U. S. DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS

COPPER ELECTROTYPING

CIRCULAR OF THE BUREAU OF STANDARDS, No. 387

U. S. DEPARTMENT OF COMMERCE
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BUREAU OF STANDARDS
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[Supersedes Circular 52, second edition]

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ISSUED AUGUST 30, 1930

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1930

For sale by the Superintendent of Documents, Washington, D. C. - - - Price 10 cents

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ABSTRACT

This circular on copper electrotyping includes simple definitions of terms and units employed in electrodeposition and the conditions for the satisfactory operation and control of copper electrotyping solutions. Conversion tables for the ordinary and scientific units are included. Tables are also given to show the weight and thickness of copper deposited at given current densities for specified periods.

The circular is written primarily for the benefit of practical electrotypers, in order to enable them to make use of the results of scientific studies in this field.

CONTENTS

I. INTRODUCTION

The second edition of Circular 52, published in 1916, was based largely upon experiments on copper electrotyping solutions that had been conducted by the National Bureau of Standards up to that time. During the past several years the International Association of Electrotypers has cooperated with the bureau in a study of various electrotyping problems. Among these is the effect of addition agents in copper electrotyping solutions. The technical details of this investigation have been recently published in the Bureau of Standards Journal of Research.[1] This revised circular has been prepared partly in order to put these results into their true perspective with regard to the entire electrotyping process, and thereby to make them more directly useful than they are in a separate publication. At the same time the text of the circular has been thoroughly revised, so as to incorporate the present views of the best practice. This circular will be confined to copper electrotyping baths.

Other studies on electrotyping that have been conducted at this bureau include the properties of graphite and the operation of nickel

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[1] R. O. Hull and W. Blum, Addition Agents in Copper Electrotyping Solutions, B. S. Jour. Research, 5 (RP228); September, 1930.

electrotyping solutions. The results have been published in detail.[2] Circulars on these two subjects that have been issued by the International Association of Electrotypers may be obtained on request to the Bureau of Standards.

II. OUTLINE OF THE ELECTROTYPING PROCESS

While this circular is primarily of interest to electrotypers, a brief outline of the process may be desirable for the benefit of those not familiar with this industry.

The first step in the production of an electrotype consists in the preparation of an impression or "mold" in wax of the form to be reproduced. The molding wax usually consists of ozokerite to which various susbstances have been added to produce the desired physical properties. The molten wax is poured upon one side of a metallic plate, consisting of lead, copper, or aluminum. The wax-coated metal is termed a "case." After taking the impression of the form by the use of suitable pressure at a slightly elevated temperature, usually by means of a hydraulic press, the resultant "mold" is "trimmed" and "built up" to produce the desired degree of relief in the finished plate.

The mold is then coated with graphite, applied by a wet or a dry process, or both. After washing out the excess of graphite, the form is either introduced directly into the depositing bath, or, in some cases, is given a preliminary treatment (so-called "oxidizing") with copper sulphate solution and fine iron filings, whereby a thin film of copper is deposited by "immersion" upon the graphite. The baths are usually contained in lead-lined wooden tanks, with copper cross bars, from which the anodes and cathodes are suspended. Electrical connection to the graphited cathode surface is made by means of the suspending hook by either of two methods. In the one known as the "case connection," the hook is in direct contact with the metallic plate of the case, portions of the wax being removed in order to bring the metal and the graphite surface into electrical contact, while the back of the case is insulated with wax. In the method now more generally employed, and known as the "face connection," the hook is in contact with a small copper plate imbedded in the wax near the top of the form and in contact with the graphite surface. In the latter method the metallic plate itself is not in the circuit, and there is less tendency for copper to deposit upon any accidentally exposed portions of it.

After the copper is deposited to the desired thickness (usually 0.006 to 0.010 inch (0.15 to 0.25 mm)) the case is taken from the bath, and the copper "shell" is loosened by means of hot water. After trimming the edges, the back of the shell is treated with soldering fluid (usually an acidified solution of zinc chloride) and coated with "tin foil" containing about 35 per cent of tin and 65 per cent of lead, after which it is laid face downward upon a heated pan. After the tin foil is melted upon the back of the shells, molten electrotype metal (usually containing from 3 to 4 per cent each of tin and antimony and from 92 to 94 per cent of lead) is poured over them to the desired depth. The electrotypes thus produced are cleaned, cut, and

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[2] W. Blum and J. H. Winkler, Nickel Electrotyping Solutions, Trans. Am. Electrochem. Soc., 53, p. 419; 1928. J. H. Winkler and W. Blum, The Properties of Graphite Used in Electrotyping, Trans. Am. Electrochem. Soc., 53, p. 435; 1928.

These researches are also summarized in Principles of Electroplating and Electroforming, by W. Blum and G. B. Hogaboom, published by the McGraw Hill Book Co. (2d ed.); 1930.

trimmed to the desired size, "finished" to a plane surface and shaved to the proper thickness. They may be subsequently curved if desired.

In many cases, for the most perfect reproduction of halftone or other work in low relief, molding in thin sheet lead at high pressures is practiced. The lead mold thus produced is cleaned with alcohol to remove grease, and is then treated with a dilute solution of chromic acid or a chromate. This forms a thin film of lead chromate, which prevents the deposited metal shell from adhering too tenaciously. The subsequent steps are similar to those involved when wax molds are used.

For the better classes of work, especially color process halftones, or for plates requiring very severe service, nickel electrotypes (commonly called "steel" or "nickel steel") are frequently employed. In their preparation, a thin layer of nickel (usually about 0.001 inch or 0.025 mm) is first deposited upon the wax or lead mold, copper is then deposited back of the nickel, and the resultant nickel-copper shell is treated as above. The true "nickel electrotype" thus made should not be confused with a nickel-plated electrotype in which nickel is deposited upon the surface of a finished copper electrotype.

During recent years a thin coating of chromium,[3] usually about 0.0002 inch (0.005 mm) has been often applied to nickel or copper electrotypes that are to be used for very long runs, for example in the printing of cartons and labels.

III. METHODS OF EXPRESSING CONDITIONS

1. METHODS OF EXPRESSING TEMPERATURE

The thermometer usually employed in scientific work is the centigrade thermometer, on the scale of which the melting point of ice is 0° and the boiling point of water (at a pressure of one atmosphere) is 100°, while on the Fahrenheit scale the corresponding points are 32° and 212°, respectively. In general, preference is given to the centigrade scale in scientific work, 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.

(*a*) To convert centigrade to Fahrenheit temperatures, multiply the degrees centigrade by 9/5 and add 32°.

Example.—To convert 20° C., to Fahrenheit

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

(*b*) 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 may be readily seen from Tables 1 and 2 in the Appendix.

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[3] The following publications of the Bureau of Standards on chromium plating may be obtained by sending the indicated sums to the Superintendent of Documents, Washington, D. C.:
Technologic Paper 346, Electrodeposition of Chromium from Chromic Acid Baths. Price 15 cents.
RP131. Throwing Power in Chromium Plating. Price 10 cents.
Health Hazards in Chromium Plating (Treasury Department). Price 5 cents.

2. METHODS OF EXPRESSING DENSITY

For testing the density of solutions either a Baumé (Bé) or specific gravity (sp. gr.) hydrometer may 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 solution and the water being at definitely stated temperatures. 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 $\frac{60°}{60°}$ 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. The specific gravity hydrometer is almost exclusively used for scientific work, and is the basis of the tables of composition given in the Appendix. For the benefit of persons still using Baumé hydrometers tables (Tables 3 and 4) for the conversion of degrees Baumé to specific gravity and vice versa will be found in the Appendix of this circular.

3. METHODS OF EXPRESSING COMPOSITION

In view of the almost universal use of the metric system in scientific work, reference will be made in this circular to that system. Since, however, the common United States units are generally employed in electrotyping and similar commercial work, the values will also be expressed in such units. 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 Bureau of Standards Circular No. 47. The relations between the values most commonly used in this work will be found in Tables 5 and 6 in the Appendix.

In this connection emphasis should be laid upon the great practical advantages connected with the use of the metric system throughout in electrotyping, rather than the conversion of the results obtained by titration of the solutions (for example, in grams per liter) into customary units (for example, ounces per gallon) before adjusting the composition.

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 liter is practically equal to 1 cubic decimeter or 1,000 cubic centimeters) facilitates the calculation of the capacity of tanks or vats; and (3) the simple relation between the units of weight, volume, and capacity (1 kilogram is practically equal to the weight of a cubic decimeter or 1 liter of water at its maximum density) renders very convenient the calculation of the weight of a given voume of water or of any liquid of known specific gravity.

In order to actually use the metric system in regulating the solutions the electrotyper should secure a meter rule (or a 60 cm four-fold rule) and either a set of metric weights to use on an ordinary scale or else a platform scale with metric graduations. Such scales can be secured with beams graduated in both metric and customary units. A copper measure, holding, say, 10 liters, will also be found convenient in removing portions of the solutions. The names of firms handling suitable metric apparatus will be furnished by this bureau upon application.

Tables and charts illustrating the use of the metric system, as well as a paper metric scale (which may be used to measure the dimensions of the tanks), are also furnished free by this bureau upon request.

(*a*) To obtain the approximate capacity of a tank in gallons divide the cubical contents (expressed in cubic inches) by 231.

Example.—A rectangular tank that is 59 inches long, 30 inches wide, and 24 inches deep (up to the height of the solution) has a capacity of $59 \times 30 \times 24 = 42{,}480$ cubic inches, which divided by $231 = 184$ gallons; or for practical purposes 185 gallons.

(*b*) To obtain the approximate capacity of a tank in liters, multiply together the three dimensions (expressed in centimeters) and divide the product by 1,000.

