitted deposits. A pit is associated with the presence and retention of gas bubbles, usually hydrogen, on the cathode surface, which prevent deposition of metal at that point. A pit may start at the cathode surface, in which case it constitutes a pore, through which corrosion may occur. In other cases the pit may originate during deposition and may not extend to the basis metal. Even then, however, the pit is an incipient weak spot, because the coating is thinner there. The pits are objectionable from the standpoint of appearance, especially because after being buffed they may cause drag marks and be even more conspicuous.

Evolved hydrogen is the most common immediate cause of pits, but in special cases release of dissolved air or other gases may initiate pitting. If a solution becomes very cool, *e.g.*, at night, it dissolves more air. When it is warmed by passage of current or otherwise, some of the air is released, and if the bubbles cling to the surface, they may cause pits.

Evolution of hydrogen is not in itself a cause of pitting; in fact certain baths operated with very low efficiency and much hydrogen evolution, such as the chromic acid bath, show little tendency toward pitting. In order for hydrogen to form a pit, it must be evolved at a given point and be retained there long enough for the metal to deposit around it. The local discharge of hydrogen is governed very largely by the hydrogen overvoltage on that part of the surface. Its retention there is influenced by the surface tension of the solution with respect to hydrogen.

The local evolution of hydrogen may be favored by the presence of (1) inclusions or other discontinuities in the cathode surface, (2) suspended particles that may lodge on the cathode, (3) inorganic impurities, such as iron compounds that may be preferentially deposited on the cathode, or (4) organic impurities, such as decomposition products of addition agents, which may possibly change the surface tension of the solution or may be codeposited on the cathode.

The principal remedies for pitting in nickel deposition are addition of hydrogen peroxide and wetting agents, and purification with activated carbon. Hydrogen peroxide, H_2O_2, used in dull-nickel baths, furnishes a material that is more easily reduced at the cathode than is the hydrogen or nickel ion. Hence at those points at which hydrogen might otherwise be discharged and cause pitting, the hydrogen peroxide is reduced. One evidence of such reduction, especially at low current densities, is the decrease in cathode efficiency in the presence of hydrogen peroxide or other oxidizing agents. The hydrogen peroxide may also oxidize harmful organic matter and will oxidize ferrous ions to ferric. One objection to hydrogen peroxide is that it is unstable and hence decomposes slowly, apart from its desired oxidizing action. Hence it must be added at fairly frequent intervals in small concentrations if the contamination persists, and time should be allowed for it to act.

One advantage of hydrogen peroxide is that the end product of its reduction is water, and hence is harmless. Other oxidizing agents that might be employed may leave harmful or inert compounds which may accumulate in the bath. Persulfates and permanganates are in this class. Chromic acid is definitely harmful.

Because hydrogen peroxide oxidizes many organic materials, it is not compatible with bright-nickel baths that contain certain organic additions. In such baths it is therefore customary to employ wetting agents (page 85). Care must be exercised to ensure that the wetting agents used do not react or otherwise interfere with the particular brighteners used. In general, sulfates of long-chain or slightly branched hydrocarbons are used, or substituted aryl sulfonates with shorter chains.

Impurities and Their Removal. Nickel baths and especially the bright plating baths are very susceptible to the effects of metallic impurities, such as iron, copper, zinc, and chromium, and to certain organic compounds. As above noted, these may increase the tendency for pitting. In addition they may change the character of the deposits, especially at relatively low current densities. For example, small concentrations of zinc or cadmium yield bright-nickel deposits, but larger amounts produce dark streaks.[1] One objection to the use of cadmium as a brightener is that it may yield "passive" nickel deposits.

It was early shown that in the ordinary nickel baths copper is most deleterious, as it causes dark deposits, especially on the lower part of cathodes. Zinc is nearly as harmful, but iron in fairly high concentrations does not necessarily cause cracking or curling provided the pH is properly adjusted. However, at high pH values the dissolved iron is likely to be oxidized and precipitated as brown ferric hydroxide, $Fe(OH)_3$, or a basic salt. Such precipitates in suspension are likely to cause pores or pits in the nickel.

The importance of pure nickel solutions has been increased in bright-nickel plating, where slight variations in color or luster are more important. Research Project No. 5 of the American Electroplaters' Society on this subject is in progress at Michigan State College under D. T. Ewing. In a preliminary report[2] it was

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[1] THOMPSON, M. R., *Trans. Am. Electrochem. Soc.*, vol. 42, p. 79, 1922, and vol. 23, p. 359, 1923.

[2] EWING, D. T., and GORDON, W. D., *Proc. Am. Electroplaters' Soc.*, p. 213, 1947, and EWING, D. T., ROMINSKI, R., and KING, W., *Proc. Am. Electroplaters' Soc.*, p. 119, 1948.

shown that some loss of appearance, ductility, and protective value are produced in a Watts bath with as little as 0.025 g/l of copper, equivalent to about 0.05 per cent of the nickel content of the bath or to about 0.01 per cent of copper in the nickel sulfate.

Fortunately, simple methods are now available for the removal of most harmful impurities in nickel baths.[1] It is possible to remove iron and copper by increasing the pH of the solution. This treatment causes the salts of these metals to hydrolyze and to precipitate as hydroxides or basic salts at a lower pH than nickel hydroxide is precipitated. For this purpose it is desirable first to oxidize the dissolved iron to ferric salt, which hydrolyzes at a lower pH than does ferrous. Much of the harmful organic matter can also be removed in this treatment. Part of it may be directly oxidized, *e.g.*, by hydrogen peroxide, and the balance may be removed by adsorption on the precipitated ferric hydroxide.

It is also possible to remove copper, iron, lead, and zinc by electrolysis of the nickel bath under carefully controlled conditions. Because copper and lead are more noble than nickel, they deposit preferentially at a low current density. On the other hand, zinc and iron are deposited, along with some nickel, at relatively higher current densities. An ingenious arrangement has been described[2] in which a corrugated cathode is employed with a plane anode. Under these conditions, a lower current density exists in the hollows than on the ridges of the cathode. Hence the copper, lead, iron, and zinc are removed simultaneously, the copper and lead in the hollows and the zinc and iron on the ridges. By having such a cell in continuous operation while a portion of the plating bath is passed through it, it is possible to keep the concentrations of these impurities below harmful values.

Since the bright-nickel baths usually contain desirable organic substances, it is not practicable to oxidize the deleterious organic impurities without attacking the desired addition agents. It is therefore customary to remove at intervals all organic matter by filtration through activated carbon, after which new additions of brighteners and wetting agents are made.

Operating Conditions. The four important variables that can be controlled in the operation of a given nickel bath are pH, temperature, current density, and agitation. As these factors are mutually interdependent, and as their optimum values vary according to the type of bath and of deposit, it is not possible to

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[1] Diggin, M. B., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 33, p. 513, 1946.

[2] Case, B. C., *Proc. Am. Electroplaters' Soc.*, p. 228, 1947.

specify preferred values for each factor. Instead, an effort will be made to indicate the directions of their effects upon the bath operation and character of the deposits.

pH. In the early operation of relatively weak nickel baths at room temperature and low current densities, it was often stated that the baths should be *neutral*, as judged, for example, by litmus paper. When pH control was first applied to nickel plating, it was found that most commercial nickel plating was then conducted at a pH of 5.0 to 6.0, even in the Watts bath, at relatively high temperatures and current densities. Subsequently it was reported[1] that better results were obtained in the Watts-type bath by operating at a pH of 1.5 to 3.0. This so-called "low pH bath" has come into extensive use even though its cathode efficiency is low. In the development of bright-nickel plating it was found that an intermediate pH, *e.g.*, from 2.5 to 4.5, is usually advantageous. For a given bright bath, however, the pH should be maintained within about ±0.3 pH of the value found to be optimum for that bath.

The choice of pH is governed by the type of bath and the desired properties of the deposit. In general in dull-nickel baths an increase in pH, especially above 5.0, leads to the production of harder deposits, probably as the result of more precipitation and inclusion of basic material at the still higher pH that then exists in the cathode film. Conversely, the low pH deposits are likely to be softer. To some extent this distinction is overcome by the fact that higher current densities are usually applied in low pH baths; hence the pH of the cathode film approaches that in the high pH baths.

The control of pH is best effected by balancing the conditions of operation so as to avoid large or rapid changes in pH. The principal cause of a change in pH is a difference in anode and cathode efficiency. By maintaining a large area of *clean*, high-purity nickel anodes and an adequate content of chloride in the bath, the anode efficiency is likely to be slightly greater than the cathode efficiency. Hence the pH tends to increase. This is usually a desirable trend, because the pH can then be adjusted at intervals by small additions of hydrochloric or sulfuric acid, which are more convenient to add than a basic material such as nickel carbonate. Another advantage of a slightly excessive anode efficiency is that thereby the solution tends to be *self-sustaining*,

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[1] PHILLIPS, W. M., *Trans. Am. Electrochem. Soc.*, vol. 58, p. 387, 1930.

i.e., the excess of dissolved nickel will at least partially counteract the loss by drag out. Drag in of acid of alkali may also change the pH.

Temperature. In general, it is possible to apply higher current densities in warm than in cold baths. This advantage of high temperature depends upon several factors, including (1) higher solubility of the nickel or other salts, (2) higher conductivity, (3) a reduced polarization at both the anode and cathode, and (4) an increased anode and cathode efficiency. Among the possible disadvantages of a high temperature are (1) an increased tendency for hydrolysis and precipitation, especially of impurities such as iron and zinc that may then cause pitting, (2) a tendency to precipitate or coagulate brightening agents, (3) excessive evaporation, (4) production of passive deposits, and (5) lower throwing power. In practice, it is customary to use moderately high temperatures, usually from 40 to 50°C (104 to 140°F), but in special cases higher temperatures are employed.

Current Density. The permissible current density is governed by the factors just discussed. At room temperature, especially in dilute baths, current densities of 5 to 20 amp/ft^2 (0.5 to 2 amp/dm^2) are employed. In stronger, warm baths current densities up to 60 amp/ft^2 (6 amp/dm^2) can be used. Higher average current densities are possible in certain baths, especially on regular shapes, but on many articles the maximum current density is three or more times the average, and hence burning occurs unless a relatively low average current density is used.

Agitation. The effect of agitation is the same as an increase in nickel concentration and in hydrogen-ion concentration (*i.e.*, a decrease in pH) and hence permits higher current densities. In practice, the degree of agitation furnished in conveyor tanks is not sufficient to affect the permissible current density greatly and is chiefly advantageous in yielding more uniform plating on different pieces and greater convenience in handling. One objection to rapid agitation of nickel baths is the stirring up of suspended particles and consequent roughness. The customary use of violent air agitation in nickel electrotyping baths is permissible, because some roughness on the *back* of electrotype shells (the layer last deposited) is not objectionable, but it would be on electroplated coatings. Air agitation in nickel-plating baths is much more extensively used in England than in the United States. When frequent or continuous filtration of nickel-plating baths is applied, rapid agitation can be employed without causing roughness.

Properties of Nickel Deposits. The physical properties of electrodeposited nickel are of special interest because there is a very wide range in properties, control of which fosters special applications of nickel, *e.g.*, in electroforming. While many data on these properties have been published and summarized,[1] little information was previously reported on the effects of operating conditions on each property. A recent report[2] summarized studies made by the American Electroplaters' Society on dull-nickel deposits. These results lead to the following conclusions regarding the range of properties and the effects of operating conditions.

Hardness. This varies in different nickel deposits from about 130 to 430. In the Watts-type bath, a minimum hardness was obtained at a pH of 3, above and below which harder deposits were obtained. This minimum hardness is not observed in other nickel baths, *e.g.*, the all-chloride or all-sulfate bath. The hardest deposits are obtained at a high pH.

At a pH of 3, a minimum hardness was obtained when the current density was about 40 amp/ft^2 (4 amp/dm^2).

Harder nickel deposits are obtained from an all-chloride bath or an acetate bath than from the Watts type.

At a given pH and current density in the Watts bath an increase in temperature decreases the hardness. At a pH of 3 a minimum hardness was obtained at 55°C (131°F).

Tensile Strength. In general, the tensile strength is about parallel to the hardness and ranges from 56,000 to 160,000 lb/in.^{2} (3,900 to 11,000 kg/cm^2).

Ductility. The ductility, as measured by elongation, is roughly inversely proportional to the hardness and tensile strength.

Electrical Resistivity. The electrical resistivity of deposited nickel is influenced by the content of inclusions such as oxide and also of cobalt. It shows a minimum at a pH of 3.

Magnetic Properties. As previously reported, these may vary with the conditions of deposition. Hence it is necessary to anneal nickel coatings at 400°C (750°F) before measuring their thickness by their magnetic attraction (page 122).

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[1] Brenner, A. and Jennings, C. W., *Plating*, vol. 35, p. 52, 1948.

[2] Brenner, A., and Jennings, C. W., *Proc. Am. Electroplaters' Soc.*, p. 31, 1948, and *Plating*, vol. 35, pp. 1228 and 1234, 1949.

Structure. Deposits from the Watts bath are usually columnar, while those from the all-chloride or all-sulfate are finer grained.

Composition. Nickel deposits usually contain oxygen and hydrogen, probably present as basic nickel compounds such as $Ni(OH)_2$. Chloride may be present in the deposits from all-chloride baths. These inclusions no doubt influence the hardness and tensile strength.

Effect of Heat-treatment. Heating of all nickel deposits, *e.g.*, to 1000°C (1832°F), decreases their hardness, tensile strength, density, and electrical resistivity and increases their ductility.

Nickel Anodes. The use of nickel baths containing chloride has practically eliminated the use of nickel anodes containing less than 99 per cent of nickel, such as were formerly employed. At present the principal types of nickel anodes are the rolled and the cast. In special cases, cathode sheets from nickel-refining baths have been used as anodes, as they are the purest and cheapest form of nickel. The principal objections to them are their low thickness, usually not over 0.25 in. (6 mm), which increases the amount of scrap nickel, and the presence of laminations, which may cause fine lacy particles to be detached and cause rough deposits.

Most of the rolled nickel anodes are so-called "depolarized"; *i.e.*, they contain a small amount of nickel oxide, which probably assists their uniform corrosion. The low sulfur content must be closely controlled. The cast-nickel anodes and some types of rolled anodes contain a small amount of carbon, which facilitates their uniform casting and also aids in their corrosion.

No commercial nickel anodes dissolve without leaving some insoluble residue, consisting chiefly of finely divided nickel, and nickel oxide, NiO, from the rolled anodes and of carbon from the cast anodes. In high pH baths some nickel peroxide, NiO_2, may form on the anodes. It is necessary to prevent this residue from becoming suspended in the solution and being carried to the cathode, where it may cause rough deposits. The practical means of retaining the residue is by the use of anode bags. For most purposes these are made of a good grade of cotton cloth, which is not appreciably attacked by nickel-plating solutions. Care should be taken to remove any sizing material, such as dextrin, from the cloth, as it may introduce deleterious organic material into the nickel baths. In special cases other fabrics, such as glass cloth or a plastic cloth such as Vinyon, have been employed, but the cotton is usually preferred. One objection to the use of anode bags is that they tend to retain the more concentrated solution which forms at the anode and thereby to increase anode polarization.

If the anode bags are good filters, *i.e.*, allow no insoluble material to pass through them, the rolled and cast anodes both yield good service. Practically, it is found that the residue of nickel oxide from the rolled anodes is somewhat finer and more easily detached than the carbon from the cast anodes. The carbon tends to form a fairly adherent, spongy coating on the cast anodes and to retain fine particles that might otherwise become detached.

Deposition of Nickel on Different Basis Metals. Because nickel is most extensively applied to numerous basis metals, the cycles employed will be considered briefly in this section, even though they may also involve differences in preparation or the deposition of a metal layer prior to the nickel or may be equally adaptable to plating of metals other than nickel.

Plating on Steel. Nickel can be plated directly on steel or over a thin or a thick layer of copper. Because extensive corrosion tests and experience have shown that the copper layer exerts less protective value than an equal thickness of nickel, the present trend is toward the elimination of the copper. When a thin layer, *e.g.*, 0.0001 in. (0.0025 mm), of copper is applied, it is chiefly used as a step in the cleaning procedure and not because of any protective value of the copper. When bright nickel is used, a relatively thick layer of either bright copper or dull copper, subsequently buffed, can be used to produce a smoother subsurface for the bright nickel.

Typical steps in the preparation of steel for plating are referred to on page 219.