Example.—Suppose a rectangular tank is 150 cm long, 75 cm wide, and 60 cm deep. Then the tank has a capacity of $150 \times 75 \times 60 = 675{,}000$ cubic centimeters, or 675 liters; or for practical purposes 680 liters.

For all practical purposes, it will be sufficiently accurate to express the capacity to the nearest 5 gallons, or 20 liters. It will probably be found convenient after determining the capacity of each tank to paint it upon the tank, thus avoiding remeasurement.

(*c*) In order to facilitate the removal of a definite percentage of the solution in a tank, a vertical scale, in inches (or centimeters), may be scratched upon the lead lining of the tank, starting from the bottom. If, then, the normal height of the solution is 24 inches (60 cm), and it is desired to remove 10 per cent of the solution, all that is necessary is to siphon or dip out the solution till the level is lowered 2.4 inches (6 cm).

IV. GENERAL PRINCIPLES OF ELECTRODEPOSITION

1. DEFINITION OF ELECTRICAL TERMS

(a) CURRENT

The current (or current strength) is the rate at which the electricity passes through the circuit. It is expressed in amperes.

The ampere is defined as that current which, under specified conditions, deposits a definite weight (1.118 mg) of silver in one second. In practice, the current is measured in terms of amperes by means of a suitable ammeter.

(b) RESISTANCE

The resistance of the circuit to the passage of an electrical current, is expressed in ohms.

The ohm is defined as equal to the resistance at 0° C. of a uniform column of mercury having a mass of 14.4521 g and a length of 106.3 cm.

(c) ELECTROMOTIVE FORCE

The electromotive force (or voltage, or potential difference) represents the electrical pressure used to force the electricity through the circuit. It is expressed in volts.

The volt is that electromotive force which will produce a current of 1 ampere in an electrical circuit of which the resistance is 1 ohm. The standard for the volt is the Weston normal cell, the electromotive force of which at 20° C. is 1.0183 volts. The electromotive force is usually measured in terms of volts by means of a suitable voltmeter.

The voltage measured at the dynamo is always higher than the voltage measured between two other parts of the circuit; for example, between an anode and cathode. The latter voltage is called the potential difference between these two points.

(d) RELATION BETWEEN FUNDAMENTAL UNITS

The values of these electrical units have been so chosen that a very simple relation exists between them. This relation (based on Ohm's law) may be expressed:

$$\text{Current} = \frac{\text{electromotive force}}{\text{resistance}} \text{ or } I = \frac{E}{R}$$

or in terms of the above units

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

It is possible, therefore, to double the current either by doubling the voltage used or by reducing the resistance to one-half the former value.

Example.—If in a given electrical circuit an electromotive force of 10 volts is applied, and the total resistance of the circuit is 2 ohms, the resultant current will be

$$\frac{10 \text{ volts}}{2 \text{ ohms}} = 5 \text{ amperes}$$

In case the voltage is doubled we have

$$\frac{20 \text{ volts}}{2 \text{ ohms}} = 10 \text{ amperes}$$

If, on the other hand, the resistance is decreased to one-half, we also obtain twice the original current; that is,

$$\frac{10 \text{ volts}}{1 \text{ ohm}} = 10 \text{ amperes}$$

(e) CURRENT DENSITY

The current density is the current per unit area, and is usually expressed either in amperes per square decimeter or amperes per square foot. In any given case the average current density at the anode or cathode can be readily calculated by dividing the total current by the exposed area of the anode or cathode. If two baths are in series the current density in each bath is obtained by dividing the total current by the anode or cathode area in that bath.

Example.—Suppose that 500 amperes is passed through a bath in which the area of the cathode is 10 square feet, or 93 square decimeters. The cathode current density is then

$$\frac{500}{10} = 50 \text{ amp./ft.}^2$$

or

$$\frac{500}{93} = 5.4 \text{ amp./dm}^2$$

(f) QUANTITY OF ELECTRICITY

The quantity of electricity that passes is equal to the current multiplied by the time. The fundamental unit is the coulomb, which is the quantity of electricity that passes when a current of 1 ampere flows for 1 second. The common commercial unit is the ampere-hour (equal to 3,600 coulombs); that is, the quantity of electricity which passes when a current of 1 ampere flows for 1 hour.

(g) POWER

The power expended in the passage of an electrical current is equal to the product of the applied electromotive force and the current. When the electromotive force is expressed in volts and the current in amperes, the power is obtained in watts.

A watt is the power involved when a current of 1 ampere is passed through a circuit by the application of 1 volt. The usual commercial unit is the kilowatt, equal to 1,000 watts, or to 1.34 horsepower.

(h) ENERGY

The energy consumed in such operations is equal to the applied power multiplied by the time. The units usually employed are the watt-hour and the kilowatt-hour, which are equal to the energy consumed when a power of 1 watt or 1 kilowatt, respectively, is applied for 1 hour. The kilowatt-hour is the usual basis of payment for electrical energy.

2. APPLICATION TO ELECTRODEPOSITION

In general, in the electrodeposition of metals (as in electroplating and electrotyping) a current of electricity is caused to pass through a solution between two metallic surfaces, dissolving metal from the one and depositing it upon the other. (In some processes, for example, in chromium plating, insoluble anodes are used.)

(a) ELECTROLYTE

The electrolyte is the conducting solution, which contains, in addition to water, a compound (usually a salt) of the metal to be deposited, together with, in most cases, one or more substances added to improve the conductivity of the solution or the character of the deposit. Thus, in the regular acid copper bath, the principal constituent is copper sulphate (a salt formed by the action of sulphuric acid upon copper), while sulphuric acid is added to increase the conductivity of the solution and to improve the character of the deposited metal.

(b) ELECTRODES

The conductors through which the current enters and leaves the solution are known as electrodes.

The electrodes through which a positive current enters the solution, and from which the metal is dissolved, are called anodes.

The electrodes through which a positive current leaves the solution, and upon which the metal is deposited, are the cathodes.

(c) CURRENT EFFICIENCY

If a definite current is passed through a suitable solution for a specified time, under the ideal conditions, a definite weight of the metal will be dissolved from the anode and the same weight of metal will be deposited upon the cathode.

Under any given conditions the amount of metal deposited is proportional to the quantity of electricity that passes. The weight of metal deposited by 1 ampere-hour (3,600 coulombs) differs with different metals. From the acid copper sulphate bath 1 ampere-hour should deposit at 100 per cent efficiency 1.186 g (0.0418 ounce) of copper; therefore, 24 ampere-hours, or 1 ampere-day, should deposit 28.46 g, or almost exactly 1 ounce of copper.

The ratio of the weight of metal actually dissolved from the anode, or deposited upon the cathode, to the weight, with 100 per cent efficiency, represents the current efficiency at the anode or cathode, respectively.

Example.—Twenty-four ampere-hours (or 1 ampere-day) should deposit 28.46 g (or almost exactly 1 ounce) of copper. If, in any case, such a current actually deposits only 27.90 g of copper, the cathode current efficiency is $\frac{27.90}{28.46}$, or 98 per cent.

(d) RESISTANCE

As above noted (p. 7), the current produced by a given voltage, or the voltage required to produce a given current, is determined by the resistance of the circuit. The lower the resistance of the circuit, the lower the voltage and also the power required to produce a given current and to deposit a given weight of metal. In any such circuit the resistance is made up of two parts—the external resistance (of the leads and connections) and the internal resistance (the resistance of the solution itself).

The external resistance should be reduced to the practical minimum by the use of sufficiently large copper bars and rods for conductors and by securing the best possible contacts (permanent wherever feasible). An abnormally high resistance at any point or in any connection is indicated by undue heating at or near that point. It is generally considered good practice in such work to pass not more and preferably less than 800 amperes per square inch, or 125 amperes per square centimeter of cross section of the copper rods.

The internal resistance of the bath may be decreased (*a*) by addition of appropriate materials to the solution, (*b*) by raising the temperature of the solution, (*c*) by decreasing the distance between the anodes and the cathodes, or (*d*) by increasing the size of the electrodes. In general, however, in the last case the total current is increased, although the current density is decreased.

(e) ARRANGEMENT OF BATHS

When two or more baths are so arranged that the anodes in one bath are directly connected to the cathodes in the next, the baths are said to be in series. In such a case the internal resistance of the circuit is equal to the sum of the internal resistances of the separate baths, and the current that flows through the two baths is the same. If the resistances of the two baths are equal, the voltages between the anodes and cathodes in each bath will be equal to each other and approximately equal to one-half the voltage derived from the generator. If in any such case the voltages on the two baths are not approximately equal, it is evident that the composition of the solution tions, or the size of or distance between the electrodes in the two baths, is not the same. If the cathode areas in the two baths are appreciably different, the current density, and, therefore, the character of the deposits will vary.

When the baths are arranged independently—that is, the anodes and cathodes in each are directly connected to the generator—they are in parallel. In such a case the voltage on each bath is approximately that of the generator, and the current that passes through each circuit is inversely proportional to the resistance of each.

Example.—Suppose that two baths are connected in parallel to a generator producing current at 6 volts. If the total resistance of one bath is 0.01 ohm and of the second bath is three times as great (that is, 0.03 ohm) the current flowing through the first bath will be three times as great as that through the second.

1. $6/0.01 = 600$ amperes.
2. $6/0.03 = 200$ amperes.