Plating on Cast Iron. The possible advantages of a copper layer are illustrated by the fact that the best adhesion of nickel to cast iron is almost invariably obtained when at least a thin layer of copper is first applied. The difficulty of plating on cast iron is undoubtedly associated with the presence of free carbon or graphite in the iron. If this is firmly embedded, nickel does not deposit so readily upon the carbon or carbides as on the iron crystals. Copper from cyanide baths is more likely to deposit upon the carbon and in any crevices on the surface, than is nickel. If, in an effort to remove carbon from the surface, the latter is overpickled, a weak layer of metal may remain, which yields poor effective adhesion. Cathodic cleaning in molten caustic is sometimes effective; and pickling in hydrofluoric acid may be helpful. At best, the adhesion of nickel to cast iron is not so good as to steel, since the intermediate copper layer, even if perfectly adherent, is usually weaker than the nickel and hence separation may occur within the copper layer.

Plating on Copper and Brass. It is the most common practice to apply nickel directly to copper or brass, followed by the customary thin coating of chromium. It has been conclusively shown that chromium coatings applied directly to brass furnish much less protection against corrosion than when a nickel layer is first applied. Occasionally a flash of copper is applied, especially to leaded brass, before nickel plating.

Plating on Zinc and Zinc-base Die Castings. It has been shown in extensive tests that adherent coatings of nickel can be directly applied to zinc die castings by using a *high-sulfate* nickel bath,[1] The principle of this bath is the addition of sufficient sodium sulfate (containing the *common-ion* sulfate) to reduce the nickel-ion activity and increase the cathode polarization. Thereby zinc is prevented from passing into solution and precipitating dark, spongy nickel. Exposure tests have shown that such nickel coatings furnish good protection against the corrosion of zinc. This high-sulfate nickel bath has excellent conductivity and throwing power and has hence been successfully used in the barrel plating of small brass articles. The deposits are semibright and somewhat brittle.

In spite of the above facts, practically all nickel plating on zinc is preceded by a copper layer from a cyanide bath. This procedure is justified by the fact that on the customary irregular shapes plated, there is a tendency for zinc to pass into solution even in the high-sulfate nickel bath, at points of low current density. This behavior not only leads directly to dark deposits in those areas, but also contaminates the nickel bath with zinc, which leads to dark nickel deposits over the entire surface. The zinc does not tend to deposit copper at a significant rate from the cyanide bath, the throwing power of which is sufficiently good to ensure rapid, complete covering of the zinc with copper. The Rochelle salt bath (page 296) and certain bright copper baths may be used for this copper plating on zinc.

A relatively thick layer of copper is required because there is a tendency, even at room temperature, for copper in contact with

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[1] THOMPSON, M. R., *Trans. Am. Electrochem. Soc.*, vol. 47, p. 163, 1925.

zinc to diffuse into the zinc and to form a brittle alloy layer.[1] The presence of a fairly thick copper layer, *e.g.*, at least 0.0003 in. (0.0075 min), ensures an excess of copper at the interface, which tends to counteract any brittle alloy layer.

Plating on Aluminum. The most common practice involves the treatment of aluminum or its alloys with a sodium zincate dip, which may also contain copper and which produces a thin adherent coating of zinc, upon which copper from a cyanide bath is generally deposited. Nickel and chromium can then be applied in the usual way.

Recently is was found[2] that very adherent deposits of zinc, cadmium, or tin may be produced on aluminum by immersing the latter in solutions containing hydrofluoric acid or fluorides. The latter exerts a solvent effect on the film of aluminum oxide normally present on aluminum or its alloys, just as does the free alkali normally present in the sodium zincate dip.

It is also possible first to *anodize* aluminum, *i.e.*, to treat it anodically in an appropriate bath so as to form an oxide film on the surface and then, after a suitable chemical treatment, to deposit a metal such as nickel. Such a process appears to contradict the usual criterion of a clean surface for plating. Studies have shown that some of the aluminum oxide layer remains under the plated coating. The latter obtains its adhesion to the basis metal through pores in the oxide coating.[3] Owing to the fact that both copper and nickel accelerate corrosion of any exposed aluminum, plated aluminum does not usually resist corrosion in severe industrial or marine atmospheres.

Plating on Magnesium. Plating of nickel or other metals on magnesium or its alloys is rendered difficult by the high activity of magnesium and its consequent tendency to deposit nickel or other heavy metals by immersion. Owing to the large difference in solution potentials of magnesium and of the metals such as copper, nickel, or chromium that may be plated upon the magnesium, corrosion of the latter is greatly accelerated if there are any pores or discontinuities in the coatings. Consequently, plated magnesium is not now recommended for use under even mild conditions of exposure. Until it can be shown that nearly impervious plated coatings can be produced and maintained on magnesium or its alloys, it is doubtful whether any proposed detailed cycles for

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[1] CASTELL, W. F., *Trans. Electrochem. Soc.*, vol. 66, p. 427, 1934.

[2] HEIMAN, S., *Trans. Electrochem. Soc.*, vol. 95, p. 205, 1949.

[3] BENGSTON, H., *Trans. Electrochem. Soc.*, vol. 88, p. 307, 1945.

such plating warrant present industrial application. The principles, without the details, of suggested methods will be discussed as a guide to further research.

In a method suggested by Loose,[1] the magnesium is cleaned in an alkaline bath, etched in a solution containing chromic acid, and then dipped into a solution containing hydrofluoric acid. A residual film of sparingly soluble magnesium fluoride retards deposition of nickel by immersion. Plating is then conducted in a solution of the type of No. 5 (page 380) which contains free fluoboric acid.

In another procedure suggested by Delong,[2] the magnesium is cleaned, then pickled in phosphoric or acetic acid, cleaned anodically in trisodium phosphate, pickled in hydrochloric acid, and dipped in an alkaline zinc solution containing pyrophosphate and fluoride. Copper is then deposited from a Rochelle salt bath, and followed by nickel or other metals.

Typical Nickel Baths. The following formulas represent the principal types used in nickel deposition. The exact concentrations and operating conditions may require modification for specific applications, but the values given may serve as a guide.

1. PLAIN NICKEL (DILUTE, COLD BATH)

	N	g/l	oz/gal
Nickel sulfate, $NiSO_4$, $6H_2O$	0.9	120	16
Ammonium chloride, NH_4Cl	0.25	15	2
Boric acid, H_3BO_3	0.25M	15	2

pH, 5.3
Temperature, 20–30°C (68–86°F)
Current density, 0.5–2 amp/dm^2 (5–20 amp/ft^2)

2. WATTS-TYPE, WARM BATH

	N	g/l	oz/gal
Nickel sulfate, $NiSO_4$, $6H_2O$	1.8	240	32
Nickel chloride, $NiCl_2$, $6H_2O$	0.4	45	6
Boric acid, H_3BO_3	0.5M	30	4

pH, for operation at a high pH, 4.5–5.5; low pH, 1.5–3.0
Temperature, 43°C (110°F)
Current density, 2–7 amp/dm^2 (20–65 amp/ft^2)

3. BRIGHT NICKEL

Typical Watts bath (No. 2) plus two or more types of addition agent and a wetting agent
pH, 2.3–4.5
Temperature and current density as in 2

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[1] LOOSE, W. S., *Trans. Electrochem. Soc.*, vol. 81, p. 213, 1942.

[2] DELONG, H. K., *Metal Finishing*, vol. 46, p. 46, 1946.

4. Nickel Plating Directly on Zinc or Barrel Plating on Brass
(High-sulfate bath)

	N	g/l	oz/gal
Nickel sulfate, $NiSO_4, 6H_2O$	0.5	70	9
Ammonium chloride, NH_4Cl	0.25	15	2
Sodium sulfate, Na_2SO_4	1.0	160	22
Boric acid, H_3BO_3	0.25*M*	15	2

pH, 5.5
Temperature, 20–30°C (68–86°F)
Current density, 1.5–3.0 amp/dm² (14–28 amp/ft²)

5. Nickel Plating on Magnesium (page 379)

	N	g/l	oz/gal
Nickel sulfate, $NiSO_4 \cdot 6H_2O$	0.45	60	8
Boric acid, H_3BO_3	0.56*M*	35	4.7
Ammonium fluoride, NH_4F	0.57	65	8.7

pH (adjusted with hydrofluoric acid), 5.5
Temperature, 40°C (104°F)
Current density, 10–30 amp/ft² (1–3 amp/dm²)

6. Nickel Electrotyping

	N	g/l	oz/gal
Nickel sulfate, $NiSO_4, 6H_2O$	0.5	70	9
Ammonium chloride, NH_4Cl	0.1	5	0.7

pH, 6.0 for wax molds; 5.6 for lead molds
Temperature, 20–30°C (68–86°F)
Current density, 1–2 amp/dm² (10–20 amp/ft²)

7. Nickel Plating on Stereotypes

	N	g/l	oz/gal
Nickel chloride, $NiCl_2 \cdot 6H_2O$	1.1	135	18
Nickel acetate, $Ni\ (C_2H_3O_2)_2$	1.2	105	14

pH, 4.6
Temperature, 46°C (115°F)
Current density, 5 amp/dm² (47 amp/ft²)

8. Bright Cobalt-nickel Bath

	N	g/l	oz/gal
Nickel sulfate, $NiSO_4 \cdot 6H_2O$	1.8	240	32
Nickel chloride, $NiCl_2 \cdot 6H_2O$	0.38	45	6
Cobalt sulfate, $CoSO_4 \cdot 7H_2O$	0.11	15	2
Boric acid, H_3BO_3	0.5*M*	30	4
Ammonium sulfate, $(NH_4)_2SO_4$	0.04	2.5	0.3
Nickel formate, $Ni\ (COOH)_2$	0.67	50	6.7
Formaldehyde, HCHO (40 per cent)		2.5	0.3

pH, 4.5
Temperature, 55°C (131°F)
Current density, 3 amp/dm² (28 amp/ft²)

9. Hard Deposits, All-chloride Bath[1]

	N	g/l	oz/gal
Nickel chloride, $NiCl_2 \cdot 6H_2O$	2.5	300	40
Boric acid, H_3BO_3	0.25*M*	30	4

Temperature, 50°C (122°F)

Current density, 5–10 amp/dm^2 (50–100 amp/ft^2)

10. High-speed Nickel Bath[2]

	N	g/l	oz/gal
Nickel sulfate, $NiSO_4 \cdot 6H_2O$	1.5	200	27
Nickel chloride, $NiCl_2 \cdot 6H_2O$	1.5	175	23
Boric acid, H_3BO_3	0.65*M*	40	5.3

pH, 1.5

Temperature, 46°C (113°F)

Current density, 11 amp/dm^2 (100 amp/ft^2)

11. Wood's Nickel Strike[3]

	N	g/l	oz/gal
Nickel chloride, $NiCl_2 \cdot 6H_2O$	2	240	32
Hydrochloric acid (sp gr 118)	...	125 (ml)	16 (fl oz)
(Equivalent to HCl)	1.4	52	7

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[1] Wesley, W. A., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 33, p. 504, 1946.

[2] Pinner, W. L., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 33, p. 506, 1946.

[3] *Metal Ind.* (*N.Y.*), vol. 36, p. 330, 1938.

CHAPTER XXI

GROUP 8: PLATINUM-GROUP METALS

GENERAL CONSIDERATIONS

The six metals ruthenium, rhodium, palladium, osmium, iridium, and platinum have many similar properties and are usually found together in their ores. A large part of their present production is obtained from Canadian nickel ores, chiefly from the residues from electrolytic nickel refining. While these six metals have certain similarities to iron, cobalt, and nickel, their valences and compounds are more complex. All these metals are relatively scarce and expensive, but at present palladium is the cheapest. While each of the metals has been deposited from aqueous solutions, only three, *viz.*, rhodium, palladium, and platinum, have been used or suggested for commercial plating and hence warrant present consideration.

In general, the platinum metals have high melting points and are relatively resistant to oxidation and to attack by most acids. Most of their commercial uses depend upon these properties, *e.g.*, the extensive use of platinum for crucibles, vessels, and electrodes in chemical and electrochemical processes. If it were possible to produce relatively thin but completely impervious coatings of platinum upon common metals such as steel, copper, or nickel, plated laboratory vessels might replace much of the solid platinum. A few unpublished tests by W. E. Bailey at the National Bureau of Standards showed that the usual thin decorative platinum coatings contain fine cracks (similar to those in chromium) and are very porous. While it may be possible by further investigations to reduce this porosity, the production of platinum plated vessels is not now promising.

The extensive use of rhodium plating on reflectors depends upon the resistance of the rhodium to tarnish, even at the fairly high temperatures produced in powerful searchlights.[1] Although the reflectivity of rhodium (page 429) is less than 80 per cent, as

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[1] Kushner, J. B., *Metals and Alloys*, vol. 11, p. 137, 1940. Anon., *Metal Finishing*, vol. 38, p. 532, 1940.

compared with 95 per cent for silver, the rhodium surface will maintain a high reflectivity over longer periods.

The proposed use of rhodium plating over silverware to protect it against tarnish has not been very successful, although it is used on silver-plated glass and china. Even though electrodeposited rhodium is relatively hard (over 500 Brinell), the very thin coating (a few millionths of an inch) that is permitted by the high cost of rhodium is easily penetrated by scratches, through which tarnish of the silver may take place. One reason the rhodium was proposed for this purpose is that its color is white and more nearly resembles silver than does the color of platinum or palladium.

In former years platinum plating was applied to jewelry, including white gold, but at present rhodium plating is more extensively used when a white tarnish-resistant surface is desired.

Because it is relatively cheap, palladium plating has been proposed and has found some applications on jewelry and as a preliminary coating before rhodium plating. Its color is not so white as that of rhodium. Palladium and rhodium have relatively low specific gravities (12.16 and 12.41) as compared with 21.44 for platinum. Hence a given thickness of one of the former metals corresponds to only about 60 per cent of the weight of that same thickness of platinum. As, however, palladium is not so hard or so resistant to tarnish or chemical attack as are platinum and rhodium, it is not a satisfactory substitute for those metals.

An excellent review of platinum plating, with some references to rhodium and palladium, was presented by R. H. Atkinson[1] to the First International Electrodeposition Conference. A more recent summary was published by K. Schumpelt.[2]

The present methods of plating may be summarized as follows:

PLATINUM DEPOSITION

The best known and most used bath for platinum plating is based on solutions described in 1855 by Roseleur. The following formulas are typical, although the exact proportions used may vary widely:

1.	*N*	g/l	
Chloroplatinic acid, $H_2PtCl_6 \cdot 6H_2O$	0.1	13	32 dwt/gal
(Equivalent to platinum, Pt^{IV})	0.1	5	12 dwt/gal
Ammonium phosphate, $(NH_4)_2HPO_4$	1.0	45	6 oz/gal
Sodium phosphate, $Na_2HPO_4 \cdot 12H_2O$	2.0	240	32 oz/gal

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[1] *J. Electrodepositors' Tech. Soc.*, vol. 13, paper 25, 1937.

[2] *Trans. Electrochem. Soc.*, vol. 80, p. 489, 1941.

2.	*N*	g/l	
Chloroplatinic acid, $H_2PtCl_6 \cdot 6H_2O$	0.08	10.5	27 dwt/gal
(Equivalent to platinum, Pt^{IV})	0.08	4	10 dwt/gal
Ammonium phosphate, $(NH_4)_2HPO_4$	1.0	45	6 oz/gal
Boric acid, H_3BO_3	0.25	15	2 oz/gal

To prepare either solution, the three compounds are dissolved in water separately. The ammonium phosphate is then added to the chloroplatinic acid. This produces a yellow precipitate of ammonium chloroplatinate, $(NH_4)_2PtCl_6$. Without filtering this solution, the sodium phosphate (or boric acid) is added, and the mixture is boiled gently for a few hours, *i.e.*, until the odor of ammonia can no longer be detected and the solution acquires a pale lemon-yellow color.

The resultant solution contains the platinum in the platinic state (Pt^{IV}), in the form of an ammino compound. It is used with platinum anodes at a temperature of about 70°C (158°F) and a current density of 0.2 to 0.5 amp/dm^2 (2 to 5 amp/ft^2). As the platinum anodes are insoluble, it is necessary to replenish the solution by the addition of chloroplatinic acid or ammonium chloroplatinate. This will result in an objectionable accumulation of chlorides in the bath.

An alkaline platinum bath, also based on early publications, was described by E. C. Davies and A. R. Powell,[1] who recommend the following formula:

3. PLATINATE BATH

	N	g/l	
Sodium hexahydroxyplatinate, $Na_2Pt(OH)_6 \cdot 2H_2O$	0.2	18.5	45 dwt/gal
(Equivalent to platinum, Pt^{IV})	0.2	10	25 dwt/gal
Sodium hydroxide, NaOH	0.13	5	0.7 oz/gal
Sodium oxalate, $Na_2C_2O_4$	0.08	5	0.7 oz/gal
Sodium sulfate, Na_2SO_4	0.4	30	4 oz/gal

To prepare this solution, the platinum salt (made by boiling a mixture of sodium chloroplatinate and sodium hydroxide, cooling, and adding ethyl alcohol) is dissolved in hot water, and the other three compounds are separately dissolved and added. The bath is operated at 65 to 80°C (149 to 176°F) and a current density of about 0.8 amp/dm^2 (7.5 amp/ft^2). Anodes of platinum or of copper heavily plated with platinum are used. The bath is replenished by additions of the platinum salt and sodium hydroxide. Sodium carbonate is likely to accumulate in the bath, as a result of absorption of carbon dioxide.