(f) INSULATION

In order to avoid irregularities in operation, and losses of electrical energy, precautions should be taken to provide suitable insulation between the anode and cathode bars, and between them and the lead linings or other metallic connections. The strips of wood generally used on the edge of the tanks to support the electrode rods readily become impregnated with the solutions and permit leakage of electricity from anodes to cathodes or to the linings. For such purposes strips of nonpermeable insulating material, such as alberene stone, hard rubber, glass, porcelain, wood impregnated with wax, etc., are preferable. By the use of tanks constructed of stoneware or similar material, the possibility of electrical leakage is greatly reduced. No metallic connection other than the electrical conductors should exist between tanks or to the earth. To avoid electrical leakage each pipe leading into the tanks should have a suitable insulating joint, the simplest form of which is a few inches of rubber hose.

V. DEPOSITION OF COPPER FROM ACID SULPHATE SOLUTIONS

1. GENERAL CONSIDERATIONS

The acid copper bath such as is used in electrotyping, is one of the simplest solutions employed in electrodeposition, as it has in addition to water, only two essential constituents—copper sulphate (or "bluestone") and sulphuric acid (or "oil of vitriol"). The same type of solution is used on a very large scale for copper refining, in which the anodes consist of relatively impure copper, while the copper that is deposited in the process is very pure. An acid copper bath can not be employed for plating copper directly on steel. For that purpose cyanide solutions are used. In recent years there has been a greatly increased use of the acid plating solution to produce intermediate layers of copper, expecially in the automobile industry. This bath is also used for plating on nonmetallic surfaces, such as of plaster and wood, that have been rendered impervious and conducting. In the electroforming of tubes, sheets, and other articles, acid copper solutions are employed.

The acid solutions used for these various purposes are very similar in composition, and it might at first seem that the information derived from other processes would be directly applicable to electrotyping. This is not the case, as the conditions of operation and the requirements of the product are different in electrotyping than in the other processes. The desirable conditions for electrotyping are as follows:

(*a*) A copper shell of the customary thickness (0.006 inch or 0.15 mm), should be deposited in not more than two hours, and preferably in less than one hour.

(*b*) The deposit should be relatively hard and tough.

(*c*) Slight roughness on the back of the shell is usually unobjectionable, but marked "treeing" should be avoided.

(*d*) The copper should "cover" a graphited wax mold in as short a time as practicable.

(*e*) The throwing power should be good; that is, the copper should deposit as uniformly as possible in the depressions of the mold, because the bottoms of the depressions form the printing surface.

The principal factors which affect the rate of covering and of subsequent deposition, and the properties of the deposit, are (1) the composition of the bath, (2) the temperature of the bath, (3) the current density, and (4) the degree of agitation.

2. PROPERTIES OF THE COPPER DEPOSITS

By varying one or more of the above conditions, marked changes may be produced in the structure and physical properties of the deposited copper. These, in turn, may affect the service obtained from the plate. It is difficult to correlate the wearing quality of the plate with any simple measurable properties. The resistance of the copper to deformation, as measured, for example, by the Brinell or Rockwell hardness test, may influence the ability of the plate to resist flattening if the pressure on the printing press is unduly high. The thickness of the shell and the properties of the "backing up" metal also influence the resistance of the plate to deformation. Under favorable conditions in surface printing, however, there should be very little occasion for the plates to be subjected to high pressures.

If then the normal wearing out of the plates is caused by abrasion, a test of abrasion resistance would be desirable. No simple satisfactory test of this kind has been devised, The "scratch-hardness" test may serve as an indication of wear resistance. In this test a diamond or sapphire point is drawn across the surface under a definite load, and the width of the scratch is then measured with a microscope. The harder material yields a narrow scratch, and vice versa. At best, however, the results of this test are not very reproducible, especially in the hands of different observers.

It is possible to measure the ultimate tensile strength and percentage elongation of strips of the deposited copper in a small testing machine. From the measured width and thickness of the test samples the tensile strength can be computed in pounds per square inch (lbs./in.^{2}) or in kilograms per square centimeter (kg/cm^2). Results of numerous tests have shown that copper deposited under different conditions may vary in tensile strength from 20,000 to 65,000 lbs./in.^{2} (1,400 to 4,500 kg/cm^2) and in elongation from 4 to 35 per cent (in a gage length of 2 inches or 5 cm).

In general, it was found that an increase in tensile strength is accompanied by an increase in scratch hardness. Thus, for example, a deposit with a tensile strength of about 20,000 lbs/in.^{2} (1,400 kg/cm^2) yielded, under the conditions used, a scratch with a width of about 12 "microns" (thousandths of a millimeter); while one with a strength of about 60,000 lbs./in.^{2} (4,200 kg/cm^2) gave a scratch with a width of about 9 microns. It is not possible, however, to derive any exact relation between the tensile strength and the scratch hardness.

Microscopic examination of the deposited copper shows that it is always crystalline. In general, the initial deposit consists of very fine grains, while the subsequent layers are coarser. Copper that is deposited slowly from warm solutions in the absence of addition agents usually consists of relatively large conical crystals, the presence of which can be detected with the naked eye. Such copper is soft and has a low tensile strength. If the current density is increased, or if addition agents are present, the crystals are smaller and have a random arrangement. Such copper is harder and more brittle and has a higher tensile strength.

In general, it may be assumed that satisfactory copper electrotype shells will have a tensile strength of 35,000 to 50,000 lbs./in.^{2} (2,500 to 3,500 kg/cm^2) and an elongation of at least 5 to 10 per cent. Unless otherwise stated, the conditions proposed in this circular apply to the production of copper with such properties.

3. COMPOSITION OF THE SOLUTIONS

(a) COPPER SULPHATE AND SULPHURIC ACID

The only essential constituents in addition to water are copper sulphate (blue vitriol) and sulphuric acid (oil of vitriol). Both of these materials are readily obtainable in a sufficiently pure form for this purpose. The small amounts of iron, nickel, arsenic, or other impurities in commercial copper sulphate are not likely to have injurious effects. Pure copper sulphate crystals contain 25.46 per cent copper, and the commercial salt usually contains at least 25 per cent of copper.

Commercial sulphuric acid may contain small amounts of iron, arsenic, and other impurities. If it is very dark in color, it probably contains organic matter, such as may be formed by the action of the concentrated acid on wood or paper. The organic matter may serve as a harmful addition agent. Unless, therefore, light-colored commercial acid is available, it may be preferable to employ pure sulphuric acid. The fact that under normal operating conditions no copper sulphate is required after the bath is prepared, while sulphuric acid is added at intervals, may justify the use of pure acid. Frequent additions of very impure acid may lead to the accumulation of deleterious impurities in the bath.

Concentrated sulphuric acid usually has a specific gravity of about 1.84 (66° Baumé) and contains about 93 per cent of sulphuric acid. As the concentrations of acid in the baths are generally expressed in avoirdupois ounces per gallon (oz./gal.) or in grams per liter (g/l), while the acid is measured by volume, it is convenient to know the volume of acid corresponding to a given weight. If the specific gravity of sulphuric acid is 1.84, 1 pint of sulphuric acid weighs 1.84 times as much as a pint of water. The latter weighs practically 1 pound (actually 1.04 pounds); and a fluid ounce (1/16 pint) of water weighs about 1 avoirdupois ounce.

For practical purposes we may consider that for each pound of sulphuric acid required in the solution 5/9 of a pint should be added, or for each avoirdupois ounce about 5/9 of a fluid ounce. Suppose that a 200-gallon bath is to be prepared and is to contain 10 oz./gal. (75 g/l) of sulphuric acid. This represents 2,000 ounces or 125 pounds of sulphuric acid. This is equivalent to $5/9 \times 125 = 69.3$ pints of acid, or $\frac{69.3}{8} = 8.7$ gallons of acid.

It is possible to vary the concentrations of copper sulphate and sulphuric acid over wide limits and still get fairly satisfactory deposits. The best results, however, are obtained by having relatively high concentrations of both of these constituents. The dissolved copper sulphate furnishes copper ions which must be present for deposition of copper. In general, a high concentration of copper sulphate increases the permissible rate of deposition; that is, the limiting current density that can be used without producing "burnt" deposits. The sulphuric acid increases the conductivity and thus reduces the voltage required to produce any desired current density. It also increases the anode corrosion, which may even become excessive and cause accumulation of copper sulphate. The sulphuric acid increases the throwing power and decreases the tendency for the formation of roughness and trees. It also produces finer grained deposits.

It is not possible, however, to increase indefinitely the concentrations of both the copper sulphate and sulphuric acid. As shown in Table 7 in the Appendix, at ordinary temperature about 53 oz./gal. (395 g/l) of copper sulphate can be dissolved in water. If, however, sulphuric acid is also present in considerable amount, the solubility of the copper sulphate is decreased. The maximum total concentration of these two constituents is about 43 oz./gal. (325 g/l). At higher temperatures the possible total concentration is greater, but when such a solution cools the copper sulphate is likely to crystallize out. If these crystals form on the copper anodes, they may practically insulate the anodes and prevent the passage of any current.

Numerous experiments have shown that in a warm agitated solution containing about 33 oz./gal. (250 g/l) of copper sulphate ($CuSO_4 . 5H_2O$) and about 10 oz./gal. (75 gl/) of sulphuric acid (H_2SO_4), as high current densities can be used without burning as can be produced with 6 volts. This is the potential usually available on each tank when the tanks are operated in parallel.

(b) ADDITION AGENTS

When baths containing only copper sulphate and sulphuric acid are operated under the above conditions at high current densities, the deposits are usually somewhat rough and relatively soft. As previously indicated, slight roughness is not objectionable. It is usually desirable, however, to produce copper that is as hard as can be deposited without being brittle. Certain "addition agents" have been found to be beneficial for this purpose.