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[1] *J. Electrodepositors' Tech. Soc.*, vol. 13, paper 26, 1937.

A third type of bath, in which there is no accumulation of salts, was described by W. Keitel and H. E. Zschiegner.[1] The platinum is added in the form of diammino platinous nitrite, $Pt(NH_3)_2(NO_2)_2$. Their recommended formula is as follows:

4. Amminonitrite Bath

	N	g/l	
Diamminoplatinous nitrite	0.1	16	40 dwt/gal
(Equivalent to platinum^{II})	0.1	10	25 dwt/gal
Ammonium nitrate, NH_4NO_3	1.25	100	13 oz/gal
Sodium nitrite, $NaNO_2$	0.15	10	1.3 oz/gal
Ammonium hydroxide, NH_4OH(sp gr 90)		50(ml)	6.5 fl oz/gal

This bath is operated with platinum anodes at a temperature of 95°C (203°F) and a current density of 20 amp/dm^2 (186 amp/ft^2) for 15-sec *flash* coatings or of 7 amp/dm^2 (65 amp/ft^2) for thicker coatings. Although the platinum in this bath has a valence of II, the cathode efficiency is low (about 10 per cent) and indefinite, hence it is hard to predict the time necessary to deposit a given thickness of platinum.

A more recently proposed bath[2] is a combination of the phosphate and amminonitrite, with the following composition:

5. Phosphate + Ammonio-nitrite Bath

	N	g/l	
Sodium phosphate, $Na_2HPO_4 \cdot 12H_2O$	0.83	100	13.4 oz/gal
Ammonium phosphate, $(NH_4)_2HPO_4$	0.45	20	2.7 oz/gal
Diamminoplatinous nitrite	0.04	6.5	16 dwt/gal
(Equivalent to platinum, Pt^{II})	0.04	4	10 dwt/gal

This bath is operated similarly to bath 4.

PALLADIUM DEPOSITION

In an extensive review of palladium deposition, R. H. Atkinson and A. R. Raper[3] recommend two processes, in the first of which soluble palladium anodes are used. In the second process platinum anodes are used and the anode and cathode compartments are separated by a diaphragm.

In the soluble anode process the bath contains sodium palladous nitrite, $Na_2Pd(NO_2)_4$, equivalent to 10 g/l (25 dwt/gal) of metallic palladium and 30 g/l (4 oz/gal) of sodium chloride, NaCl. It is

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[1] *Trans. Electrochem. Soc.*, vol. 59, p. 273, 1931.

[2] Private communication from K. Schumpelt.

[3] *J. Electrodepositors' Tech. Soc.*, vol. 8, paper 10, 1933.

operated at a pH of 8 at 40 to 50°C (104 to 122°F) and a current density of 0.1 amp/dm^2 (1 amp/ft^2). With palladium anodes, the anode and cathode efficiencies are nearly 100 per cent and no replenishment is required except to replace drag out.

In another bath of this type [1] the following formula is used:

	N	g/l	
Sodium phosphate, $Na_2HPO_4 \cdot 12H_2O$....	0.83	100	13.4 oz/gal
Ammonium phosphate, $(NH_4)_2HPO_4$....	0.45	20	2.7 oz/gal
Sodium chloropalladite, Na_2PdCl_4......	0.08	12	1.5 dwt/gal
or Palladium diamminnonitrite, $Pd(NH_3)_2(NO_2)_2$..................	0.08	9	1.1 dwt/gal
(Equivalent to palladium, Pd^{II})........	0.08	4	10 dwt/gal

The constituents are dissolved, and the solution is boiled till the dark red color changes to a light yellow, which indicates the formation of an ammino palladous compound. It is operated at 2 to 4 amp/ft^2 (0.2 to 0.4 amp/dm^2) at somewhat above room temperature.

The diaphragm in the process of Atkinson and Raper is made of porous clay tiles of low resistance. The solution in the cathode compartment contains 40 g/l of palladosammine chloride, $Pd(NH_3)_2Cl_2$; 35 ml/l of ammonium hydroxide, NH_4OH (sp gr 0.88); and 10 g/l of ammonium chloride, HN_4Cl. The anode solution contains 10 g/l of ammonium carbonate, $(NH_4)_2CO_3$; 20 g/l of ammonium sulfate, $(NH_4)_2SO_4$; and 50 ml/l of ammonium hydroxide (sp gr 0.88). The bath can be operated over a wide range of temperature. For example, at 20°C (68°F) a current density of 0.5 amp/dm^2 (5 amp/ft^2) is used, and at 70°C (158°F) a current density of 2 amp/dm^2 (20 amp/ft^2). This process is recommended for thick deposits of palladium.

Palladium can be stripped from silver by making it anodic in a solution containing 100 g/l of sodium chloride and 3.6 g/l of hydrochloric acid.

RHODIUM DEPOSITION

The principal baths used for rhodium plating consist of rhodium sulfate, $Rh_2(SO_4)_3$, or rhodium phosphate, $RhPO_4$, with an excess of sulfuric or phosphoric acid.[2] While the solution is simple, it is

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[1] Private communication from K. Schumpelt.

[2] FINK, C. G., and LAMBROS, G. C., *Trans. Electrochem. Soc.*, vol. 63, p. 181, 1933. ATKINSON, R. H., and RAPER, A. R., *J. Electrodepositors' Tech. Soc.*, vol. 9, p. 77, 1933. WEISBERG, M., *Metal Finishing*, vol. 38, pp. 587, 647, 1940, and vol. 39, p. 16, 1941.

not easy to prepare, because it is difficult to dissolve metallic rhodium or to prepare pure soluble rhodium compounds. A detailed method for making the rhodium-plating solution, starting with the fusion of metallic rhodium with lead, is described by L. Cinnamon.[1]

The present rhodium baths contain from 1 to 2 g/l of rhodium, introduced as the sulfate or phosphate, and from 20 to 40 g/l of sulfuric acid or phosphoric acid. Both sulfuric and phosphoric acids may be present. The baths are usually operated at room temperature, 20 to 25°C (70 to 80°F), and with a current density of about 7 amp/dm^2 (65 amp/ft^2). The cathode efficiency is generally less than 10 per cent, especially in the range for bright deposits. The efficiency increases as the temperature is raised, the metal content is increased, or the acidity is decreased.

Because these acid solutions attack many basis metals (which also precipitate spongy rhodium), it is advisable to deposit the rhodium over nickel, silver, or gold. Nickel is usually preferred as the undercoat on reflectors.

Because rhodium is insoluble in all acids, it is very difficult to strip defective coatings. One method is to use an acid that will dissolve the underlying metal through pores in the rhodium, which then later flakes off. It was reported by R. H. Atkinson[2] that rhodium and also platinum can be dissolved from silver by immersion in a fused mixture of sodium and potassium cyanide. This stripping action can be accelerated by making the article anodic in the fused bath.

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[1] *Proc. Am. Electroplaters' Soc.*, vol. 25, p. 205, 1937.

[2] *J. Electrodepositors' Tech. Soc.*, vol. 13, paper 25, 1937.

CHAPTER XXII

ALLOY DEPOSITION

GENERAL PRINCIPLES

In this chapter an effort will be made to explain as simply as possible the known principles of alloy deposition and to illustrate them by more detailed data regarding a few important applications of alloy plating. Because brass plating is by far the most extensive industrial application of alloy deposition, particular consideration will be given to it. For convenience, many references to alloy deposition have been included in other chapters, *e.g.*, tungsten alloys under tungsten deposition (page 349) and nickel-cobalt alloys under nickel (page 368).

In spite of an enormous literature on alloy deposition, admirably assembled by C. L. Faust,[1] there are comparatively few present commercial uses of alloy deposits. One important but often overlooked factor is that the industrial deposition of an alloy must be justified by some significant advantages, since, in general, the control of alloy deposition is more involved and troublesome than that of single metals. It is possible that the introduction of a second metal into the bath and hence into the deposit may be advantageous by (1) improving the bath operation or (2) changing one or more properties of the deposit, such as color, luster, hardness, ductility, and resistance to corrosion, *e.g.*, at high temperatures.

The study of the effects of impurities in plating baths has shown that small concentrations of certain metals may have significant effects on the deposition of other metals, with which they may or may not codeposit. There is no sharp distinction between the effects of large and of small metallic additions to a deposit. For convenience, however, the term *alloy deposition* will here be used to refer especially to those deposits which contain more than 1 per cent of the minor metal. Any deposits consisting of two or more metals that are so finely divided that they cannot be distinguished

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[1] *Trans. Electrochem. Soc.*, vol. 78, p. 383, 1940.

with the unaided eye will be considered as *alloys*, regardless of the metallurgical form in which the metals may be present. Most of the discussion will be confined to alloys of two metals, *i.e.*, to *binary*, or *bimetallic*, systems, because their deposition is better understood and they are more likely to be applied commercially. The difficulties of controlling a trimetallic bath are usually greater than those of a bimetallic bath.

While the major factors that influence the codeposition of two metals have been fairly well defined,[1] there have been few quantitative applications of these principles to known systems of alloy deposition, much less to new or unknown systems as a guide or basis of prediction. Virtually all alloy plating that is conducted commercially, especially brass plating, is based on empirical study and experience and not upon any far-reaching predictions derived from theoretical considerations.

The principal factors that determine if two metals can be codeposited from an aqueous solution and the ratio of the metals in the resultant deposit produced at any given temperature and current density are as follows: (1) the static or equilibrium potential of each metal in that type of bath; (2) the cathode polarization of each metal in the presence of the other, *i.e.*, the cathode polarization existing during codeposition; (3) the concentration of each metal and of its ions in the solution used and especially in the cathode film; (4) the solution potential, *i.e.*, the dissolving tendency of the alloy deposit that is or may be formed; (5) the hydrogen overvoltage on the resultant cathode alloy surface. In addition, the results will be influenced by the effects of temperature and current density upon each of the above properties. Even though the direction of the effect of each single variable can often be predicted, it is not yet possible to estimate the magnitude of such changes, especially if two or more conditions are simultaneously varied. This brief outline indicates the complexity and difficulty of making an exhaustive study of any single alloy-plating system. The importance and relation of each of the above factors will now be considered.

Equilibrium Potentials. Consideration of the electromotive series (page 44 and Table 10, Appendix) shows that in solutions of equivalent ion activities, *e.g.*, in simple salt solutions, the normal potentials of but few of the metals are very close together. It is obvious that, if the standard potentials of two metals, *e.g.*, zinc

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[1] FAUST, C. L., *Trans. Electrochem. Soc.*, vol. 80, p. 301, 1941.

and copper, vary widely, in this case by 1.10 volts, *i.e.*, from −0.76 to +0.34 volts, it is so much easier to deposit copper than zinc that it is very unlikely that the two metals will deposit simultaneously from simple solutions, *e.g.*, the sulfates. If on the other hand the standard potentials of two metals are close together, *e.g.*, tin (−0.14 volt) and lead (−0.12 volt), it is about as easy to deposit one as the other, and hence from a simple bath such as the fluoborate, alloys of lead and tin can be readily deposited (page 410).

These same relations would still hold if the zinc and copper were present in a complex salt solution in which the ratio of the two metal-ion activities was about the same as in the simple solutions. The formation of complex salts and ions of any metal always results in a decrease in the metal-ion activity. Fortunately, from the standpoint of alloy deposition, the relative change in ion activity by the formation of complexes of a given type is usually different for two metals. For example, in the formation of complex cyanide solutions from which brass is deposited, the static potential of copper becomes so much more negative with respect to its standard potential than does that of zinc that the two potentials approach each other and may even be reversed. In the latter case it would be possible to cause zinc to deposit chemically upon immersed copper, just the opposite of what happens in a sulfate bath. These relations may be illustrated by hypothetical potential values for cyanide solutions of copper and zinc.

Suppose that with appropriate concentrations of copper, zinc, and cyanide, the equilibrium potentials of the two metals were each made equal to −1.00 volt. In that case, the potential of copper[1] would have been reduced from +0.18 to −1.00 volt, *i.e.*, a total of 1.18 volts, corresponding to a reduction in cuprous ion activity of 1.18 volt/0.058 volt = $10^{-21}N$. The potential of the zinc would have been changed from −0.76 to −1.00 or 0.24 volt, which corresponds to a change in zinc-ion activity of 0.24 volt/0.029 volt = $10^{-8}N$. As far as equilibrium potentials are concerned, it is just as easy to deposit copper as zinc from such a hypothetical solution. If, *e.g.*, by addition of more cyanide, the equilibrium potential of the copper in such a bath became more negative than that of zinc, it would be easier initially to deposit zinc than copper.

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[1] In cyanide solutions copper is in the cuprous state, Cu^{I}. The standard potential of a copper-cuprous ion electrode is about +0.18 volt instead of +0.34 volt, the value for cupric copper.

These principles illustrate the reasons for the frequent use of complex salt solutions for the deposition of alloys. It should be emphasized that it is not necessary to make the static potentials of the two metals exactly equal in the complex solution, much less to reverse their normal order. It is necessary that, for example, by complex ion formation, the static potentials of the two metals become close enough to each other that with a reasonable ratio of the two metal-salt concentrations (*e.g.*, a ratio not greater than 10 to 1) it is possible to deposit both of the metals at some convenient current density.

Cathode polarization. If a system were devised in which two metals had equilibrium potentials close enough to each other, initial simultaneous deposition would occur in some ratio, fixed only by the concentrations of the two metals and hence of their ions in that bath. If there were no cathode polarization of deposition of either metal, then the two metals would deposit in this same ratio at all current densities. These conditions are never approached in any actual alloy systems, because, in general, the cathode polarization curves of any metals in their complex salts have appreciable slopes; *i.e.*, the polarization increases with an increase in current density.

At least three types of systems may exist as a result of these differences in the respective cathode polarization curves of two metals in a given type of bath, as represented diagrammatically in Fig. 53, in each of which, for simplicity, the equilibrium potentials of the two hypothetical metals A and B are given the same values of e_H, which for illustration may differ by only 0.2 volt. In this particular illustration, metal B is initially more noble, *i.e.*, more positive, than metal A.

Case (*a*) of Fig. 53 illustrates the condition in which the cathode polarization of metal B is so much less than that of metal A that there is no potential at which the two polarization curves overlap. In that case, in the light of the factors thus far considered, the codeposition of A and B is impractical.

Case (*b*) represents polarization curves for the two metals that are nearly parallel. At any cathode potential up to A, only metal B is deposited. When potential A is reached, metal A starts to deposit, and as the cathode potential and resultant current density are increased, the proportion of metal B in the deposit, which is equal to the ratio of the two ordinates for the respective current densities of A and B at a given potential, decreases. In such a system the content of metal B in the deposit is always greater than that of A but approaches equality (*i.e.*, 50 per cent of each) as the potential and current density are increased.

In Case (*c*), the polarization of metal B is greater than that of A; hence at potentials beyond the intersection of the two curves the proportion of B increases.

In the above, oversimplified explanation, it was assumed that the deposition of one metal was not influenced by that of the other and that the behavior of the bivalent system could therefore be predicted from that of the separate metals. It is not possible to measure directly the current density and cathode potential of each separate metal during their codeposition. It is possible, however, to make a current density-potential curve for the alloy deposition and to analyze the deposit produced at each current density. From these data it is possible to determine the proportion of the

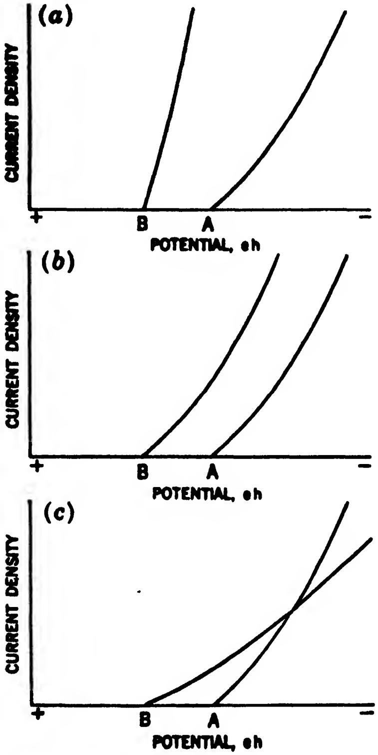

FIG. 53. Possible types of polarization curves in alloy deposition. Case (*a*), the curves for the two metals do not overlap. Case (*b*), the two curves overlap. Case (*c*), the two curves cross.

current that is used in the deposition of each metal and to plot corresponding separate polarization curves for each.

If in a given system such curves agreed closely with those based on measurements with the separate metals, each in a corresponding solution containing only the salt of that metal, the above simple predictions would be verified. In the few studies in which such comparisons have been made, it has been found that the metal ratios in the deposit may vary widely from those predicted from the separate cathode polarization curves. Such discrepancies may result from abnormalities in either the solution or the deposit.

Two separate cyanide solutions of copper and zinc in which the static potentials of copper and zinc are each -1.00 volt may contain quite different ratios of free and combined cyanide. If these two solutions are mixed, the resultant ratio of free and combined cyanide may change the actual and relative potentials of copper and zinc in the mixed solution. In consequence, the separate polarization curves of the two metals in the mixed solution (if they could be measured) would then be different from those obtained in the separate solutions.

The Deposition Potential of the Resultant Alloy. These considerations assume that, when codeposited, each metal acts as if the other were not present. This condition can exist only if the resultant *alloy* is a mechanical mixture, however finely divided, of the two metals. If the deposit is a true alloy, its solution pressure and hence the minimum potential at which it can be deposited are different from that of either of the separate metals. Because the structure of alloys determines both their cathodic and anodic behavior, the principal types of alloys will be briefly discussed.

Mixtures. As indicated above, it is possible for two metals to be intimately mixed and still preserve their original properties. If such an alloy is made anodic, the less noble of the two metals, *e.g.*, *A*, will dissolve at the potential characteristic of that metal and will continue to dissolve at that same potential until the residue of more noble metal *B* so completely envelopes it that further solution of *A* is retarded or prevented. This condition is represented by curve I in Fig. 54. The term *atomic per cent* used in Fig. 54 refers to the ratio of the number of atoms of the metal and not to the proportions by weight. For example, a tin-lead alloy with 50 atomic per cent of each metal contains an equal number of atoms of each, hence 119 parts of tin and 207 parts of lead by weight. The per cent *by weight* of each metal in this alloy would be 119/(119 + 207) = 119/326 = 36 per cent of tin and 64 per cent of lead. The use of atomic per cents in such diagrams instead of weight per cents serves to point out the existence of intermetallic compounds (see below). In depositing two metals from a system represented by Curve I the behavior could probably be predicted from the separate polarization curves.

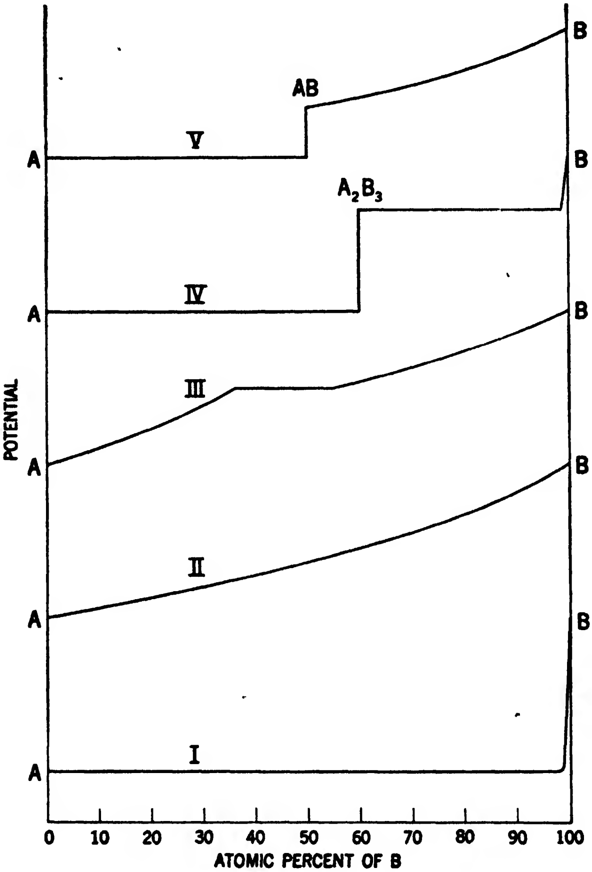

FIG. 54. Equilibrium potentials of different types of alloys. Curve I, metals *A* and *B* form no compounds or solid solutions. Curve II, metals *A* and *B* form solid solutions in all proportions. Curve III, metals *A* and *B* form two solid solutions, each with a limited range. Curve IV, the two metals form a definite compound A_2B_3. Curve V, the two metals form a compound *AB*, which forms solid solutions with *B*. (*According to Allmand and Ellingham, "Applied Electro-chemistry," 2d ed., Edward Arnold & Co., London,* 1924.)

Solid Solutions. Many binary alloys consist of a solution of one metal in the other, similar to ordinary solutions, except that the resultant alloy is solid at ordinary temperature. When such alloys are made anodic, the minimum dissolving potential becomes more noble as the concentration of the more noble metal *B* increases, as in Curve II of Fig. 54. Conversely it requires a less negative potential to deposit alloys with higher contents of *B*. Certain alloys may contain two different solid solutions, as in Curve III of Fig. 54, *e.g.*, a solution of *A* in *B* in one part of the system and of *B* in *A* in the other part.

Intermetallic Compounds. Some alloys consist of or contain definite compounds of the two metals, which behave electrochemically as a single metal. Thus in Curve IV of Fig. 54, the alloy contains a compound of *A* and *B*, represented by the formula A_2B_3, *i.e.*, containing 40 atomic per cent of *A* and 60 atomic per cent of *B*. If more than 40 per cent of *A* is present, *A* forms a separate constituent, and if more than 60 per cent of *B* is present, pure *B* is mixed with the compound. The important point is that such an alloy dissolves (and therefore may deposit) as if it were either a single substance (the compound), or a mixture of one metal and the compound.

Such data as are depicted in Fig. 54 represent the equilibrium potentials of these alloys and do not necessarily show what potentials are involved in their deposition. They do, however, indicate the minimum equilibrium potentials at which a given alloy will deposit. Just as with single metal deposition, the polarization is more important than the equilibrium potentials.

Experience has shown that the codeposition of two metals may take place along polarization curves that are (1) intermediate between those for the separate metals or (2) more negative than either of the metals. The third possibility, *i.e.*, depositing two metals at less negative potentials than either one alone, has not been reported and is highly improbable.

The deposition of an alloy at a potential less negative than that required for the less noble metal alone represents "depolarization" of the deposition of the latter metal. For this to occur it is necessary that the resultant alloy consist of a solid solution or a compound from which the less noble metal dissolves less readily than when alone. It is well known that metallic sodium cannot be deposited from an aqueous solution upon a solid cathode but it can be deposited upon a mercury cathode, with which it forms an alloy called an *amalgam*. If salts of both mercury and sodium are present in an aqueous solution, an alloy of the two metals, *i.e.*, sodium amalgam, can be deposited. The sodium in this alloy reacts much less rapidly with water than does pure sodium, and hence it is easier to deposit the alloy than pure sodium. There are many systems from which an alloy can be plated that contains a metal which cannot be separately deposited. Notable recent examples are the codeposition of molybdenum or tungsten with iron, cobalt, or nickel (page 349). Because no data are available on the standard potentials of molybdenum or tungsten, it is not now possible to state whether these alloy deposits represent simple effects of depolarization or other factors such as hydrogen overvoltage are responsible (see below).

It is even more difficult to explain the deposition of alloys at potentials more negative than the polarization curves of either of the separate metals. Such a behavior indicates a retardation of the deposition, especially of the more noble metals. This cannot be accounted for by the equilibrium potentials of the alloys, which are never more negative than the potential of the less negative metals. The excessive chemical polarization (page 46) in such alloy deposition may be related to the form and behavior of the complex ions present.

Hydrogen Overvoltage. Alloy deposition is still further complicated by the fact that in every aqueous solution there are hydrogen ions, any discharge of which reduces the cathode efficiency of metal deposition. In a strict sense every plating bath of a single metal is an *alloy bath,* since both metal and hydrogen may be discharged and the hydrogen may dissolve in or form compounds with the metal deposited. These same possibilities exist in a solution containing two metals, from which both metals and also hydrogen may be deposited.

As previously explained (page 53), the proportions in which hydrogen and a metal are discharged from a given bath depend upon (1) the respective ion activities of hydrogen and of the metal in that solution and (2) the respective polarization curves for discharge of metal and of hydrogen on that metal surface. For example, zinc may be deposited at high cathode efficiencies from low pH baths because hydrogen has a high overvoltage on zinc and hence is not evolved rapidly at the potential at which zinc is deposited.

In the presence of two metals that may be codeposited, the hydrogen overvoltage on the resultant alloy may be different from that on either of the constituent metals. There are indications, but not conclusive evidence, that the failure to deposit certain metals such as tungsten and molybdenum in a pure state from aqueous solutions is caused partly by the low overvoltage of hydrogen on such metals and the resultant low or zero cathode efficiency. Conversely, if the hydrogen overvoltage on an alloy, *e.g.*, of tungsten and cobalt, is relatively high, it may then be possible to deposit such an alloy. The situation is still further complicated by the effect of surface finish on the hydrogen overvoltage. If the initial deposit of a metal or alloy is rough or spongy, the hydrogen overvoltage and the metal cathode efficiency are decreased. In the absence of data on the relative hydrogen overvoltages on any given two metals or on their deposited alloy, no quantitative predictions of effects of such variables as pH can be made for a given alloy system.

Effects of Operating Conditions. *Metal Concentrations.* In general, an increase in the ratio B/A of metal concentrations in the bath increases the proportion of B in the deposit but not proportionally. This metal ratio in the solution is especially important, and it is difficult to control if, even in the complex bath used, one metal is still much nobler than the other. For example, in a cyanide bath containing silver and cadmium, the silver is still the more noble, so that the ratio of Ag/Cd in the solution must be made much smaller than the ratio desired in the deposit. If, for example, a *nontarnishing* alloy with 90 per cent of silver and 10 per cent of cadmium is desired, the bath must contain relatively more cadmium, *e.g.*, 60 per cent of cadmium and 40 per cent of silver. It is very important to note that there is no simple relation between the ratio of two metals in a bath and in a deposit produced from that bath under any specified conditions. The actual ratios must be determined by experiment. It is unusual and purely coincidental for an alloy deposit to be obtained with the same ratio of metals in the deposit as in the solution. The actual concentrations of each metal in the bath are less important than their ratio. In general, just as with single metals, an increased metal concentration permits the use of higher current densities.

Concentration of Complexing Constituent. As previously mentioned, alloy deposition is usually made possible by the formation of complex metal salts and ions, in which the equilibrium potentials of the two metals are closer together than in their simple salt solutions. When this procedure is used, the complex-forming addition decreases the ion activity of the more noble metal to a greater extent than of the less noble metal. Hence, in general, further addition of the complexing reagent makes it relatively easier to deposit the less noble metal and therefore increases its proportion in the deposit. For example, an increase in the free cyanide content of a brass bath usually increases the proportion of zinc in the brass deposit.

Current Density. In general, raising the current density increases the proportion of the less noble metal in the deposit. For example, an increase in current density in a brass bath increases the proportion of zinc in the deposit. This relation exists if the respective polarization curves of the two metals during codeposition are similar to those in Fig. 53 (2). If, however, the two curves should cross each other as in Fig. 53 (3), an increase in current density will first increase the proportion of the less noble metal *A* but beyond the intersection an increase in current density will have the reverse effect. In general, the composition of an alloy deposit will vary on different parts of an irregularly shaped article, because of the variations in current density.

Temperature. The effect of an increase in temperature upon the codeposition from a given bath will depend upon such factors as its effects on (1) the two polarization curves, (2) the respective cathode efficiencies, and (3) the tendency of the two metals to form an alloy. In general, a rise in temperature aids the deposition of the more noble metal; *e.g.*, it increases the proportion of copper in a brass deposit.

Addition Agents. Any substances that are used to produce brighter, smoother, or more dense alloy deposits may change the ratio of metals in the deposit if they affect the factors discussed above. If they form or assist in forming complex ions, their effects will be similar to those of other complex-forming additions.

Anodes for Alloy Deposition. In alloy deposition it is usually necessary for the anodes to perform the functions of a soluble anode in a plating bath, *i.e.*, to introduce the current, to control its distribution on the cathode, and to supply metal to replace that deposited. In addition, in an alloy bath it is necessary, for the most efficient operation, for the anode to supply the two metals in the same amount and ratio as they are deposited. To the extent that this objective is realized, the control of the alloy bath is simplified. It must be emphasized that the composition or behavior of the anodes in an alloy bath does not *directly* determine the composition of the alloy deposit produced under given conditions in any short interval of time. Under these conditions the deposit composition depends solely upon the bath composition, which, as above stated, rarely has the same metal ratio as in the deposit. From a given bath, *e.g.*, a brass bath, under specified conditions an alloy deposit of the same composition will be initially obtained regardless of whether the anode is insoluble, *e.g.*, platinum, or consists of copper, zinc, or brass. After a certain period of operation with any other than brass anodes, the bath composition will change and consequently that of the deposit also. If, for example, a deposit containing 80 per cent of copper and 20 per cent of zinc is desired, the anodes must contain or, better, must yield to the solution the two metals in this same proportion and with an anode efficiency equal to the cathode efficiency, in order to maintain a constant composition of the bath and of the deposit.

It is not conveniently possible to measure the anode and cathode efficiencies in alloy deposition unless by a coincidence the equivalent weights of the two metals are very close together. In the latter case the cathode efficiency depends upon the total weight of the two metals deposited and not upon their ratio. This situation is illustrated by deposits of cobalt plus nickel, with almost identical equivalent weights, or of cobalt plus tungsten, in which the respective equivalent weights are 29.47 (for Co^{II}) and 30.65 (for W^{VI}). However, in most cases the equivalent weights differ widely. For example, in brass plating, that of cuprous copper, Cu^{I}, is 63.6 and that of zinc, Zn^{II}, is 32.7. Hence, if the current were equally divided between the two metals and the cathode efficiency of each was 100 per cent, the resultant deposit would contain not 50 per cent by weight of each metal, but 66 per cent of copper and 34 per cent of zinc. Under these conditions 2 amp-hr would deposit at 100 per cent efficiency 2.37 g of copper and 1.22 g of zinc, or a total of 3.59 g of brass. If in a given experiment only 1.8 g of brass *of this composition* was deposited, it would be correct to say that the cathode efficiency was 50 per cent. If, however, the 1.8 g of brass deposit contained, not 1.19 g of copper and 0.61 g of zinc, but these metals in some other ratio, such as 1.40 g of copper and 0.40 g of zinc, it would be more troublesome to compute the cathode efficiency. In this case the deposition of the copper would require $1.40/2.37 = 0.59$ amp-hr, and that of the zinc would require $0.40/1.22 = 0.33$ amp-hr. The total quantity of electricity used in depositing metal was therefore $0.59 + 0.33 = 0.92$ amp-hr. If a total of 2 amp-hr was applied, the average cathode efficiency was $0.92/2.00 = 46$ per cent.

If the cathode efficiency of the alloy deposition is practically 100 per cent and if the equivalent weights of the two metals are not close to each other, it is possible to compute the composition of the deposit from its weight and the number of ampere-hours used. This method proved useful with alloys of lead and tin.[1]

The computation of anode efficiency is similar to that of cathode efficiency but is complicated by the fact that metal particles may become detached from the anode, the loss in weight of which is not then a measure of the anode efficiency. It is therefore preferable to compute the anode efficiency from the cathode efficiency and any changes in concentration of the two metals in the bath.

In principle, it is desirable to employ anodes that have the same composition as that of the deposit and that dissolve uniformly and completely. Whether or not this behavior occurs depends upon both the composition and constitution of the alloy used in the anode. If it consists of a pure solid solution or a pure compound (page 394), it is probable that the two metals will dissolve from it in the same ratio in which they are in the anode, leaving little residue or sludge. If, however, as is more commonly true, two or more phases are present in the alloy anode, these are less likely to dissolve at the same rate. If they do not so dissolve, the bath composition will change and sludge will also be produced. Part of this sludge may result from the deposition of the more noble metal in the bath upon the less noble constituent of the alloy anode. Often it is possible to employ alloy anodes over long periods by adding to the bath a substance that will tend to make the anode corrosion more uniform without unfavorably affecting the alloy deposition.

Because for certain alloy baths it is difficult to secure satisfactory solution of alloy anodes, the two separate metals can be used as anodes. If the solution potentials of these two metals are fairly close in the bath used, it may be possible to hang the two kinds of anodes on the same bar and to control their relative rates of solution by adjusting the areas of each. In most cases when separate anodes of two metals are used, their solution potentials are so far apart that at any conveniently applied potential only the less noble metal will dissolve. In that case it is preferable to have the two kinds of anodes in separate anode circuits, in one or both of which a resistance is placed, to control the potential and

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[1] Blum, W., and Haring, H. E., *Trans. Am. Electrochem. Soc.*, vol. 40, p. 287, 1921.

thereby also the current density for each of the separate metals. Even though this arrangement is often practicable, it is more critical and more troublesome to operate. For example, care must be used to avoid too high a potential difference between the two anode bars; otherwise one may act as an intermediate electrode and receive a deposit.