It has long been known that when certain materials are added to baths used in metal deposition, the deposits are smoother and harder. Especially in copper deposition a large number of such addition agents have been proposed, although only a few of them have come into extensive use. The one most commonly used is glue or gelatin, which is added to almost all copper refining baths in order to produce a smoother deposit and thus decrease the tendency for short circuits between the anodes and cathodes, which are relatively close to each other. The concentration of glue is very low, usually not over about 3 parts per 1,000,000 of solution, which is equivalent to about 0.0004 oz./gal., or 3 mg/l. Recently experiments were conducted on this subject at the Bureau of Standards by R. O. Hull, research associate of the International Association of Electrotypers. The details have been published in the Journal of Research.[4] The experiments showed that glue is the most effective of the additions tried; that is, it requires a smaller concentration to produce an appreciable effect upon the smoothness and hardness of the copper. This very fact is a disadvantage, however, as there is no satisfactory method of determining this small content of glue by analysis, and an excess is likely to be detrimental and to form very brittle deposits. The most favorable concentration of glue for the conditions used in electrotyping was found to be about 0.0013 oz./gal. (0.01 g/l). The use of glue for this purpose is not recommended, as it requires frequent replenishment, and it is difficult to avoid getting an excess.

It was found that both urea and dextrin (which latter may be added as such, in commercial glucose which contains a small amount of dextrine, or as starch, which is converted to dextrin) produce smooth deposits, which, however, are usually rather soft. Hence, these addition agents are not particularly suited for use in electrotyping.

The addition agent that was found to be most satisfactory is phenolsulphonic acid. This is a compound produced by treating concentrated phenol (carbolic acid) with an equal volume of concentrated sulphuric acid. The mixture may be allowed to stand at ordinary temperature for about 48 hours; or combination may be hastened by heating the mixture to the temperature of boiling water (212° F. or 100° C.) for about 1 hour. A convenient quantity of the reagent can be prepared by pouring 2 quarts (or 4 pounds) of phenol into an earthenware, lead, or copper vessel, slowly adding 2 quarts (about 7.5 lbs.) of concentrated sulphuric acid, and mixing thoroughly. If the phenol is very pure, it is solid at ordinary temperature. In that case the container should be immersed in warm water till the phenol has liquefied and can be poured out. Concentrated phenol is very poisonous and is corrosive to the skin. Care should be taken in handling it and any that splashes on the hands should be washed off at once.

After the mixture has stood for 48 hours, or been heated for 1 hour and allowed to cool, about 2 quarts of water is added to make the solution less viscous. Each pint of this mixture is equivalent to about 5 avoirdupois ounces of phenol.

It was found that the best concentration of the phenolsulphonic acid is that equivalent to about 0.13 oz./gal. or 1 g/l of phenol. For a bath containing 250 gallons, this is equivalent to 32 oz. of phenol, or to about 6 pints (3 quarts) of the above mixture. The maximum

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[4] See footnote 1, p. 2.

effect of the initial addition is not observed for a few days, by which time the solution has acquired a deep green color. In operation the concentration of addition agent gradually decreases, partly from evaporation and partly from oxidation. It is not necessary to make frequent additions, as good results are obtained over a fairly wide range of concentration. In the absence of chemical analyses it will probably be safe to add each week about 5 per cent of the original amount. Thus for a 250-gallon bath, a weekly addition of about 5 fluid ounces of the mixture may be made. Such additions should, of course, be governed also by the appearance and hardness of the shells. In general, it will be found that the phenolsulphonic acid produces smooth, hard shells, especially when these are deposited in warm solutions at high current densities.

Addition agents do not increase the electrical efficiency of the copper baths; as the cathode efficiency in all copper baths is close to 100 per cent. The addition agents have little, if any, effect upon the conductivity of the solutions. Deposition at a high current density always requires a higher voltage than is needed for a lower current density under the same conditions. The use of an addition agent must therefore be justified by an improvement in the deposit, and especially by a saving in time.

(c) CHANGES OCCURRING IN THE COMPOSITION OF THE SOLUTIONS

Since the commercial copper sulphate and sulphuric acid, as well as the copper anodes, are usually fairly pure, and since, moreover, a small amount of the solution always adheres to the cathodes and is subsequently replaced, there is no marked tendency for impurities to accumulate in the solution. Under the ideal conditions the same amount of copper should dissolve at the anodes as is deposited upon the cathodes, and the solution should remain practically constant in composition. In practice, however, it is usually found that the content of copper sulphate increases while that of free acid decreases; which change is accompanied by an increase in the density of the solutions. This change is explained by the fact that in such cases more copper is dissolved from the anodes than is deposited upon the cathodes. This effect is especially marked when low anode current densities are employed, and can therefore be remedied or at least reduced by the use of a smaller anode surface. In general, for these copper baths, it is not necessary or desirable to have the anode surface greater than that of the cathodes.

Other factors may also cause changes in the composition of the solutions. Thus, the evaporation which always takes place will in itself cause an increase in both density and acidity if it is not corrected by the occasional addition of water to constant level. When the cases (cathodes) are removed from the baths a certain amount of the solution always adheres to them. The mechanical losses thus produced cause a decrease in both density and acidity if, as is customary, the bath is maintained at constant level by the occasional addition of water. Since, in practice, however, the solutions usually increase in density and decrease in acidity, it is evident that the chemical changes discussed in the last paragraph more than balance the mechanical losses. In any event, it is desirable at intervals to determine and adjust the composition of the solution to that desired. Even though, as previously pointed out, the composition of the solution, under otherwise uniform conditions, does not in itself have a marked influence upon the character of the deposits, it is essential that the solution be kept nearly uniform in composition, since changes in it influence the current density produced with a given voltage. Adjustment of the solution usually consists in (*a*) the replacement of a portion of the solution with water to reduce the content of copper sulphate, and (*b*) the addition of the requisite amount of sulphuric acid. Observations on electrotyping baths indicate that to maintain a constant composition of such solutions it is seldom, if ever, necessary to add any copper sulphate.

(d) METHOD OF REGULATING THE COMPOSITION

(1) Determination of the Density.—Before testing the solutions they should always be adjusted to the normal level of the baths by the addition of water if necessary, and thoroughly mixed. The hydrometer should be read always in the same way, preferably by floating it in a glass jar or cylinder containing the solution. By placing the eye slightly below the level of the solution, and then gradually raising the eye, the surface, first seen as an ellipse, becomes a straight line, the intersection of which with the hydrometer scale should be taken as the reading of the hydrometer. For practical purposes with colored solutions, and especially for comparison, the readings will usually be sufficiently accurate if made by observing the hydrometer scale above the surface of the liquid. The density should always be taken at approximately the same temperature, preferably that for which the hydrometer is graduated. If the solution is warm, the sample should be cooled to room temperature before measuring the density or acidity.

(2) Determination of Acidity.—*Principle.*—The amount of free sulphuric acid in the electrolyte is determined by measuring the volume of an alkali solution of known strength which is required to neutralize the acid present in a measured volume of the copper sulphate solution. An indicator (methyl orange) is added to the solution in order to show, by its change in color, when all the acid is neutralized by the alkali. This method was published by Wogrinz[5] in 1913. Even before that time it was used in a few electrotyping establishments in this country.

Apparatus.—The only essential pieces of apparatus for making this test are a pipette to measure the copper sulphate solution, a burette to measure the standard alkali, and a few flasks. Suitable apparatus and the necessary solutions can be secured for a moderate charge from some local chemist or chemical supply house.

Solutions (*alkali*).—A sodium hydroxide (caustic soda) solution of any known and convenient strength may be employed. It is, however, probably most convenient to obtain a normal solution, 1 ml of which will neutralize 0.049 g of sulphuric acid. If, therefore, a sample of 10 ml (or 1/100 of a liter) of the copper solution be titrated, each ml of the sodium hydroxide required is equivalent to 4.9 g per liter (or for most practical purposes 5 g/l or 0.67 oz./gal.) of sulphuric acid. If solutions of other strength are employed, the calculations should be correspondingly changed. Since the sodium hydroxide may change in strength on standing (owing to its attacking the glass

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[5] Chem. Ztg., **37**, p. 869; 1913.

of the container) it should either be renewed or restandardized by a chemist at intervals of about six months. Attack of the glass may be prevented by lining the dry bottle with a heavy coat of paraffin or ozokerite. The bottles should be closed with a rubber stopper.

Methyl orange solution, containing 1 part of methyl orange in 1,000 parts of water, is used as an indicator; that is, it changes color when all the sulphuric acid is neutralized.

Titration.—To carry out the titration, measure with a pipette 10 ml of the copper sulphate solution to be tested (after the bath has been thoroughly mixed) and run it into a small flask. Add to it about 1 ml of the methyl orange solution and dilute with water to about 150 ml. Adjust the sodium hydroxide solution to the zero mark in the burette. Run the sodium hydroxide solution into the copper sulphate solution slowly, with constant shaking, until the pink or purple color of the solution just disappears. If a decided green color or appreciable precipitate appears, too much alkali has been added and a new portion should be titrated. Note the reading of the burette at the end of the titration. After completing the titrations, empty and rinse the burette and put a little vaseline on the stopcock.

Calculation.—To find the number of grams per liter of sulphuric acid in the copper solution, multiply by 5 the number of milliliters of normal alkali used in the above titration. The number of ounces per gallon is equal to two-thirds (0.67) the number of milliliters of alkali used.

(3) ADJUSTMENT OF COMPOSITION.—Having determined the specific gravity and the acidity of any such solution, it is a simple matter to adjust the composition to that desired, provided the specific gravities of solutions of known content of copper sulphate and sulphuric acid are known. Such a table, prepared [6] by this bureau, is given as Table 8 in the Appendix. It was found that the denisty of these solutions at any temperature depends only upon the total content of copper sulphate plus sulphuric acid. (This relation appears to be a coincidence, and does not apply to solutions of other salts.) In Table 8 (Appendix) are shown the amounts of copper sulphate plus sulphuric acid (in grams per liter and ounces per gallon) in solutions of given specific gravity [7] at 77° F. (25° C.).

In order to determine the amount of copper sulphate (crystals) present in any solution of known specific gravity and acidity, all that is necessary is to deduct the determined acid content from the total content corresponding to the observed specific gravity as given in Table 8. Thus, if the solution has a specific gravity of 1.20, it contains 339 g/l of copper sulphate plus sulphuric acid. If it contains 60 g/l of sulphuric acid, the copper sulphate content is $339 - 60 = 279$ g/l.

The usual process of adjusting such a solution may be carried out as follows:

1. Determine from Table 8 the amount of copper sulphate (in g/l) in the solution.
2. Divide the difference between the desired copper sulphate content and the amount present, by the amount present, to obtain the percentage of the solution to be replaced with water.

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[6] For details, see B. S. Scientific Paper No. 275.

[7] The specific gravities given in the table are for 25°/4° C. For all practical purposes, however, the values obtained at room temperatures with hydrometers calibrated, for example, at 60°/60° F. may be used. If a Baumé hydrometer is used the corresponding specific gravity should be determined from Table 3.

3. Subtract this percentage of the sulphuric acid from the amount originally present, and finally deduct the remainder from the amount of acid desired in order to obtain the amount (g/l or oz./gal. of acid to be added.

4. Multiply the number of grams per liter required by the number of liters in the tank and divide by 1,000 to determine the number of kilograms of acid to be added.

5. To determine the number of pounds of acid to be added for each 100 gallons of solution in the bath multiply the number of grams per liter required by 0.83.

Example.—Suppose a bath containing 680 liters (180 gallons) was found to have a specific gravity of 1.20 and to contain 60 g/l of sulphuric acid, and it is desired to adjust it to a specific gravity of 1.19 and an acid content of 75 g/l.

From Table 8 it may be noted that a solution with a specific gravity of 1.20 contains 339 g/l of copper sulphate plus sulphuric acid; therefore, the present solution contains 339 − 60 = 279 g/l of copper sulphate.

Similarly, a solution with a specific gravity of 1.19 contains a total of 321 g/l; therefore, the desired solution contains 321 − 75 = 246 g/l of copper sulphate.

$$\begin{array}{rl} & 279 \text{ g/l (copper sulphate present)} \\ \text{subtract} & \underline{246} \text{ g/l (copper sulphate desired)} \\ \text{Difference} & 33 \text{ g/l} \end{array}$$

$$\frac{33 \text{ (difference)}}{279 \text{ (amount present)}} = 11.8 \text{ per cent,}$$

or for practical purposes 12 per cent.

Therefore, remove 12 per cent of 680 liters (82 liters) or of 180 gallons (15.6 gallons) of the solution from the tank. Since 12 per cent of the sulphuric acid present is thereby removed, there is left only 88 per cent of the original acid, or the equivalent of only 60 − 7 = 53 g/l. To obtain 75 g/l it is therefore necessary to add 75 − 53 = 22 g/l or 22 × 0.134 = 2.9 oz./gal. of sulphuric acid.

A bath containing 680 liters will, therefore, require 680 × 22 = 14,960 g., or practically 15 kgs. of sulphuric acid. One containing 180 gallons will require 180 × 2.9 = 522 ounces or $\frac{522}{16} = 33$ pounds of acid. This is equal to $\frac{33}{1.8} = 18$ pints = 9 quarts of acid. After this is added the tank should be filled with water to the desired level and thoroughly mixed.

(4) DETERMINATION OF PHENOLSULPHONIC ACID.—The method for the determination of phenolsulphonic acid is rather involved, and can not be carried out except by a person with considerable experience in chemical analysis. Electrotypers will probably find it advisable to make arbitrary additions as above suggested. When chemical assistance is available, an occasional analysis, for example every few months, may lead to more uniform results. The following method is described briefly for the benefit of any chemists who have occasion to make such analyses.

The result of this analysis may be expressed as the "total phenol equivalent." It includes free phenol, that combined as phenolsulphonic acid, and any hydroquinol or quinone formed in the bath by oxidation of phenol. The method depends upon the fact that free bromine combines with phenol or its sulphonic acid to form tribromophenol

$$C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr.$$

Under similar conditions hydroquinol and quinone probably also form addition compounds. Hence the result, expressed as "phenol equivalent" is only a rough guide to the total concentration of addition agent present.

The method is applied to the copper bath as follows: Dilute a 10 ml sample of the solution to 50 ml and add 2 g of 20-mesh granulated zinc to precipitate the copper. When the copper is removed, filter the solution into a 200 ml flask and add 10 ml of a 0.1*N* "bromine solution" and 50 ml of concentrated hydrochloric acid. (The bromine solution contains 2.8 g/l of potassium bromate, and 12 g/l of potassium bromide. It is standardized against 0.1 *N* thiosulphate under the same conditions as are used for the determination.) Close the flask with a rubber stopper and heat it in a water bath to 50° C. (122° F.) for one-half hour. Cool, add 2 ml of a 10 per cent solution of potassium iodide, shake well, and titrate the liberated iodine (using starch indicator) with 0.1 *N* thiosulphate, which has been similarly standardized against 0.1 *N* dichromate (4.9 g/l $K_2Cr_2O_7$). From the volumes of thiosulphate used in this titration and in the standardization of the bromine solution, the phenol equivalent of the solution may be calculated. One milliliter of 0.1 *N* bromine solution is equivalent to 0.00157 g of phenol.

(5) NOTES.—1. In the above operations and calculations extreme accuracy is not required, since all that can be accomplished is to keep the composition of the solutions approximately constant. The chief value of such tests will be to enable the operator to avoid obtaining defective work, or in cases where the work may prove defective to determine immediately whether the composition of the solution or some other condition is at fault.

2. A permanent record of all titrations and of all changes in or additions to the solutions should be kept. Such records will ultimately furnish valuable information regarding the operation of the bath, and may reduce the necessity for frequent analyses.

4. TEMPERATURE OF THE SOLUTIONS

(a) EFFECT OF TEMPERATURE OF DEPOSITION

A rise in temperature of the solution may affect the character of the deposit in two ways: (1) By increasing the conductivity of the solution and, therefore, the current density produced by a given voltage; and (2) by causing a change in the physical properties of the deposited copper, even with the same current density. The first effect is particularly significant with respect to seasonal variations, since at lower temperatures of the baths (as after a cold night) the copper will not deposit as rapidly (at a given voltage) as at normal temperatures. From the standpoint of economy, the use of relatively high temperatures in the baths is desirable, because of the increased conductivity and consequent saving of power.

In the regular electrotyping operations where copper is deposited upon graphited wax molds, the permissible maximum temperature is limited by the softening point of the wax. Owing to the great variations in the composition of molding wax, it is impossible to state any definite limits, but it appears probable that for such work the highest safe temperature will not exceed 40° C. (104° F.).

In the studies made by this bureau upon solutions containing no addition agents, the temperature was varied from 25° to 40° C. (77° to 104° F.). Within this range it was found that the temperature has a more marked influence upon the character of the deposited metal than any other single factor. In all cases, under otherwise similar conditions, a rise in temperature from 25° to 40° C. caused a decided decrease in the tensile strength and in the hardness of the copper, accompanied by a much coarser crystalline structure. This effect of temperature was most marked with medium current density (35 to 55 amp./ft.^{2} or 4 to 6 amp./dm ^{2}), and with high acid content. In some cases this change in temperature reduced the tensile strength from 40,000 to 20,000 lbs./in.^{2} (2,800 to 1,400 kg/cm^2). In order to obtain satisfactory deposits from plain solutions at medium current density the solution should, therefore, be maintained between 25° and 35° C. (77° and 95° F.), and even with high current densities the temperature should not exceed 35° C. (95° F.). As previously noted, the use of addition agents, such as phenolsulphonic acid, permits higher temperatures and current densities to be used, as the tendency to form soft deposits is thereby counteracted.

(b) REGULATION OF THE TEMPERATURE

(1) THE AMOUNT OF HEAT PRODUCED.—Whenever an electrical current is passed through any solution, the amount of heat produced in a given time is directly proportional to the resistance of the solution and to the square of the current; in other words, H (heat produced) $= I^2R$. Obviously, the lower the resistance of the solution the less heat will be produced in it when a given current is passed. If, however, the resistance of the solution is lowered (for example, by the addition of sulphuric acid) and the voltage is maintained constant, the current produced will be greater, and since the heat evolved is proportional to the square of the current, the increased production of heat due to the increased current will be greater than the decrease due to reduced resistance. This may be illustrated by a simple example.

Example [8].—(*a*) Suppose the resistance is 0.02 ohm, and a voltage of 4 volts is employed, then the current passing will be $\frac{4}{0.02} = 200$ amperes. In this case the heat produced in 1 second is equal to I^2R or $(200)^2 \times 0.02 = 800$ joules (energy units.)[9]

(*b*) Suppose now that the resistance is reduced to one-half (that is, to 0.01 ohm) and the voltage is retained at 4 volts. Then the current produced will be $\frac{4}{0.01}$ or 400 amperes, and the heat produced will be equal to $(400)^2 \times 0.01 = 1{,}600$ joules.

(*c*) Suppose that after reducing the resistance to 0.01 ohm, as in (*b*), the voltage is reduced to 2 volts, thus producing $\frac{2}{0.01} = 200$ amperes;

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[8] In these calculations, used solely for illustration, the external resistance has been neglected.