A somewhat simpler arrangement involves the use of only one metal as anode and the addition of compounds of the other metal to replenish the bath. If the concentration of the latter metal in the deposit is low, this method is convenient, as any anions such as carbonate or cyanide introduced with the added metal compound are then unlikely to accumulate in the bath and may even compensate for drag out.

If insoluble anodes are used, *e.g.*, of platinum, and the metals are replenished entirely by additions of metal compounds, the associated anion, *e.g.*, cyanide or hydroxide, may accumulate in the bath. If, as in gold-alloy plating, the concentrations of heavy metals, *e.g.*, of gold and copper, are much less than of the other salts such as potassium cyanide and carbonate, the use of insoluble anodes may be practicable. One general objection to the use of insoluble anodes in a cyanide bath is that thereby cyanide may be oxidized to cyanate and ultimately to carbonate.

TYPICAL ALLOY PLATING BATHS

Brass Plating. Deposition of brass, which is an alloy of copper and zinc, is extensively used in industry for two main purposes. It is commonly applied to zinc, steel, and cast-iron hardware to give it the appearance of brass. For this purpose the color of the brass deposit is the primary consideration, and its composition or other properties are incidental. The coatings are usually rather thin, *e.g.*, about 0.0002 in. (0.005 mm), and exert little protection against corrosion under severe conditions. The application of lacquer over the brass coatings increases their useful life. It is important to note that the color of deposited brass is usually somewhat different from that of cast or rolled brass of the same composition. For example, to match the color of "yellow brass" with 70 per cent of copper and 30 per cent of zinc, a deposit may contain about 80 per cent of copper and 20 per cent of zinc.

The other large application of brass plating is to facilitate adhesion of rubber to steel, probably by combining with the sulfur or sulfur compounds in the rubber. In this use the composition of the brass deposit is fairly critical and is usually kept between 25 and 33 per cent of zinc.[1] The deposits are generally thin, *i.e.*, less than 0.0001 in. (0.0025 mm).

Among the early studies of brass plating is that by A. L. Ferguson and E. G. Sturdevant.[2] Recent papers on brass plating were published by H. P. Coats,[3] and by A. K. Graham.[4]

Bath Composition. All brass plating is done from cyanide baths that contain copper and zinc as the double cyanides, also carbonate and sometimes free caustic. The copper may be assumed to be present as the sodium cuprocyanide, $Na_2Cu(CN)_3$, and the zinc as $Na_2Zn(CN)_4$. Just as with zinc baths, if free alkali is present, some of the zinc may be present as sodium zincate, Na_2ZnO_2, but there is no means of defining the concentrations of these two compounds of zinc. The free cyanide is usually defined as the cyanide content in excess of the two double cyanides.

Suppose that the solution is made up according to the following formula, suggested by Coats:

	N	g/l	oz/gal
Cuprous cyanide, CuCN	0.25	22.5	3
Zinc cyanide, $Zn(CN)_2$	0.25	15	2
Sodium cyanide, NaCN	0.90	45	6

To form $Na_2Cu(CN)_3$ will require two equivalents of NaCN for one equivalent of CuCN; therefore $0.25 \times 2 = 0.50N$ NaCN will be combined with the copper. To form $Na_2Zn(CN)_4$ requires one equivalent of NaCN for each equivalent (*i.e.*, one-half the molar concentration) of zinc; hence $0.25N$ NaCN is used to combine with the zinc. The combined alkali cyanide is therefore equal to $0.50 + 0.25 = 0.75N$, and the uncombined or free cyanide is equal to the total alkali cyanide minus the combined alkali, cyanide, *i.e.*, to $0.90 - 0.75 = 0.15N$ free NaCN, or to $0.15 \times 49 = 7.4$ g/l or 1 oz/gal of free NaCN.

In the above bath, the copper content is $0.25N$; *i.e.*, $0.25 \times 64 = 16$ g/l or 2.1 oz/gal. The zinc content is also $0.25N$; *i.e.*, $0.25 \times 65/2 = 8.1$ g/l or 1.1 oz/gal. The weight ratio of Cu/Zn in the bath is $16/8.1 =$ approximately 2, or 66 per cent of copper and 34 per cent of zinc.

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[1] COATS, H. P., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 24, p. 5, 1937.

[2] *Trans. Am. Electrochem. Soc.*, vol. 38, p. 167, 1920.

[3] *Trans. Electrochem. Soc.*, vol. 80, p. 445, 1941.

[4] *Proc. Am. Electroplaters' Soc.*, p. 143, 1948.

In addition to the essential copper and zinc compounds and free cyanide, the brass baths always contain carbonate, formed by decomposition of the cyanide, and also ammonia, formed by hydrolysis of the cyanide (page 285). Frequently small amounts of ammonia are added to the bath to control its operation.[1] The ammonia probably changes the composition of the complex copper and zinc compounds.

While it is possible to produce from appropriate baths alloy deposits containing the whole range from nearly pure zinc to nearly pure copper, most of the yellow brass plating yields deposits containing from 20 to 38 per cent of zinc. It has been shown[2] that the yellow brass deposits have the same cubic structure and lattice spacing as the cast, recrystallized brass of the same composition. This is *Alpha* brass, consisting of a solid solution, which may contain up to 38 per cent of zinc. Under other conditions it is possible to deposit brass with more than 38 per cent of zinc, which exists in other crystal forms. The important fact is that electrodeposited brass (and most other alloy deposits) have the same X-ray structure as cast alloys of the same composition; in other words, they are true alloys.

The reported effects of various operating conditions upon the composition of the brass deposits are, in general, consistent with the principles of alloy deposition explained previously. Apparent exceptions are probably the result of simultaneous changes in two or more factors. One confusing factor is the production of *red brass* as a result of either too much copper or too much zinc (then called *zinc pink*) in the deposit. No adequate explanation for this effect of too high zinc has been given. It may be associated with intermittent deposition of metallic copper by chemical replacement of the zinc in the deposit by copper. If so, this behavior would involve an intermittent process, such as occurs in some bright-nickel baths.

The principal factors in brass plating are as follows:

1. *Bath Composition.*

a. Increasing the ratio of Cu/Zn in the bath increases the copper content of the deposit.

b. Increasing the free cyanide decreases the copper content of the deposit.

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[1] Pan, L. C., *Trans. Electrochem. Soc.*, vol. 74, p. 425, 1938.

[2] Raub, E., and Krause, D., *Z. Elektrochem.*, vol. 50, p. 91, 1944, and *Monthly Rev. Am. Electroplaters' Soc.*, vol. 32, p. 880, 1945.

c. Addition of sodium hydroxide decreases the copper content of the deposit.

d. Addition of ammonia tends to decrease the copper content of the deposit and is especially beneficial in that it yields brass deposits of more nearly uniform color over a wide range of solution composition and current density.[1]

e. Addition of arsenic as As_2O_3 (previously dissolved in NaOH to form sodium arsenite, Na_3AsO_3,) increases the zinc content of the deposit, and some arsenic is deposited with the brass. Nickel salts have effects similar to arsenic.

f. Phenol, C_6H_5OH, tends to reduce the zinc content of the deposit.

g. The pH of brass baths is usually from 11 to 13. An increase in pH to above 12 increases the zinc content of the deposits. The pH can be controlled by adding NaOH to increase it or $NaHCO_3$, sodium bicarbonate, to decrease it. Addition of ammonium hydroxide will not raise the pH above 11.

2. *Temperature.* An increase in bath temperature permits the use of higher current densities. A temperature above 50°C (122°F) is not desirable, because then the rate of decomposition of the cyanide is increased. An increase in temperature increases the copper content of the deposits.

3. *Current Density.* Usually an increase in current density decreases the copper content of the deposits, but in specific cases a reverse effect has been reported. The latter effect is more probable if the free cyanide is very high. In general, relatively low current densities are used, *e.g.*, 5 amp/ft^2 (0.5 amp/dm^2). Higher current densities reduce the cathode efficiency, which is usually not over 75 per cent.

4. *Anode Behavior.* As noted above, the composition or behavior of the anodes does not have a direct or immediate effect upon the composition of the deposit. For satisfactory continuous operation it is necessary to introduce from the anodes the same weights of copper and zinc as are deposited or slightly more to compensate for drag out. In all commercial brass plating, brass anodes are employed, with a composition close to that of the desired deposits. For rubber adhesion, brass anodes with about 70 per cent of copper and 30 per cent of zinc are used, and for ornamental brass plating, anodes with about 80 per cent of copper and 20 per cent of zinc.

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[1] PAN, L. C., *Monthly Rev. Am. Electroplaters' Soc.*, vol. 25, p. 13, 1938.

The rate of solution and appearance of the anodes depend largely on the bath composition, especially the free cyanide. If either the free cyanide or the pH is too low, a white film, probably of zinc cyanide, forms on the anodes. The anode current density is usually not over 5 amp/ft² (0.5 amp/dm²).

Typical Brass Baths:

1. FOR RUBBER BONDING

	N	g/l	oz/gal
Cuprous cyanide, CuCN	0.29	26.2	3.5
Zinc cyanide, $Zn(CN)_2$	0.19	11.3	1.5
Sodium cyanide, NaCN	0.90	45.0	6.0
Equivalent to			
Free cyanide, NaCN	0.13	6.4	0.85
Copper, Cu^{I}	0.29	18.8	2.5
Zinc, Zn	0.19	6.2	0.85

Solution ratio, Cu/Zn = 18.8/6.2 = 3.0/1
or 75 per cent of copper and 25 per cent of zinc
Temperature, 35–50°C (95°–122°F)
Current density, 0.5 amp/dm² (5 amp/ft²)

2. YELLOW BRASS, DECORATIVE

	N	g/l	oz/gal
Cuprous cyanide, CuCN	0.30	27	3.6
Zinc cyanide, $Zn(CN)_2$	0.15	9	1.2
Sodium cyanide, NaCN	1.10	54	7.5
Sodium carbonate, Na_2CO_3	0.60	30	4
Equivalent to			
Free cyanide, NaCN	0.35	17	2.3
Copper, Cu^{I}	0.30	19	2.5
Zinc, Zn	0.15	5	0.65

Solution ratio, Cu/Zn = 19/5 = 3.8/1
or 79 per cent of copper and 21 per cent of zinc
Temperature, 35–50°C (95–122°F)
Current density, 0.5 amp/dm² (5 amp/ft²)

Bronze Plating. Although bronze is strictly an alloy of copper and tin, much of the so-called bronze plating in the United States consists of copper-rich brass, which may contain about 90 per cent of copper and 10 per cent of zinc.

A typical bronze bath of this type has the following composition:[1]

COPPER-ZINC BRONZE BATH (90–10)

	N	g/l	oz/gal
Cuprous cyanide, CuCN	0.6	54	7.2
Zinc cyanide. $Zn(CN)_2$	0.13	7.5	1.0

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[1] GRAHAM, A. K., *Proc. Am. Electroplaters' Soc.*, p. 143, 1948.

COPPER-ZINC BRONZE BATH (90–10)—*Continued*

	N	g/l	oz/gal
Sodium cyanide, NaCN	1.45	71	9.5
Rochelle salt, $NaKC_4H_4O_6 \cdot 4H_2O$	0.32	45	6.0
Sodium carbonate, Na_2CO_3	0.56	30	4.0
Equivalent to			
Metallic copper, Cu^I	0.6	37.5	5.0
Metallic zinc, Zn	0.13	4.2	0.56
Free cyanide, NaCN	0.09	4.5	0.6

Solution ratio Cu/Zn = 37.5/4.2 = 9/1
or 90 per cent copper and 10 per cent zinc.
pH, 10.3
Temperature, 110–130°F (25–55°C)
Current density, 10–20 amp/ft² (1–2 amp/dm²)

Small additions of ammonia, *e.g.*, 1 to 5 ml/l of 28 per cent NH_4OH, are made to control the color.

The use of a copper-cadmium bath for bronze plating has also been suggested[1] because it is easier to control. It is operated with copper anodes, and cadmium oxide (dissolved in sodium cyanide) is added when needed. A proposed formula is as follows:

COPPER-CADMIUM BRONZE BATH

	N	g/l	oz/gal
Cuprous cyanide, CuCN	0.25	23	3
Cadmium oxide, CdO	0.03	2	0.25
Sodium cyanide, NaCN	0.70	34	4.5
Sodium carbonate, Na_2CO_3	0.3	15	2
Equivalent to			
Metallic copper, Cu^I	0.25	16	2.1
Metallic cadmium, Cd	0.03	1.7	0.22
Free cyanide, NaCN	0.17	8.5	1.1

Temperature, 75°F (24°C)
Current density, 2–4 amp/ft² (0.2–0.4 amp/dm²)

It is possible to deposit alloys of copper and tin, of which more application has been made in England than in the United States. Bronze deposits containing 90 per cent of copper and 10 per cent of tin may be produced and also *speculum* metal deposits, which are white and contain about 50 per cent of tin and 50 per cent of copper. The latter alloy is harder than pure tin and has been suggested for plating tableware.

A typical formula and conditions for tin-bronze plating are as follows:

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[1] HOGABOOM, G. B., JR., and HALL, N., "Guide Book," p. 82, Metal Finishing Co., 1947.

COPPER-TIN BRONZE BATH

	N	g/l	oz/gal
Cuprous cyanide, CuCN	0.40	36	4.8
Sodium cyanide, NaCN	0.53	26	3.5
Sodium stannate, $Na_2SnO_3 \cdot 3H_2O$	0.94	63	8.4
Equivalent to			
Free cyanide, NaCN	0.13	6.4	0.85
Copper, Cu^{I}	0.40	26	3.5
Tin, Sn^{IV}	0.94	28	3.7

Solution ratio, Cu/Sn = 26/28 = 0.93/1.00
or 48 per cent of copper and 52 per cent of tin
pH, 12.5
Temperature, 65°C (149°F)
Current density, 5 amp/dm^2 (50 amp/ft^2)

Bronze anodes can be used, but copper and tin anodes on separate circuits are recommended.

This bath illustrates the fact that the ratio of metals in the deposit, in this case Cu/Zn = about 9, may be widely different from that in the bath, in which Cu/Sn = 0.9. Evidently it is much easier to deposit copper than tin from such a bath.

A proposed bath for speculum plating has the following composition:[1]

SPECULUM-PLATING BATH

	N	g/l	oz/gal
Sodium stannate, $Na_2SnO_3 \cdot 3H_2O$	1.5	100	13.3
Cuprous cyanide, CuCN	0.14	13	1.7
Sodium hydroxide, NaOH	0.38	15	2.0
Sodium cyanide, NaCN	0.50	25	3.3
Equivalent to			
Tin, Sn^{IV}	1.5	45	6
Copper, Cu^{I}	0.14	9	1.2

Solution ratio, Cu/Sn = 9/45 = 0.2
Temperature, 65°C (149°F)
Current density, 2.5 amp/dm^2 (25 amp/ft^2)

This bath is operated with copper and tin anodes on separate circuits, on which the current density is controlled to maintain the composition of the baths and deposits and to retain the characteristic green film on the tin anodes.

Copper-zinc-tin Alloys. In recent years several baths have been developed from which white alloys containing copper, zinc,

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[1] MANGLES, R., JONES, F. V., PRICE, J. W., and CUTHBERTSON, J. W., *J. Electrodepositors' Tech. Soc.*, vol. 21, p. 19, 1946. CUTHBERTSON, J. W., *J. Electrodepositors' Tech. Soc.*, vol. 23, p. 143, 1948.

and tin can be deposited. These deposits are sometimes called *white brass*, or other trade names are applied. Their successful use illustrates the fact that rather complicated processes can be conducted commercially. Fortunately, it is not necessary to maintain a given composition very closely, as long as a white deposit is obtained. Typical deposits from one proprietary bath designated as "bright alloy" are reported to contain about 56 per cent of copper, 16 per cent of zinc, and 28 per cent of tin. They are produced from baths containing the double cyanides of copper and zinc and sodium stannate, together with an organic brightener.[1] White alloys of copper, cadmium, and tin have also been deposited.[2]

Silver-cadmium Alloys. The interest in alloys of silver and cadmium relates largely to the possibility of depositing *non-tarnishing* silver, containing, for example, 90 per cent of silver and 10 per cent of cadmium. While such alloys and also those with a high content of cadmium and a low content of silver can be deposited,[3] no extensive commercial use of such alloys has developed. One reason is that their control is made more difficult by the necessity of having a high proportion of cadmium in the bath, in order to deposit an alloy with a low cadmium content. Another objection is that, although the deposited alloy does not readily darken to form black silver sulfide, it does turn dull as the result of tarnish of the cadmium.