[9] A joule is an energy unit equal to 0.2387 calorie (heat unit). A calorie is the amount of heat required to raise the temperature of 1 g. of water 1° C.

that is, the same current (and rate of deposition) as in (*a*). In this case the heat produced is equal to $(200)^2 \times 0.01 = 400$ joules. In other words, by reducing the resistance to one-half, without changing the voltage, the heat produced is twice as great, while a reduction of the resistance to one-half without changing the current causes a production of only one-half the amount of heat. An appreciation of the above relation should remove the prevalent misunderstanding as to whether reducing the resistance of a solution increases or decreases the heating effect.

(2) THE TEMPERATURE REACHED IN THE BATH.—The above considerations refer only to the total heat evolved, and not to the temperature of the bath, which is the factor to be controlled. The actual temperature of the bath is influenced by (1) the amount of heat liberated in the bath, (2) the volume of the bath (the larger the bath the less is the rise in temperature produced by a given amount of heat), (3) the heat lost by radiation and conduction (which depends largely on the temperature of the surroundings and the construction of the tank), and (4) the heat used in evaporating part of the solution (which depends principally on the temperature, volume, and distribution of the air used for agitation). Without a knowledge of all these factors, it would be impossible to calculate the resultant temperature of the bath in any particular case. As is well known, however, the tendency under usual operating conditions is for the temperature to rise above that desired, especially in warm weather.

(3) CONTROL OF TEMPERATURE.—In order to maintain an approximately uniform temperature, all such baths should be provided with suitable means for heating or cooling the solutions, such as a lead coil (electrically insulated), through which either hot water, steam, or cold water can be circulated. The use of live steam to heat the solutions or of ice to cool them, as sometimes practiced, is at best a temporary expedient and is almost certain to cause irregularities in the composition and operation of the baths. The most difficult problem is that of maintaining, in warm weather, the temperature recommended; that is, not above 40° C. (104° F.) when a considerable amount of work is being done in the bath. It is recognized that this can be accomplished only by careful attention, and by the use of considerable amounts of air and cooling water or of a number of large baths which are agitated even during the periods between their actual use. In large plants, especially when high current densities are used, it is customary to lower the temperature of the cooling water by means of small refrigeration units.

5. COMPOSITION AND PHYSICAL PROPERTIES OF THE ANODES

The exact composition of the copper anodes used in such work is of little practical importance, since at the present time the amounts of impurities likely to be present in commercial copper are so small as to have little or no effect upon the operation of the baths. Moreover, as previously noted, the accumulation of impurities in the baths (even when used for years) is practically prevented by what amounts to a constant renewal of solutions in the process of removing the portion of the solution adhering to the cathodes and the portions required to adjust the density at intervals.

The actual source of the copper is of little or no significance. In this connection the distinction should be emphasized between, on the one hand, the source and method of refining the copper; and, on the other hand, the method of preparing the copper for use as anodes. In general, copper occurs in nature either in the free state as metallic copper; or in compounds, such as sulphides or carbonates. In the first form, which is found principally in the Lake Superior region, the copper requires only a mechanical treatment and melting before casting into bars of nearly pure copper, the so-called "lake copper." The ores containing compounds of copper (such as occur in the Western States) contain numerous impurities, including gold and silver, and require, in general, a much more complicated treatment, involving as a rule mechanical separation, smelting, and subsequent refining by electrolysis. In the preparation of rolled or cast copper, the metal must first be melted and cast, in which operation any differences in structure due to the original method of refining entirely disappear.

The state (or physical condition) of the copper may, however, play an important part. Of the three available classes of copper anodes, viz, cast, electrolytically deposited, and rolled, the latter are at present used most extensively in electrotyping. In acid baths cast copper anodes give rise to the formation of fine particles, consisting principally of metallic copper. This behavior may be attributed to the fact that the crystalline structure of the cast copper is usually coarser than that of rolled copper. Small amounts of impurities, such as copper oxide that may be present in cast copper, are likely to be concentrated on the grain boundaries. When these dissolve they permit fine particles of copper to become detached from the anodes.

Electrolytically deposited copper, which may be bought in the form of sheared "cathode sheets" produced in copper refining, dissolves more uniformly than cast copper, and nearly as well as rolled copper. If it is purchased directly from copper refiners in the approximate sizes required, it is somewhat cheaper than rolled copper, and has proved satisfactory in numerous plants.

It is not desirable to use more than one kind of copper anodes in the same tank. Either rolled or electrolytic anodes are satisfactory when used alone. When used in the same tank the rolled anodes dissolve somewhat more readily and, hence, the electrolytic anodes are not uniformly attacked.

The introduction of fine particles from the anodes is objectionable on account of the loss of copper, and the "fouling" of the solution, with danger of such particles lodging upon a cathode and forming nuclei for irregular growths. It is probable that the presence of this fine copper slime also increases the consumption of sulphuric acid, owing to the purely chemical solubility of such fine copper in copper sulphate—sulphuric acid solutions agitated with air. In any case it is desirable to filter the solutions at intervals. A wool filter should be used. The pumps, pipes, and filter should be constructed of lead or hard rubber, which are not appreciably attacked by these solutions.

It is the usual practice to insert the copper hooks into holes drilled in the anodes, and to pour molten lead or type metal into a suitable mold surrounding the connection. In such cases the lead should extend up on the hook to a point considerably above the solution level. Such an arrangement insures good electrical contact between the hook and anode, and also protects the hook against corrosion by the solution.

6. CHARACTER AND CONDITION OF THE CATHODE SURFACE

In general, commercial electrotypes are deposited either upon lead or upon graphited wax molds. The former require no special consideration, since the lead is itself a conductor and requires the addition of no conducting surface. In the use of wax molds, however, there is good reason to believe that many of the practical difficulties encountered in the production of electrotypes are due to defects or irregularities in the composition of the molding wax or of the graphite, or in the method of taking the impression or coating it with graphite. Information regarding graphite is contained in the paper referred to on p. 3. As opportunity offers, the properties of molding wax will be studied.

Under proper conditions it is possible to so coat the molds with graphite that no preliminary treatment with iron filings and copper sulphate is required. Most electrotypers have found, however, that the common process of metallizing the forms with copper sulphate and iron filings (usually called "oxidizing") is an advantage. This preliminary coating with copper not only saves time, but also produces a shell of more uniform thickness, owing to the subsequent simultaneous electrodeposition of copper at all parts of the plate. There is, however, some danger of scratching the forms, especially in halftone work. This danger can be eliminated by using a gentle stream of water instead of a brush to stir the iron filings and copper sulphate on the surface of the mold.

7. CONDITIONS FOR COVERING GRAPHITED WAX MOLDS

If the so-called oxidizing is not employed, it is desirable to use those conditions which will produce rapid covering of the graphited surface. This saves time, yields shells of more uniform thickness, and reduces any tendency for the graphite to be washed off of the uncovered portions.

A few experiments were made with the apparatus used for measuring the rate of covering of nickel upon graphited wax, and described in the articles referred to on p. 3. In this method the time required for the metal to cover a graphite surface having an area 1 by 6 inches (2.5 by 15 cm) was noted. For copper solutions a constant potential of 2 volts was employed. Under the most favorable conditions this voltage produced a final current density when the graphited area was covered, of about 150 amp./ft.^{2} (16 amp./dm ^{2}).

It was found that, within otherwise favorable limits, variations in the composition of the bath have very little effect upon the time of covering, which was from 11 to 14 minutes. A change in temperature from 75° to 105° F. (25° to 40° C.) increased the covering time from 12 to 42 minutes, and at still higher temperatures, under the conditions used, the covering was incomplete. From these experiments it appears probable that in large plants it might be advantageous to keep a separate tank for covering, and to maintain the solution in it at a lower temperature than that used in the regular tanks.

8. CURRENT DENSITY AND AGITATION

Next to the temperature, the current density is the most important of the factors determining the properties of the deposited copper. This is readily understood, since, as previously stated, the current density determines the rate of deposition of the copper, and, under otherwise uniform conditions, the size of the individual crystals. The latter in turn determines largely the hardness, tensile strength, and ductility of the deposited copper. In general, it may be stated that the finer the grains or crystals the greater the tensile strength and, therefore, probably the hardness of the metal. The ductility of thin strips of electrolytically deposited copper increases with increased tensile strength up to a tensile strength of about 40,000 lbs./in.^{2} (2,800 kg/cm^2) and then decreases; that is, copper with a higher tensile strength is relatively brittle. It is well known that an increase in the current density up to a certain limit causes a decrease in the size of the crystals, while with higher current densities the deposit becomes coarse and irregular with the characteristic "burnt" appearance. The generally accepted explanation of the latter effect is that with too high current densities the solution adjacent to the cathode becomes impoverished in copper. In accordance with this view the obvious method of avoiding the difficulty and of obtaining coherent deposits with high current densities, is to insure a fresh supply of copper sulphate in the solution near the cathode. This can be accomplished (*a*) by having the solution rich in copper sulphate, and (*b*) by constantly bringing fresh portions of the solution to the surface of the cathode. As is well known, the latter operation is commonly accomplished by suitable agitation of the solution, usually performed in electrotyping baths by means of a current of air. That this method is efficient in permitting more rapid deposition of the copper is shown by the fact that in practice, in "still" baths, the current density that can be employed is seldom over 30 amp./ft.^{2} (3 amp./dm^2), and usually much less; while in baths agitated with air, current densities of 75 amp./ft.^{2} (8 amp./dm^2) are common in commercial work, and under favorable conditions much higher current densities can be used. The extreme possibilities of the effect of agitating the solutions are shown in results obtained by Bennett[10] who, by very rapidly rotating a small cathode, was able, with current densities up to 4,000 amp./ft.^{2} (430 amp./dm^2) to obtain coherent deposits of copper having unusually high tensile strength. While any such degree of agitation is manifestly impracticable in electrotyping baths, the results are of interest as indicating the desirability of having the highest convenient degree of agitation, especially between the anode and cathode surfaces. Good, uniform agitation is absolutely essential for the satisfactory deposition of copper at high current densities. The air used for agitation should be free from oil. Clean air can be obtained from certain types of air compressors; with others oil-traps are required.

In early experiments without addition agents, very thorough agitation was used and current densities from 25 to 100 amp./ft.^{2} (2.5 to 10.5 amp./dm.^{2}) were employed. It was found that at low temperature (75° F. or 24° C.) the tensile strength increases with increased current density. At high temperature (105° F. or 40° C.) an increase in current density from about 25 to 40 amp./ft.^{2} (2.5 to 4.5

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[10] Trans. Am. Electrochem. Soc., **21**, p. 253; 1912.

amp./dm^2) causes a decrease in tensile strength; and an increase in current density from 40 to 100 amp./ft.^{2} (4.5 to 10.5 amp./dm^2) produces an increased tensile strength. It is therefore recommended that, at low temperature, current densities from about 40 to 60 amp./ft.^{2} (4.5 to 6.5 amp./dm^2) be employed; and, at high temperature, from about 75 to 120 amp./ft.^{2} (8 to 13 amp./dm^2). For uniform results it is essential that the current be measured by means of an ammeter. While the voltmeter is a useful and important adjunct to such baths, it does not serve to maintain uniform current conditions, unless all other conditions are absolutely uniform. By the use of an ammeter it is possible not only to measure directly the current, but also to ascertain whether other conditions are uniform, since in a solution of definite composition and temperature and with electrodes of a given size and distance apart a definite voltage will always produce a given current density.

As previously noted (p. 13) it is possible by the use of various addition agents to increase the permissible current density and thereby the rate of deposition. The addition agents do not, however, increase the cathode efficiency; that is, the weight of metal deposited per ampere-hour. With suitable addition agents such as phenolsulphonic acid, it is possible to use current densities up to about 230 amp./ft.^{2} (25 amp./dm^2); that is, about twice the maximum that is used in the regular baths. With such high current densities it is obvious that special care is required to avoid excessive heating of the solutions or other abnormal behavior.

In these baths it requires approximately 20 amp.-hr./ft.^{2} (2.2 amp-hr./dm^2) to deposit 0.001 inch (0.025 mm) of copper; or about 120 amp-hr./ft.^{2} (13 amp-hr./dm^2) to deposit the customary thickness of 0.006 inch (0.15 mm). Hence, it will require about one hour for such a deposit at 120 amp./ft.^{2} (13 amp./dm^2) or about one-half hour at twice that current density.

9. DISTANCE BETWEEN ELECTRODES

One of the important factors in determining the current density is the distance between the anodes and cathodes. From the standpoint of economy it is obvious that reducing this distance decreases the resistance of the bath and, therefore, decreases the voltage (and power) required to produce a given current density. Practically, however, the minimum distance is determined by the convenience of handling the cases without mechanical injury and the possibility of producing a uniform and satisfactory agitation between electrodes very close together. In general, it may be stated that the better the agitation the closer may the electrodes be placed. It was found impossible to detect any marked effect of the distance itself (from 2.5 to 6 inches (6 to 15 cm)) upon the quality of the copper. In some cases, especially for forms with deep recesses, the greater distance is an advantage, as then the distribution of metal is more uniform. For most purposes a distance of 3 inches (7.5 cm) will probably be satisfactory.

10. DISTRIBUTION OF THE COPPER

As previously stated, the rate of deposition of the copper, and, therefore, the average thickness of the deposits produced in a given time depend almost entirely upon the current density employed.

From a knowledge of the weight of copper deposited from such solutions by one ampere-hour (1.186 g) and the specific gravity of copper (8.9), it is a simple matter to calculate the theoretical weight and thickness of copper deposited by a given current in a specified time. Tables 9, 10, and 11 give such data (in metric and customary units) calculated upon the assumption that the current efficiency is 100 per cent and that the copper is uniformly distributed over a plane surface. The tables give, respectively, the maximum weight and average thickness of copper produced by a given current in a given time, and conversely the minimum time required to produce a deposit of specified thickness with a given current density.

Since the current efficiency in acid sulphate baths under normal conditions is seldom less than 95 per cent, and is frequently 98 or 99 per cent, no correction need be made for this factor in practical work.

On the other hand, it should be emphasized that the assumption that the copper will be uniformly distributed, even over a plane surface, is never realized in practice, at least when deposited directly upon graphited wax molds. Owing to the appreciable time required for "covering" (usually 15 to 20 minutes), it should be expected that those portions first covered will have the thickest deposits. While this factor no doubt has some influence, it is almost invariably found in practice that the copper on such shells is much thicker on the bottom and two vertical edges than in the center or near the top edge. Even when considerable care was used, it was found that differences in thickness of from 20 to 30 per cent were found in different parts of the plane portion of the form. This behavior, which may be explained by the greater current density near the edges, is most marked when the tank and the anodes are appreciably larger, and especially deeper, than are the corresponding cathode surfaces. For this, as well as other reasons, it is therefore not desirable to use anodes larger than the cathodes, or to use very deep tanks.

Even more marked than the above differences are those observed in different parts of the type surface, as determined from a study of a considerable number of finished plates from different plants. Probably all electrotypers have realized that upon a type surface the copper is not as thick as upon the plane surface near the edges; but they may be surprised to learn that in shells having a thickness on the plane surface of 0.006 to 0.008 inch (0.15 to 0.2 mm) the copper on the printing surface is usually only 0.002 to 0.004 inch (0.05 to 0.10 mm) in thickness. It is obvious, therefore, that any specification by which an electrotyper agrees to furnish a shell of a stated thickness is misleading unless the average thickness is referred to.

The various factors influencing the distribution and uniformity of the copper on such surfaces have been studied in connection with the throwing power of the solutions. In general, it may be stated that the greater the distance between the anodes and cathodes, the more uniform the deposit. It was found that there is no appreciable difference in the current density (and therefore weight of copper deposited) upon an area of given outside dimensions, whether plane, half tone, or type form. As, however, the actual surface area of a half tone or type form is greater than that of a similar flat surface, a lower average thickness of copper will be produced upon the half tone or type form by a given current and time than upon a plane form. In using Table 9 the approximate weight of copper deposited upon a given area of such a surface in a specified time (excluding the period required for covering) will be obtained. (This will include the weight of the copper on the rough edges.) In using Tables 10 and 11, however, it is necessary to make some allowance for the variation in thickness. In practice it has been found that the thickness on a smooth or halftone surface will be from 80 to 90 per cent of that derived from these tables, while upon a type form the thickness on the printing surface will be only 30 to 50 per cent of that calculated. The values in the tables are, therefore, useful chiefly in computing the relative thickness of shells produced under different conditions.

The conditions that were found to produce the best throwing power in copper deposition are (*a*) a relatively low concentration of copper sulphate, (*b*) a high concentration of sulphuric acid, (*c*) the use of addition agents, (*d*) a low temperature, and (*e*) a low current density. It may be noted that certain of these conditions, especially (*a*), (*d*), and (*e*) are unfavorable for rapid deposition. Practically, in electrotyping, it is usually preferable to employ those conditions that permit rapid deposition and thus to produce the shells in a short time, even though in doing so the deposit is less uniform in thickness than it might be if the shell were made more slowly. In effect this choice represents the deposition of slightly more copper in order to obtain some known or assumed minimum thickness of copper on the printing surface.

If, however, the form is of such shape that it is difficult to get metal into the depressions and if time is not an important consideration, the conditions used for slow deposition will be warranted and advantageous.

In general, it is desirable to produce shells of approximately the same average thickness, especially when a number of plates are to be used on the same press, or to register with each other. One way to foster such uniformity is to connect with each cathode bar an ampere-hour meter, which measures the number of ampere-hours that pass to the case. Such an instrument may be provided with a signal, such as a bell, to indicate when the number of ampere-hours have passed that are required for a certain area with a specified thickness. Whether the expense of such installations is warranted will depend upon the degree of uniformity required. It is believed that in most cases the quality (hardness and ductility) of the copper has a greater influence upon the wearing qualities than the exact thickness, provided the latter be such as to insure a coherent shell, free from holes or other imperfections.

11. SUMMARY

(*a*) PROPERTIES OF DEPOSITED COPPER.—(1) In general, the finer the crystals, the higher is the tensile strength and, therefore, probably the hardness of the copper.

(2) The ductility (as measured by the permanent elongation after fracture) increases with increased tensile strength up to a tensile strength of about 40,000 lbs./in.^{2} (2,800 kg/cm^2) and then decreases; that is, the copper becomes relatively brittle.

(3) It is believed that copper with a tensile strength of 35,000 to 50,000 lbs./in.^{2} (2,500 to 3,500 kg/cm^2) and an elongation of 5 to 10 per cent will be found satisfactory for electrotype plates.

(*b*) AGITATION.—The best possible agitation should be employed, especially between the anodes and cathodes.

(*c*) Composition of Solutions.—(1) The solution should contain from 8 to 11 oz./gal. (60 to 80 g/l) of sulphuric acid, and from 32 to 35 oz./gal. (240 to 270 g/l) of copper sulphate. The specific gravity of the solution should be from 1.18 to 1.20 (22° to 24° Bé.).

(2) If phenolsulphonic acid is used as an addition agent, its concentration should correspond to about 0.13 oz./gal. (1 g/l) of phenol.

(3) Whatever the composition employed, it should be kept as nearly constant as possible, to insure uniform working conditions.

(*d*) Temperature.—(1) A rise in temperature under otherwise uniform conditions always decreases the tensile strength. This effect is most marked with high acid content and with medium current density.