Gold Alloys. The principal use of deposited gold alloys is to produce a desired color, such as *green gold* or *rose gold*. In such cases the exact composition is less important than the color. In general, a smaller amount of silver is required in deposited green gold than in the rolled alloy of similar color and likewise of copper in rose gold. The resultant alloy deposits are usually at least 18 K, *i.e.*, contain at least 75 per cent of gold. While no extensive studies on deposition of gold alloys have been published, the following formulas are typical of those used for *colored* gold deposits.

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[1] DIGGIN, M. B., and JERNSTEDT, G. W., *Proc. Am. Electroplaters' Soc.*, p. 247, 1944.

[2] Private communication of N. HALL.

[3] FAUST, C. L., HENRY, D. J., and FRANCE, W. G., *Trans. Electrochem. Soc.*, vol. 72, p. 479, 1937. MATHERS, F. C. and JOHNSON, A. D., *Trans. Electrochem Soc.*, vol. 74, p. 229, 1938. STOUT, L. E., and THUMMEL, W. G., *Trans. Electrochem. Soc.*, vol. 59, p. 337, 1931.

GREEN GOLD

	N	g/l	
Potassium gold cyanide, $KAu(CN)_2$	0.01	2.9	7 dwt/gal
Silver cyanide, AgCN	0.001	0.13	0.3 dwt/gal
Potassium cyanide, KCN	0.6	39	5.2 oz/gal
Equivalent to			
Metallic gold, Au^I	0.01	2.0	5 dwt/gal
Metallic silver, Ag	0.001	0.1	0.25 dwt/gal

Small amounts of arsenic or lead can be added to intensify the green color.

RED ROSE GOLD

	N	g/l	
Potassium gold cyanide, $KAu(CN)_2$	0.01	2.9	7 dwt/gal
Copper (cuprous) cyanide, CuCN	0.012	1.1	0.15 oz/gal
Potassium cyanide, KCN	0.5	32.5	4.3 oz/gal
Equivalent to			
Metallic gold, Au^I	0.01	2.0	5 dwt/gal
Metallic copper, Cu^I	0.012	0.75	0.1 oz/gal

Zinc-cadmium Alloys. The deposition of a small amount of cadmium with zinc represents an attempt to obtain an alloy coating that will yield electrolytic protection to steel equivalent of that of zinc and resistance to corrosion of the coating comparable to that of cadmium. To some extent this goal has been accomplished by depositing about 10 per cent of cadmium with the zinc from a bath such as the following:

ZINC-CADMIUM BATH

	N	g/l	oz/gal
Zinc cyanide, $Zn(CN)_2$	1.2	75	10
Cadmium oxide, CdO	0.05	3	0.4
Sodium cyanide, NaCN	0.75	38	5
Sodium hydroxide, NaOH	2.25	90	12

Temperature, 35°C (95°F)
Current density, 20 amp/ft^2 (2 amp/dm^2)

Anodes containing 10 per cent of cadmium and 90 per cent of zinc are used. When the bath is not in operation, cadmium tends to cement out on the anodes. Deposits of this type were found to yield slightly better protection to steel in an industrial atmosphere than either zinc or cadmium coatings of the same thickness.[1]

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[1] BLUM, W., STRAUSSER, P. W. C., and BRENNER, A., *J. Research Natl. Bur. Standards*, vol. 16, p. 185, 1936, RP 867.

Tin-zinc Alloys. In an effort to obtain the protective value of zinc coatings and reduce the rate of attack of the coating, *i.e.*, to obtain a substitute for cadmium, alloy deposits containing from 50 to 80 per cent of tin and the balance zinc have been recently developed in England.[1] The wide difference in the normal potentials of these two metals makes it very difficult to codeposit them from simple baths, *e.g.*, acid sulfate solutions. The alloys are therefore deposited from alkaline baths containing sodium stannate and sodium zinc cyanide together with free alkali and free cyanide. The best corrosion protection to steel and best solderability are furnished with alloy coatings containing about 80 per cent of tin and 20 per cent of zinc (by weight). Deposits with 50 per cent each of tin and zinc are cheaper and contain less of the strategic metal tin, but such deposits are more difficult to control and are less readily soldered. The following bath compositions and conditions are recommended:

	For 80 per cent tin alloys			*For 50 per cent tin alloys*		
	N	g/l	oz/gal	*N*	g/l	oz/gal
Sodium stannate, $Na_2SnO_3 \cdot 3H_2O$....	1	67	8.9	1	67	8.9
(Equivalent to tin, Sn^{IV}).........	1	30	4	1	30	4
Zinc cyanide, $Zn(CN)_2$...........	0.08	4.8	0.64	0.25	15	2
(Equivalent to zinc, Zn)...........	0.08	2.5	0.33	0.25	8	1.1
Sodium hydroxide, NaOH..........	0.13	5	0.7	0.17	7	1
Sodium cyanide...................	0.45	22	3	0.81	40	5.3
Total cyanide computed as NaCN	0.53	26	3.6	1.06	52	7.2
(Free sodium cyanide, NaCN).....	0.37	18	2.4	0.56	27	3.6

Temperature, 65°C (149°F)
Current density, 1–3 amp/dm² (10–30 amp/ft²)

Cast alloy anodes having the same composition as the desired deposits are employed. An anode current density of about 2 amp/dm² (20 amp/ft²) is used and is adjusted so as to maintain the greenish yellow film that is characteristic of tin anodes in a stannate bath (page 328).

Lead-tin Alloys. As noted on page 390, it is easy to deposit alloys of lead and tin because in simple salt solutions the potentials of these in the bivalent state are so close that either one may deposit the other from its solution until an equilibrium is reached.

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[1] Mangles, R., *J. Electrodepositors' Tech. Soc.*, vol. 21, p. 45, 1946, and *Engineering*, vol. 161, p. 289, 1946. Cuthbertson, J. W., and Angles, R. M., *Trans. Electrochem. Soc.*, vol. 94, p. 73, 1948.

It was early reported[1] that lead-tin alloys can be deposited from fluoborate solutions. Interest in such deposits was renewed during the Second World War, when scarcity of tin caused electroplated lead or lead-tin coatings to be substituted for *terne plate*, *i.e.*, steel coated by hot-dipping with an alloy of lead containing 10 to 30 per cent of tin. In this connection it was shown[2] that alloy deposits with about 5 per cent of tin yield better protection against corrosion of steel than either pure lead or alloys with higher tin content. Deposits of lead-tin alloys have also been used in bearings.

The fluoborate solutions used for plating lead-tin alloys are from 1.0 to 2.0*N* in total metal content and contain from 0.5 to 1.0*N* free fluoboric acid together with an addition agent, usually glue. It is now possible to purchase strong solutions of lead and tin fluoborate and fluoboric acid, from which the alloy baths can be readily prepared. A typical modern solution for low-tin alloys is as follows:

	N	g/l	oz/gal
Lead fluoborate, $Pb(BF_4)_2$	2	381	51
Tin fluoborate, $Sn(BF_4)_2$	0.2	30	4
Fluoboric acid, HBF_4	0.5	45	6
Glue		0.5	0.07
Equivalent to			
Lead, Pb^{II}	2	207	28
Tin, Sn^{II}	0.2	12	1.6

Ratio, Pb/Sn in solution = 207/12 = 17.3
or 94 per cent of lead and 6 per cent of tin

The ratio of lead to tin in the deposit from such a bath is affected by the glue content but not much by the current density. At current densities of from 20 to 50 amp/ft^2 (2 to 5 amp/dm^2) deposits with about 5 per cent of tin were obtained. With a higher tin content in the bath an increase in current density increases the tin content of the deposit, which may be made as high as 50 or 70 per cent tin.

Nickel-cobalt Alloys. The close similarity of nickel and cobalt in both physical and chemical properties accounts for the fact that they can readily be codeposited. In fact, as noted (page 364) small amounts of cobalt are commonly present in nickel baths and are usually considered equivalent to nickel. One reason that cobalt-nickel alloys have not come into extensive use is that their

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[1] Blum, W., and Haring, H. E., *Trans. Am. Electrochem. Soc.*, vol. 40, p. 287, 1921.

[2] DuRose, A. H., *Trans. Electrochem. Soc.*, vol. 89, p. 417, 1946.

properties are quite similar to those of nickel or cobalt alone. The use of cobalt in one type of bright-nickel baths (page 368) is largely associated with the greater ease of producing bright alloy deposits from that type of bath than from any marked difference in properties or behavior of the alloy deposits from those of pure nickel.

Apart from color or brightness, commercial use of nickel-cobalt alloy deposits must rest on some superior properties such as hardness and wear resistance, resistance to tarnish and corrosion, or greater protective value against corrosion or erosion. Just as with almost all alloy deposits, the nickel-cobalt coatings are finer grained and may be less porous. Cobalt deposits are not necessarily harder than nickel, but the hard cobalt or nickel-cobalt deposits are apparently less brittle than nickel deposits of equal hardness. They therefore deserve study for special structural applications.

Published studies on the deposition of nickel-cobalt alloys[1] reveal apparent contradictions in the effects of temperature, current densities, and agitation upon the cobalt content of the deposits. It is well established that the standard potential of nickel (−0.23 volt) is more noble than that of cobalt (−0.28 volt). The reported discrepancies are to be explained, not by attempts to question the values of these standard potentials, but by consideration of the relative cathode polarizations of nickel and cobalt. In general, this polarization is greater for nickel than for cobalt, but the actual polarizations depend upon the metal concentrations, pH, temperature, and agitation. Under most conditions an increase in temperature, agitation, or current density increases the cobalt content of the deposit, even though at equilibrium the cobalt is less noble than nickel.

Nickel-zinc Alloys. Interest in the codeposition of nickel and zinc was stimulated by the *Corronizing* process, in which successive layers of nickel and zinc are deposited and are then heated to form an alloy, used to protect steel against corrosion. These two metals differ so much in their standard potentials (page 44) that it might appear impractical to codeposit them from simple solutions. Actually, the polarization of nickel deposition is so much greater than that of zinc that the two metals can be codeposited from sulfate or chloride baths.

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[1] FINK, C. G., and LAH, K. H., *Trans. Am. Electrochem. Soc.*, vol. 58, p. 373, 1930. YOUNG, C. B. F., and GOULD, N. A., *Trans Electrochem. Soc.*, vol. 69, p. 585, 1936. YOUNG, C. B. F., and EGERMAN, C., *Trans. Electrochem. Soc.*, vol. 72, p. 447, 1937.

In a study of the deposition potentials and structures of nickel zinc deposits from chloride baths, B. Lustman[1] found that the deposits are usually banded, indicating a rhythmic or alternating process. He also reported abrupt changes in potential that corresponded to a change from an alpha solid solution to a gamma solid solution.

Black Nickel Plating. In certain respects the ordinary black-nickel deposits may be considered as alloys of nickel and zinc. Since, however, they also contain an appreciable amount of sulfur, they probably consist largely of a mixture of nickel sulfide (which is black) and zinc, with possibly also some metallic nickel. It is at least possible that the presence of the zinc salt yields sufficiently negative cathode potentials to foster reduction of the thiocyanate ion, CNS^- to sulfide ion S^{--}; which then reacts with the nickel salt to form black nickel sulfide. A typical formula is as follows:

	N	g/l	oz/gal
Nickel ammonium sulfate, $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$	0.3	60	8
Zinc sulfate, $ZnSO_4 \cdot 7H_2O$	0.05	7.5	1
Sodium thiocyanate, NaCNS	0.20	15.0	2

pH, 5.5–6.0
Temperature, 25°C (77°F)
Current density, 2 amp/ft^2 (0.2 amp/dm^2)

Nickel anodes are used.

Nickel-molybdenum Alloys. The black finish known as *Moly black* is produced from a bath containing salts of nickel and of molybdenum.[2] The available evidence indicates that the molydbenum is present in the deposit as an oxide such as Mo_2O_3. If so, the deposit is not really an alloy of nickel and molybdenum, such as have been produced. A recently used solution of this type has the following composition.[3]

	N	g/l	oz/gal
Nickel sulfate, $NiSO_4 \cdot 6H_2O$	1.1	144	19
Ammonium molybdate, $(NH_4)_2MoO_4$	0.34	30	4
Boric acid, H_3BO_3	0.3*M*	22.5	3

pH, 4.5
Temperature, 70°C (160°F)
Current density, 0.25 amp/dm^2 (2.5 amp/ft^2)

It is applied over a cyanide zinc deposit.

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[1] *Trans. Electrochem. Soc.*, vol. 84, p. 363, 1943.

[2] HOFFMAN, R. A., and HULL, R. O., *Proc. Am. Electroplaters' Soc.*, p. 45, 1939.

[3] Private communication from K. T. SIMONS.

APPENDIX

Table 1. Conversion of Centigrade (C.) to Fahrenheit (F.) Temperatures

°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.
0	32	30	86	55	131	80	176
5	41	35	95	60	140	85	185
10	50	40	104	65	149	90	194
15	59	45	113	70	158	95	203
20	68	50	122	75	167	100	212
25	77						

Table 2. Conversion of Fahrenheit (F.) to Centigrade (C.) Temperatures

°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.
0	− 17.8	55	12.8	110	43.3	165	73.9
5	− 15.0	60	15.6	115	46.1	170	76.7
10	− 12.2	65	18.3	120	48.9	175	79.4
15	− 9.4	70	21.1	125	51.7	180	82.2
20	− 6.7	75	23.9	130	54.4	185	85.0
25	− 3.9	80	26.7	135	57.2	190	87.8
30	− 1.1	85	29.4	140	60.0	195	90.6
32	0.0	90	32 2	145	62.8	200	93.3
35	1.7	95	35.0	150	65.6	205	96.1
40	4.4	100	37.8	155	68.3	210	98.9
45	7.2	105	40.6	160	71.1	212	100.0
50	10.0						

TABLE 3. CONVERSION OF DEGREES BAUMÉ (BÉ.)[1] TO SPECIFIC GRAVITY (SP. GR.)

°Bé. Sp. gr.	°Bé. Sp. gr.	°Bé. Sp. gr.	°Bé. Sp. gr.	°Bé. Sp. gr.
0 = 1.000	8 = 1.058	16 = 1.124	24 = 1.198	32 = 1.283
1 = 1.007	9 = 1.066	17 = 1.133	25 = 1.208	33 = 1.295
2 = 1.014	10 = 1.074	18 = 1.142	26 = 1.218	34 = 1.306
3 = 1.021	11 = 1.082	19 = 1.151	27 = 1.229	35 = 1.318
4 = 1.028	12 = 1.090	20 = 1.160	28 = 1.239	36 = 1.330
5 = 1.036	13 = 1.098	21 = 1.169	29 = 1.250	37 = 1.343
6 = 1.043	14 = 1.107	22 = 1.179	30 = 1.261	38 = 1.355
7 = 1.051	15 = 1.115	23 = 1.189	31 = 1.272	39 = 1.368
				40 = 1.381

TABLE 4. CONVERSION OF SPECIFIC GRAVITY (SP. GR.) TO DEGREES BAUMÉ (BÉ.)[2]

Sp. gr. °Bé	Sp. gr. °Bé	Sp. gr. °Bé	Sp. gr. °Bé	Sp. gr. °Bé
1.00 = 0.00	1.08 = 10.7	1.16 = 20.0	1.24 = 28.1	1.32 = 35.2
1.01 = 1.44	1.09 = 12.0	1.17 = 21.1	1.25 = 29.0	1.33 = 36.0
1.02 = 2.84	1.10 = 13.0	1.18 = 22.1	1.26 = 29.9	1.34 = 36.8
1.03 = 4.22	1.11 = 14.4	1.19 = 23.2	1.27 = 30.8	1.35 = 37.6
1.04 = 5.58	1.12 = 15.5	1.20 = 24.2	1.28 = 31.7	1.36 = 38.4
1.05 = 6.90	1.13 = 16.7	1.21 = 25.2	1.29 = 32.6	1.37 = 39.2
1.06 = 8.21	1.14 = 17.8	1.22 = 26.2	1.30 = 33.5	1.38 = 39.9
1.07 = 9.5	1.15 = 18.9	1.23 = 27.1	1.31 = 34.3	1.39 = 40.7
				1.40 = 41.4

[1] This scale for liquids heavier than water is defined by the formula: Baumé $= 145 - \dfrac{145}{\text{Sp. gr. } \frac{60^\circ}{60^\circ}\text{ F.}}$, where sp. gr. $\frac{60^\circ}{60^\circ}$ F represents the specific gravity of the solution at 60°F. referred to water at 60°F.

[2] Tables 3 and 4 are given in more complete and accurate form in Circular No. 19 of the National Bureau of Standards.

TABLE 5. APPROXIMATE EQUIVALENTS OF METRIC AND CUSTOMARY UNITED STATES UNITS

Length:

1 meter (m.) = 39.37 in.
1 decimeter (dm.) = 3.937 in.
1 centimeter (cm.) = 0.3937 in.
1 inch (in.) = 2.54 cm.
1 foot (ft.) = 30.48 cm.

Area:

1 square meter (m.^{2}) = 1,550 sq. in.
1 square decimeter (dm.^{2}) = 15.5 sq. in.
1 square centimeter (cm.^{2}) = 0.155 sq. in.
1 square inch (sq. in.) = 6.45 cm.^{2}
1 square foot (sq. ft.) = 9.29 dm.^{2}

Volume:

1 cubic meter (m.^{3}) = 35.31 cu. ft.
1 cubic decimeter (dm.^{3}) = 61.02 cu. in.
1 cubic centimeter (cm.^{3} or c.c.) = 0.061 cu. in.
1 cubic inch (cu. in.) = 16.39 cm.^{3}
1 cubic foot (cu. ft.) = 28.32 dm.^{3}

Capacity (liquid measure):

1 liter (l.) = 1,000 ml. (or about 1,000 c.c.)
1 liter = 1.057 qt.
1 milliliter[1] (ml.) or c.c. = 0.034 fluid oz.
1 gallon[2] (gal.) = 231 cu. in.
1 gallon = 3.785 liters
1 quart (qt.) = 0.946 liters
1 fluid ounce (fl. oz.) = 29.6 ml. or c.c.

Mass (weight):

1 kilogram (kg.) = 1,000 g.
1 kilogram = 2.205 avoirdupois lb.
1 gram (g.) = 0.0353 avoirdupois oz.
1 gram = 0.0322 troy oz.
1 avoirdupois ounce (oz.) = 28.35 g.
1 avoirdupois pound (lb.) = 453.6 g.
1 troy ounce (tr. oz.) = 31.10 g.
1 liter of water weighs 1,000 g.

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[1] The millimeter, the true unit of capacity, is at present commonly so designated on volumetric apparatus. The cubic centimeter (usually abbreviated cm.^{3} or c.c.) has a slightly different value. For all practical purposes, however, the terms *cubic centimeter* and *milliliter* are synonomous.

[2] One British Imperial gallon is equal to the volume at 62°F. of 10 lb. of water. It is equivalent to 277.41 cu. in., to 4.55 liters, or to 1.20 U. S. gallons. Therefore to convert oz./U. S. gal. to oz./Imp. gal., multiply by 1.2.

Table 6. Approximate Conversion Factors for Metric and Customary United States Units

1. **Grams per liter (g./l.) multiplied by 0.134 = avoirdupois ounces per gallon[1] (oz./gal.).**
2. **Avoirdupois ounces per gallon (oz./gal.) multiplied by 7.5 = grams per liter[2] (g./l.).**
3. **Grams per liter (g./l.) multiplied by 0.122 = troy ounces per gallon (tr. oz./gal.).**
4. **Troy ounces per gallon (tr. oz./gal.) multiplied by 8.2 = grams per liter (g./l.).**
5. **Grams per liter (g./l.) multiplied by 2.44 = pennyweights per gallon (dwt./gal.).**
6. **Pennyweights per gallon (dwt./gal.) multiplied by 0.41 = grams per liter (g./l.).**
7. **Grams per liter (g./l.) = ounces per cubic foot (oz./cu. ft.).**
8. $$\frac{\text{grams per liter}}{\text{10 multiplied by specific gravity}} = \text{percentage by weight.}$$
9. **Amperes per square decimeter (amp. dm.^{2}) multiplied by 9.29 = amperes per square foot (amp./sq. ft.).**
10. **Amperes per square foot (amp./sq. ft.) multiplied by 0.108 = amperes per square decimeter (amp./dm.^{2}).**
11. **Kilograms per square centimeter (kg./cm.^{2}) (as in tensile strength) multiplied by 14.22 = pounds per square inch (lb./sq. in.).**
12. **Pounds per square inch (lb./sq. in.) multiplied by 0.0704 = kilograms per square centimeter (kg./cm.^{2}).**
13. **Grams per square decimeter (g./dm.^{2}) multiplied by 0.328 = ounces per square foot (oz./sq. ft.).**
14. **Ounces per square foot (oz./sq. ft.) multiplied by 3.04 = grams per square decimeter (g./dm.^{2}).**
15. **Milliliters per liter (ml./l.) multiplied by 0.128 = fluid ounces per gallon (fl. oz./gal.).**
16. **Fluid ounces per gallon (fl. oz./gal.) multiplied by 7.8 = milliliters per liter (ml./l.).**
17. **Specific gravity of a metal divided by 12 = oz./sq. ft. for 0.001 in.**

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[1] **1a. Grams per liter (g./l.) multiplied by 0.161 = avoirdupois ounces per British Imperial gallon (av. oz./Imp. gal.).**

[2] **2a. Avoirdupois ounces per Imperial gallon (av. oz./Imp. gal.) multiplied by 6.2 = grams per liter (g./l.).**

TABLE 7. ATOMIC WEIGHTS OF COMMON ELEMENTS[1] (1947)

	Symbol	Atomic weight		Symbol	Atomic weight
Aluminum	Al	26.97	Magnesium	Mg	24.32
Antimony	Sb	121.76	Manganese	Mn	54.93
Arsenic	As	74.91	Mercury	Hg	200.61
Barium	Ba	137.36	Molybdenum	Mo	95.95
Bismuth	Bi	209.00	Nickel	Ni	58.69
Boron	B	10.82	Nitrogen	N	14.01
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.41	Palladium	Pd	106.7
Calcium	Ca	40.08	Phosphorus	P	30.98
Carbon	C	12 01	Platinum	Pt	195.23
Chlorine	Cl	35.46	Potassium	K	39.10
Chromium	Cr	52.01	Rhenium	Re	186.31
Cobalt	Co	58.94	Rhodium	Rh	102.91
Copper	Cu	63 54	Silicon	Si	28.06
Fluorine	F	19 00	Silver	Ag	107.88
Gold	Au	197.2	Sodium	Na	23.00
Hydrogen	H	1.008	Strontium	Sr	87.63
Indium	In	114.76	Sulfur	S	32.07
Iodine	I	126.92	Tin	Sn	118.70
Iron	Fe	55.85	Tungsten	W	183.92
Lead	Pb	207.21	Zinc	Zn	65.38
Lithium	Li	6.94			

[1] From report of International Committee on Atomic Weights, 1947.

For most calculations in electroplating, the nearest whole numbers may be employed.

TABLE 8. USUAL VALENCES OF COMMON ELEMENTS

Name	Symbol	Valence	Type of compound
Aluminum	Al	+ III	Aluminum salt and aluminate
Antimony	Sb	+ III + V	Antimonite Antimonate
Arsenic	As	+ III + V	Arsenite Arsenate
Barium	Ba	+ II	Barium salt
Bismuth	Bi	+ III	Bismuth salt
Boron	B	+ III	Borate
Cadmium	Cd	+ II	Cadmium salt
Calcium	Ca	+ II	Calcium salt
Carbon	C	+ IV	Carbonate
Chlorine	Cl	− I + V + VII	Chloride Chlorate Perchlorate
Chromium	Cr	+ II + III + VI	Chromous salt Chromic salt Chromate, chromic acid
Cobalt	Co	+ II + III	Cobaltous salt Cobaltic salt
Copper	Cu	+ I + II	Cuprous salt Cupric salt
Fluorine	F	− I	Fluoride
Gold	Au	+ I + III	Aurous salt Auric salt
Hydrogen	H	+ I	Hydride
Indium	In	+ III	Indium salt
Iodine	I	− I	Iodide
Iron	Fe	+ II + III	Ferrous salt Ferric salt

TABLE 8. USUAL VALENCES OF COMMON ELEMENTS—(*Continued*)

Name	Symbol	Valence	Type of compound
Lead	Pb	+ II	Lead salt
Magnesium	Mg	+ II	Magnesium salt
Manganese	Mn	+ II	Manganous salt
		+ VII	Permanganate
Mercury	Hg	+ I	Mercurous salt
		+ II	Mercuric salt
Nickel	Ni	+ II	Nickelous salt
		+ III	Nickelic salt
Nitrogen	N	− III	Ammonia, ammonium salt
		+ III	Nitrite
		+ V	Nitrate
Oxygen	O	− II	Oxide
Palladium	Pd	+ II	Palladous salt
		+ IV	Palladic salt
Phosphorus	P	+ III	Phosphite
		+ V	Phosphate
Platinum	Pt	+ II	Platinous salt
		+ IV	Platinic salt
Potassium	K	+ I	Potassium salt
Rhodium	Rh	+ III	Rhodium salt
Silicon	Si	+ IV	Silicate
Silver	Ag	+ I	Silver salt
Sodium	Na	+ I	Sodium salt
Sulfur	S	− II	Sulfide
		+ IV	Sulfite
		+ VI	Sulfate
Tin	Sn	+ II	Stannous salt, stannite
		+ IV	Stannic salt, stannate
Zinc	Zn	+ II	Zinc salt

TABLE 9. ELECTROCHEMICAL EQUIVALENTS[1]

Name	Valence	Equivalent weight = atomic weight + valence	Electrochemical equivalent			Weight per unit area		Thickness		Amp-hr per dm² to deposit 0.1 mm	Amp-hr per ft² to deposit 0.001 in.
			mg/coulomb	g/amp-hr	oz/100 amp-hr	g/dm² for 0.1 mm = sp gr	oz/ft² for 0.001 in.	mm for 1 amp-hr per dm²	in. for 100 amp-hr per ft²		
Antimony	3	40.6	0.415	1.495	5.3	6.7	0.56	0.0223	0.0095	4.48	10.6
Arsenic	3	24.74	0.259	0.932	3.3	5.7	0.47	0.0164	0.0069	6.12	14.4
Cadmium	2	56.21	0.582	2.097	7.4	8.6	0.71	0.0244	0.0103	4.10	9.7
Chromium	3	17.34	0.180	0.647	2.3	7.1	0.59	0.0091	0.0039	10.95	25.9
	6	8.67	0.090	0.323	1.1			0.0046	0.0019	21.90	51.8
Cobalt	2	29.47	0.306	1.100	3.9	8.9	0.74	0.0124	0.0052	8.09	19.1
Copper	1	63.54	0.659	2.372	8.4	8.9	0.74	0.0267	0.0113	3.75	8.8
	2	31.77	0.329	1.186	4.2			0.0133	0.0056	7.50	17.7
Gold	1	197.2	2.044	7.357	23.62	19.3	1.47*	0.0381	0.0162	2.63	6.2
	3	98.6	0.681	2.452	7.92			0.0127	0.0054	7.94	18.7
Indium	3	38.25	0.397	1.426	4.52	7.31	0.56*	0.0195	0.0083	5.12	12.0
Iron	2	27.93	0.289	1.042	3.7	7.9	0.65	0.0132	0.0056	7.58	17.9
Lead	2	103.61	1.074	3.865	13.6	11.3	0.94	0.0342	0.0145	2.92	6.9
Nickel	2	29.35	0.304	1.095	3.9	8.9	0.74	0.0126	0.0053	7.95	18.7
Platinum	4	48.81	0.506	1.821	5.82	21.4	1.60*	0.0085	0.0036	11.70	27.7
Rhodium	3	34.30	0.331	1.192	3.82	12.4	0.95*	0.0096	0.0042	10.4	23.8
Silver	1	107.88	1.118	4.025	12.92	10.5	0.79*	0.0383	0.0163	2.61	6.2
Tin	2	59.25	0.615	2.214	7.8	7.3	0.61	0.0303	0.0129	3.30	7.8
	4	29.63	0.307	1.107	3.9			0.0152	0.0064	6.60	15.6
Zinc	2	32.69	0.339	1.219	4.3	7.1	0.59	0.0172	0.0073	5.82	13.7

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[1] It should be emphasized that all these values are based on 100 per cent current efficiency. In applying them it is necessary to take into account the actual cathode efficiencies. For most metals such as copper, nickel, zinc, and silver, the cathode efficiencies are usually over 90 per cent. In such cases the errors involved in using this table directly are no greater than the probable uncertainties in measuring the current densities. However, in depositing chromium from chromic acid, in which the valence of chromium is 6, the average cathode efficiency is only about 14 per cent. It is therefore necessary to divide the above weights and thicknesses for Cr^{VI} by 7 or to multiply the periods by 7. The results are then only an approximation.

* Troy ounces.

TABLE 10. ELECTROMOTIVE SERIES[1]

Approximate single potentials of metals toward solutions with normal metal-ion concentration or activity. Based on the normal hydrogen electrode as zero.

	VOLTS		VOLTS
Zinc	−0.76	*Hydrogen*	0.00
Chromium	−0.56	Antimony	+0.10
Iron (ferrous)	−0.44	Arsenic	+0.32
Cadmium	−0.40	Bismuth	+0.20
Indium	−0.34	Copper	+0.34
Cobalt	−0.28	Rhodium	+0.68
Nickel	−0.23	Mercury	+0.78
Tin (stannous)	−0.14	Silver	+0.80
Lead	−0.12	Platinum	+0.90
		Go[illegible]	+1.36

---

[1] Many of these values are at best uncertain, owing in some cases to difficulty in measuring the potentials and in others to uncertainty as to the metal-ion concentration or activity in the solution used. The order in which they are arranged is probably correct, although the relative positions of cadmium and iron are in question.

These values refer only to metals in the "active" state. Where they are passive (p. 50) their potentials are more positive. Under most conditions chromium and nickel are passive and their potentials are much more positive than those in this table.

TABLE 11. HYDROGEN OVERVOLTAGE (POLARIZATION) ON METALS[1]

At 1 amp/dm^2 (9.3 amp/ft^2) at 25°C (77°F)

(Derived from data of Knobel, Kaplan, and Eiseman, *Trans. Am. Electrochem. Soc.*, vol. 43, p. 55, 1923.)

METAL	HYDROGEN OVERVOLTAGE VOLTS
Platinized platinum	0.030
Smooth platinum	0.068
Gold	0.390
Electrolytic iron	0.557
Copper	0.584
Brass	0.646
Carbon	0.700
Zinc	0.746
Nickel	0.747
Silver	0.762
Graphite	0.779
Aluminum	0.826
Tin	1.077
Lead	1.090
Cadmium	1.134

---

[1] These values are simply illustrative. The actual numerical values for any metal depend on the surface condition, the current density, and the solution used. Even the order of the metals is not constant.

TABLE 12. RESISTIVITIES[1] OF SOLUTIONS AT 25°C. (77°F.), IN OHM-CM

Name	Formula	Concentration		
		N	0.5 *N*	0.1 *N*
Hydrochloric acid	HCl	3.01	5.54	26
Sulphuric acid	H_2SO_4	4.81	9.28	40
Hydrofluoric acid	HF	....	81	280
Acetic acid	$HC_2H_3O_2$	670	870	1,900
Boric acid[2]	H_3BO_3	70,000	220,000	
Chromic acid[2]	H_2CrO_4	3.18	5.81	27
Potassium hydroxide	KOH	5.07	9.48	46
Potassium chloride	KCl	8.94	17.1	78
Potassium cyanide	KCN	8.21	15.3	70
Sodium hydroxide	$NaOH$	5.77	10.6	50
Sodium chloride	$NaCl$	11.6	21.7	92
Sodium fluoride	NaF	18.5	29.4	121
Sodium sulphate	Na_2SO_4	16.8	29.1	109
Sodium carbonate	Na_2CO_3	19.1	31.3	117
Sodium phosphate	Na_2HPO_4	31.5	52.4	199
Ammonium hydroxide	NH_4OH	970	1,280	2,700
Ammonium chloride	NH_4Cl	9.34	17.4	78
Ammonium sulphate	$(NH_4)_2SO_4$	12.8	23.0	94
Calcium chloride	$CaCl_2$	12.9	23.8	101
Magnesium sulphate	$MgSO_4$	29.9	49.5	171
Copper sulphate	$CuSO_4$	34.1	56	191
Zinc sulphate	$ZnSO_4$	33.2	53	187
Zinc chloride	$ZnCl_2$	13.4	22.6	101
Cadmium sulphate	$CdSO_4$	36.6	62	210
Cadmium chloride	$CdCl_2$	40.1	58	185
Ferrous chloride	$FeCl_2$	16.5	28.7	
Ferrous sulphate	$FeSO_4$	33.6	53	180
Ferrous ammonium sulphate	$FeSO_4.(NH_4)_2SO_4$	12.0		
Nickel sulphate	$NiSO_4$	33.8	53	195
Nickel ammonium sulphate	$NiSO_4.(NH_4)_2SO_4$	....	19.5	71
Nickel chloride	$NiCl_2$	14.1	25.0	105
Cobalt sulphate	$CoSO_4$	34.1	57	204
Cobalt chloride	$CoCl_2$	14.5	25.3	75
Silver potassium cyanide	$KAg(CN)_2$	....	16.0	
Lead fluoborate	$Pb(BF_4)_2$	9.2		

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[1] Some of these have been compiled by L. D. Hammond from various sources; others have been computed from International Critical Tables, vol. VI. Certain values have been computed from data at 18°, using known or assumed temperature coefficients. These values are probably correct to about 1 per cent.

[2] Concentrations of boric acid and chromic acid are *M*.

TABLE 13. COLOR CHANGE AND pH RANGE OF IMPORTANT INDICATORS

Indicator	Color		pH range	
	Acid	Basic	From	To
Tropeolin 00	Red	Yellow	1.3	3.0
Thymol blue	Red	Yellow	1.2	2.8
Methyl yellow	Red	Yellow	2.9	4.0
Methyl orange	Red	Orange	3.1	4.4
Bromophenol blue	Yellow	Blue	3.0	4.6
Bromocresol green	Yellow	Blue	3.8	5.4
Methyl red	Red	Yellow	4.4	6.2
Chlorophenol red	Yellow	Red	4.8	6.4
Bromophenol red	Yellow	Red	5.4	7.0
Bromothymol blue	Yellow	Blue	6.0	7.6
Phenol red	Yellow	Red	6.4	8.0
m-Cresol purple	Yellow	Purple	7.4	9.0
Thymol blue	Yellow	Blue	8.0	9.6
Phenolphthalein	Colorless	Red	8.0	9.8
Thymolphthalein	Yellow	Blue	9.3	10.5
Alizarin yellow	Yellow	Red	10.1	12.0

TABLE 14. METHODS OF STRIPPING PLATED COATINGS

Except those marked*, these methods yield by loss in weight an accuracy of about ± 10 per cent.

No.	Coating		Basis metal	Procedure	Reagent			°C	°F	Anode current density	
	Stripped metal	Intermediate			Name	Formula	Conc., g/l			amp/dm²	amp/ft²
1	Cr		Steel	Electro.	Sodium hydroxide	$NaOH$	90	20	70	2	20
2	Cr		Brass	Immer.	Hydrochloric acid	HCl	10 per cent (vol)	50	120		
		Ni	Brass								
		Ni	Steel								
3	Cr		Zinc	Electro.	Sodium sulfide	$Na_2S \cdot 9H_2O$	30	20	70	2	20
					+Sodium hydroxide	$NaOH$	20				
4	Cr	Ni	Zinc	Electro.	Sodium carbonate	Na_2CO_3	100	20	70	2	20
5	Ni		Steel	Immer.	Nitric acid	HNO_3	Fuming	20	70		
6	Ni		Steel*	Electro.	Sulfuric acid	H_2SO_4	50 per cent (vol)	20	70	2	20
		Cu	Steel								
			Brass				66 per cent (weight)				
			Zinc				sp gr 1.57				
7	Ni		Steel	Electro.	Sodium nitrate	$NaNO_3$	360	90	200	10	100
7a	Ni		Steel	Electro.	Chromic acid	CrO_3	210	85	185	1	10
					+Boric acid	H_3BO_3	30				
8*	Ni, Ni + Co		Copper	Electro.	Hydrochloric acid	HCl	10 per cent (vol)	20	70	2	20
			Brass								
9	Ni, Ni + Co		Brass	Electro.	Sodium thiocyanate	$NaCNS$	100	20	70	2	20
					+Sodium bisulfite	$NaHSO_3$	100				
10	Cu		Steel	Immer.	Chromic acid	CrO_3	500	20	70		
					+Sulfuric acid	H_2SO_4	50				
11	Cu		Steel	Electro.	Chromic acid	CrO_3	250	20	70	5	50
12	Cu		Steel	Electro.	Sodium nitrate	$NaNO_3$	180	20	70	2	20
	Brass										
13	Cu		Zinc	Electro.	Sodium sulfide	$Na_2S \cdot 9H_2O$	120	20	70	2	20
		Ni	Zinc								
14	Ag		Steel	Electro.	Sodium cyanide	$NaCN$	30	20	70	1–2	10–20
15	Ag		Nickel-brass	Immer.	Sulfuric acid	H_2SO_4 (sp gr 1.84)	95 per cent (vol)	80	176		
			Copper		+Nitric acid	HNO_3 (sp gr 1.42)	5 per cent (vol)				
			Brass								
			Iron								
16	Zn		Steel	Immer.	Hydrochloric acid	HCl	Conc. sp gr 1.18	20	70		
	Cd										
	Sn				+Antimony oxide	Sb_2O_3	1				
	Pb				or						
					Antimony chloride	$SbCl_3$	1.6				
17	Cd		Steel	Immer.	Ammonium nitrate	NH_4NO_3	120	40	105		
18	Zn		Steel	Electro.	Sodium hydroxide	$NaOH$	100	20	70	2	20
	Pb		Copper								
	Sn		Brass								
19	Pb		Brass	Immer.	Hydrochloric acid	HCl	75 per cent (vol)	80	175		
	Sn										

TABLE 15. FACTORS FOR COMPUTING AVERAGE THICKNESS FROM STRIPPING TESTS

Average thickness, in. = factor × g/cm²

METAL	FACTOR
Cadmium	0.0458
Chromium	0.0553
Cobalt	0.0442
Copper	0.0442
Gold	0.0204
Indium	0 0536
Iron	0 0499
Lead	0.0349
Nickel	0.0442
Platinum	0.0184
Rhodium	0.0316
Silver	0.0375
Tin	0.0540
Zinc	0.0553

TABLE 16. HARDNESS OF ELECTRODEPOSITED METALS

METAL	RANGE OF BRINELL HARDNESS NUMBER
Chromium	400–1,000
Nickel	150– 500
Cobalt	270– 310
Iron	160– 350
Silver	60– 130
Copper	60– 150
Zinc	40– 50
Cadmium	10– 55
Lead	3– 5

TABLE 17. REFLECTIVITIES OF TYPICAL BRIGHT METAL SURFACES[1]

Metal	Preparation or treatment	White light reflected, per cent
Aluminum	Rolled	70
	"Alzac" finish	85
	Evaporated on brass	75
	Evaporated on glass	90
Aluminum + Mg	Evaporated on glass	88
Antimony		67
Brass		74
Copper	Electroplated	62
	Cast	65
Chromium	Electroplated	66
Chromium steel	("Stainless")	62
Cadmium	Electroplated	52
Gold	Electroplated	61
Indium	Electroplated	68
Mercury	On glass	70
Monel metal	Rolled	60
Nickel	Rolled	65
	Electroplated	62
Platinum	Rolled	64
	Electroplated	69
Palladium	Rolled	61
Rhodium	Electroplated	72
Silver	On glass	90
	Rolled	93
	Electroplated	95
Stellite	Cast	69
Speculum metal	Cast	64
Tin	Cast	70
Zinc	Rolled	56

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[1] Approximate values derived from various publications and from unpublished tests at the National Bureau of Standards.

TABLE 18. SUMMARY OF SPECIFICATIONS FOR PLATED COATINGS

A. AES—ASTM Specifications

Basis metal	Spec. No. and coating	Type	Minimum thickness on significant surfaces		Salt spray, hr
			in.	mm	
1. Steel	A164–40T				
	Zinc				
		GS	0.001	0.025	
		LS	0.0005	0.013	
		RS	0.00015	0.0038	
2. Steel	A165–40T	NS	0.0005	0.013	
	Cadmium	OS	0.0003	0.0075	
		TS	0.00015	0.0038	
3. Steel	B200–45T				
	(Copper)*				
	+ lead	ES			96
	Cu		0.000015	0.00038	
	Pb		0.0010	0.025	
		MS			48
	Cu		0.000015	0.00038	
	Pb		0.0005	0.013	
		PS			24
	Cu		0.000015	0.00038	
	Pb		0.00025	0.0006	
4. Steel	A166–45T				
	(Copper)*				
	+ nickel				
	+ chromium	DS			96
	Cu + Ni		0.0020	0.050	
	Final Ni		0.0010	0.025	
	Cr		0.00001	0.00025	
		FS			72
	Cu + Ni		0.00125	0.031	
	Final Ni		0.0006	0.015	
	Cr		0.00001	0.00025	
		KS			48
	Cu + Ni		0.00075	0.019	
	Final Ni		0.0004	0.010	
	Cr		0.00001	0.00025	
		QS			16
	Cu + Ni		0.0004	0.010	
	Final Ni		0.0002	0.005	
	Cr		0.00001	0.00025	

* Use of copper is optional. If used, it must meet stated requirements.

TABLE 18. SUMMARY OF SPECIFICATIONS FOR PLATED COATINGS—(*Continued*)

A. AES—ASTM Specifications—(*Continued*)

Basis metal	Spec. No. and coating	Type	Minimum thickness on significant surfaces		Salt spray, hr
			in.	mm	
5. Copper or brass	B141–45 Nickel + chromium	FC			
	Ni		0.0005	0.013	
	Cr		0.00001	0.00025	
		KC			
	Ni		0.0003	0.0075	
	Cr		0.00001	0.00025	
		QC			
	Ni		0.0001	0.0025	
	Cr		0.00001	0.00025	
6. Zinc or zinc alloys	B142–45T (Copper)* + Nickel + chromium	FZ			48
	Cu + Ni		0.00125	0.031	
	Cu		0.0004	0.010	
	Final Ni		0.0005	0.013	
	Cr		0.00001	0.00025	
		KZ			32
	Cu + Ni		0.00075	0.019	
	Cu		0.0003	0.0075	
	Ni		0.0003	0.0075	
	Cr		0.00001	0.00025	
		QZ			16
	Cu + Ni		0.0005	0.013	
	Cu		0.0002	0.005	
	Ni		0.0003	0.0075	
	Cr		0.00001	0.00025	

* Use of copper is optional. If used, it must meet stated requirements.

TABLE 18. SUMMARY OF SPECIFICATIONS FOR PLATED COATINGS—(*Continued*)

B. British Standard Specifications, BS-1224

Basis metal	Coating	Type	Minimum thickness on significant surfaces	
			in.	mm
1. Steel	Nickel + chromium			
		Ni8S*		
	Ni		0.0008	0.020
	Cr		0.00002	0.0005
		Ni5S		
	Ni		0.0005	0.013
	Cr		0.00002	0.0005
		Ni3S		
	Ni		0.0003	0.008
	Cr		0.00002	0.0005
2. Copper or brass	Nickel + chromium			
		Ni6C		
	Ni		0.0006	0.015
	Cr		0.00002	0.0005
		Ni3C		
	Ni		0.0003	0.008
	Cr		0.00002	0.0005
		Ni2C		
	Ni		0.0002	0.005
	Cr		0.00002	0.0005

* For type Ni8S, salt spray or other porosity tests are optional.

TABLE 19. TOTAL CONCENTRATIONS OF COPPER SULPHATE PLUS SULPHURIC ACID IN SOLUTIONS OF GIVEN SPECIFIC GRAVITY

Specific gravity at $\frac{25^\circ}{4^\circ}$ C.[1]	Copper sulphate plus sulphuric acid		Specific gravity at $\frac{25^\circ}{4^\circ}$ C.[1]	Copper sulphate plus sulphuric acid	
	g./l.	oz./gal.		g./l.	oz./gal.
1.01	20	2.7	1.13	217	29.1
1.02	36	4.8	1.14	234	31.3
1.03	52	7.0	1.15	251	33.6
1.04	68	9.1	1.16	268	35.9
1.05	84	11.3	1.17	286	38.3
1.06	100	13.4	1.18	303	40.6
1.07	117	15.7	1.19	321	43.0
1.08	133	17.8	1.20	339	45.4
1.09	150	20.0	1.21	357	47.8
1.10	166	22.3	1.22	375	50.2
1.11	183	24.5	1.23	393	52.6
1.12	200	26.8			

[1] The specific gravity determined at 25°C. (77°F.) based upon the density of water at 4°C. (39.2°F.).

TABLE 20. SOLUBILITY OF COPPER SULPHATE IN THE PRESENCE OF SULPHURIC ACID AT 25°C. (77°F.)[1]

Sulphuric acid present			Solubility of copper sulphate ($CuSO_4.5H_2O$)		
N	g./l.	oz./gal.	*N*	g./l.	oz./gal.
0	....	...	2.82	352	47.2
0.5	24.5	3.3	2.61	326	43.7
1.0	49.0	6.6	2.42	304	40.8
1.5	73 5	9.9	2.28	285	38.2
2.0	98.1	13.1	2.14	267	35.8
2.5	122.6	16.4	2.00	250	33.5
3.0	147.1	19.7	1.84	230	30.8
3.5	171.6	23.0	1.70	212	28.4

[1] Derived from paper by GOODWIN, H. M., and HORSCH, W. G., *Chem. Met. Eng.*, vol. 21, p. 181, 1919.

TABLE 21. RESISTIVITY OF COPPER SULPHATE-SULPHURIC ACID SOLUTIONS[1] AT 25°C. (77°F.) IN OHM-CM

H_2SO_4 g./l. $CuSO_4.5H_2O$ g./l.	0	50	100	150	200
0	..	4.8	2.44	1.77	1.46
50	65	4.9	2.58	1.88	1.55
100	45	5.1	2 86	2.00	1.67
150	29	5.3	3.04	2.18	1.79
200	24	5.5	3.14	2.31	

[1] Calculated from RICHARDSON and TAYLOR, *Trans. Am. Electrochem. Soc.*, vol. 20, p. 179, 1911.

TABLE 22. SPECIFIC GRAVITY OF CHROMIC ACID SOLUTIONS AS A FUNCTION OF THE CrO_3 CONTENT[1]

Density $\left(\frac{15^\circ}{4^\circ}\text{ C.}\right)$	CrO_3 content			Density $\left(\frac{15^\circ}{4^\circ}\text{ C.}\right)$	CrO_3 content		
	Molarity	g./l.	oz./gal.		Molarity	g./l.	oz./gal.
1.01	0.15	15	2.0	1.18	2.57	257	34.4
1.02	0.29	29	3.9	1.19	2.72	272	36.4
1.03	0.43	43	5.8	1.20	2.88	288	38.6
1.04	0.57	57	7.6	1.21	3.01	301	40.3
1.05	0.71	71	9.5	1.22	3.16	316	42.3
1.06	0.85	85	11.4	1.23	3.30	330	44.2
1.07	1.00	100	13.4	1.24	3.45	345	46.2
1.08	1.14	114	15.3	1.25	3.60	360	48.2
1.09	1.29	129	17.3	1.26	3.75	375	50.2
1.10	1.43	143	19.1	1.27	3.90	390	52.2
1.11	1.57	157	21.0	1.28	4.06	406	54.5
1.12	1.71	171	22.9	1.29	4.22	422	56.5
1.13	1.85	185	24.8	1.30	4.38	438	58.7
1.14	2.00	200	26.8	1.31	4.53	453	60.7
1.15	2.15	215	28.8	1.32	4.68	468	62.7
1.16	2.29	229	30.6	1.33	4.84	484	64.8
1.17	2.43	243	32.6	1.34	5.00	500	67.0

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[1] From data compiled by J. A. BEATTIE for "International Critical Tables," McGraw-Hill Book Company, Inc., New York.

TABLE 23. APPROXIMATE SPECIFIC GRAVITIES OF SOLUTIONS CONTAINING FERROUS CHLORIDE AND CALCIUM CHLORIDE AT 25°C. (77°F.)

N	Calcium chloride, $CaCl_2$		Ferrous chloride, $FeCl_2.4H_2O$	
	g./l.	oz./gal.	2 *N*. 200 g./l. or 27 oz./gal.	3 *N*. 300 g./l. or 40 oz./gal.
1	56	7.5	1.15	1.21
2	111	14.9	1.19	1.24
3	167	22.4	1.23	1.28
4	222	29.8	1.27	1.31
5	278	37.2	1.30	1.35
6	333	44.7	1.34	1.39

TABLE 24. DENSITIES OF COMMERCIAL ACIDS

Name	Formula	Concentration, per cent by wt.	Sp. gr.	°Bé.	Wt. of 1 gal., lb.	Pounds of pure acid in each gallon of concentrated acid
(Water)	H_2O	100	1.00	0.0	8.3	
Acetic	$HC_2H_3O_2$	60	1 07	9.5	8.9	5.3
Hydrofluoric	HF	48	1.15	19	9 6	4.6
Hydrochloric	HCl	35	1 18	22	9.8	3.4
Nitric	HNO_3	67	1 41	42	11 9	8.0
Sulphuric	H_2SO_4	93	1 84	66	15 3	14.2

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