(2) A solution without addition agents should be maintained between 75° and 95° F. (25° and 35° C.), unless high current densities are used (over 75 amp./ft.^{2} or 8 amp./dm^2), in which case the temperature may be allowed to rise to 105° F. (40° C.).

(3) A solution with an addition agent, such as phenolsulphonic acid, may be used at temperatures up to 105° F. (40° C.) on wax molds, and up to 120° F. (50° C.) on lead molds.

(*e*) Current Density.—(1) At low temperature, the higher the current density (up to 90 amp./ft.^{2} or 9.5 amp./dm^2), the higher the tensile strength of the copper. Good results can be obtained from 40 to 90 amp./ft.^{2} (4.5 to 9.5 amp./dm^2).

(2) If the deposits are produced at a high temperature fairly high high current densities should be used. At 105° F. (40° C.) current densities up to 100 amp./ft.^{2} (10.5 amp./dm^2) may be used without addition agents, or up to 230 amp./ft.^{2} (25 amp./dm^2) with suitable addition agents.

(*f*) Thickness of Shells.—On smooth or half-tone surfaces, the thickness of copper will usually be from 80 to 90 per cent of that calculated for the current and time used. On type surfaces the copper will be only 30 to 50 per cent as thick as calculated.

VI. APPENDIX

Table 1.—*Conversion of centigrade (C.) to Fahrenheit (F.) temperatures*

°C. °F.	°C. °F.	°C. °F.	°C. °F.	°C. °F.
0=32	25= 77	45=113	65=149	85=185
5=41	30= 86	50=122	70=158	90=194
10=50	35= 95	55=131	75=167	95=203
15=59	40=104	60=140	80=176	100=212
20=68				

Table 2.—*Conversion of Fahrenheit (F.) to centigrade (C.) temperatures*

°F. °C.	°F. °C.	°F. °C.	°F. °C.	°F. °C.
0=−17. 8	40= 4. 4	85=29. 4	130=54. 4	175= 79. 4
5=−15. 0	45= 7. 2	90=32. 2	135=57. 2	180= 82. 2
10=−12. 2	50=10. 0	95=35. 0	140=60. 0	185= 85. 0
15= −9. 4	55=12. 8	100=37. 8	145=62. 8	190= 87. 8
20= −6. 7	60=15. 6	105=40. 6	150=65. 6	195= 90. 6
25= −3. 9	65=18. 3	110=43. 3	155=68. 3	200= 93. 3
30= −1. 1	70=21. 1	115=46. 1	160=71. 1	205= 96. 1
32= 0. 0	75=23. 9	120=48. 9	165=73. 9	210= 98. 9
35= 1. 7	80=26. 7	125=51. 7	170=76. 7	212=100. 0

Table 3.—*Conversion of degrees Baumé (Bé.) to specific gravity (Sp. gr.)*

°Bé. Sp. gr.	°Bé. Sp. gr.	°Bé. Sp. gr.	°Bé. Sp. gr.	°Bé. Sp. gr.
0=1. 000	6=1. 043	12=1. 090	18=1. 142	24=1. 198
1=1. 007	7=1. 051	13=1. 098	19=1. 151	25=1. 208
2=1. 014	8=1. 058	14=1. 107	20=1. 160	27=1. 218
3=1. 021	9=1. 066	15=1. 115	21=1. 169	27=1. 229
4=1. 028	10=1. 074	16=1. 124	22=1. 179	28=1. 239
5=1. 036	11=1. 082	17=1. 133	23=1. 189	29=1. 250

Table 4.—*Conversion of specific gravity (Sp. gr.) to degrees Baumé (Bé.)*

Sp. gr. °Bé.	Sp. gr. °Bé.	Sp. gr. °Bé.	Sp. gr. °Bé.	Sp. gr. °Bé.
1. 00=0. 00	1. 06= 8. 21	1. 11=14. 37	1. 16=20. 00	1. 21=25. 17
1. 01=1. 44	1. 07= 9. 49	1. 12=15. 54	1. 17=21. 07	1. 22=26. 15
1. 02=2. 84	1. 08=10. 74	1. 13=16. 68	1. 18=22. 12	1. 23=27. 11
1. 03=4. 22	1. 09=11. 97	1. 14=17. 81	1. 19=23. 15	1. 24=28. 06
1. 04=5. 58	1. 10=13. 18	1. 15=18. 91	1. 20=24. 17	1. 25=29. 00
1. 05=6. 90				

TABLE 5.—*Approximate equivalents of metric and United States units*

Length:
- 1 meter (m) = 39.37 inches.
- 1 decimeter (dm) = 3.937 inches.
- 1 centimeter (cm) = 0.3937 inch.
- 1 inch = 2.54 centimeters.
- 1 foot = 30.48 centimeters.

Area:
- 1 square meter (m^2) = 1,550 square inches.
- 1 square decimeter (dm^2) = 15.5 square inches.
- 1 square centimeter (cm^2) = 0.155 square inch.
- 1 square inch = 6.45 square centimeters.
- 1 square foot = 9.29 square decimeters.

Volume:
- 1 cubic meter (m^3) = 35.31 cubic feet.
- 1 cubic decimeter (dm^3) = 61.02 cubic inches.
- 1 cubic centimeter (cm^3) = 0.061 cubic inch.
- 1 cubic inch = 16.39 cubic centimeters.
- 1 cubic foot = 28.32 cubic decimeters.

Capacity (liquid measure):
- 1 liter (l) = 1,000 milliliters (or about 1,000 cubic centimeters).
- 1 liter = 1.057 quarts.
- 1 milliliter [1] (ml) or cm^3 = 0.034 fluid ounce.
- 1 gallon = 231 cubic inches.
- 1 gallon = 3.785 liters.
- 1 quart = 0.946 liter.

Mass (weight):
- 1 kilogram (kg) = 1,000 grams.
- 1 kilogram = 2.205 avoirdupois pounds.
- 1 gram (g) = 0.0353 avoirdupois ounce.
- 1 avoirdupois ounce = 28.35 grams.
- 1 avoirdupois pound = 453.6 grams.
- 1 liter of water weighs 1 kilogram.

TABLE 6.—*Approximate conversion factors for metric and United States units*

1. Grams per liter (g/l) multiplied by 0.134 = avoirdupois ounces per gallon (oz./gal.).
2. Avoirdupois ounces per gallon (oz./gal.) multiplied by 7.5 = grams per liter (g/l).
3. Grams per liter g/l multiplied by 0.0083 = pounds per gallon (lbs./gal.).
4. Pounds per gallon (lbs./gal.) multiplied by 120 = grams per liter (g/l).
5. $\frac{\text{Grams per liter}}{\text{10 multiplied by specific gravity}}$ = percentage by weight.
6. Percentage by weight (%) multiplied by 10 times the specific gravity = grams per liter (g/l).
7. Amperes per square decimeter (amp./dm^2) multiplied by 9.3 = amperes per square foot (amp./ft.^{2}).
8. Amperes per square foot (amp./ft.^{2}) multiplied by 0.108 = amperes per square decimeter (amp. /dm^2).
9. Kilograms per square centimeter (kg/cm^2) multiplied by 14.2 = pounds per square inch (lbs./in.^{2}).
10. Pounds per square inch (lbs./in.^{2}) multiplied by 0.07 = kilograms per square centimeter (kg/cm^2).

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[1] The milliliter, the true unit of capacity, is often designated (for example, on volumetric apparatus) as cubic centimeter (abbreviated cm^3 or sometimes cc.), from which, however, it has a slightly different value. For all practical purposes the term cubic centimeter and milliliter are interchangeable.

TABLE 7.—*Solubility of copper sulphate at 15° C. (59° F.) in the presence of sulphuric acid* [1]

Sulphuric acid present in grams per liter [2]	Solubility of copper sulphate (crystallized salt), in grams per liter	Sulphuric acid, present in grams per liter [2]	Solubility of copper sulphate (crystallized salt), in grams per liter
0	395	60	245
10	348	80	231
20	308	100	215
30	280	120	197
40	260	140	180
50	253		

[1] Derived from Pfanhauser: Herstellung von Metallgegenstände, p. 11.

[2] From the context in the original it appears that by "1 per cent sulphuric acid" is meant 10 gm/l, etc., on which basis the values given have been calculated.

TABLE 8.—*Total concentration of copper sulphate plus sulphuric acid in solutions of given specific gravity* [1]

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	45.5
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.).

NOTE.—Tables 9, 10, and 11, have been computed for 100 per cent cathode efficiency and for uniform distribution (p. 26). Suitable allowances must be made for possible variations from these ideal conditions.

TABLE 9.—*Weight of copper deposited from acid sulphate solution*

(*a*) IN METRIC UNITS [1]

Current density used amp./dm.^{2}	Weight of 1 dm.^{2} of deposit (grams)				
	1 hour	2 hours	3 hours	4 hours	5 hours
1	1. 19	2. 37	3. 56	4. 74	5. 93
2	2. 37	4. 74	7. 12	9. 49	11. 86
3	3. 56	7. 12	10. 67	14. 23	17. 79
4	4. 74	9. 49	14. 23	18. 98	23. 72
5	5. 93	11. 86	17. 79	23. 72	29. 65
6	7. 12	14. 23	21. 35	28. 46	35. 58
7	8. 30	16. 60	24. 91	33. 21	41. 51
8	9. 49	18. 98	28. 46	37. 95	47. 44
9	10. 67	21. 35	32. 02	42. 70	53. 37
10	11. 86	23. 72	35. 58	47. 44	59. 30
11	13. 05	26. 09	39. 14	52. 18	65. 23
12	14. 23	28. 46	42. 70	56. 93	71. 16
13	15. 42	30. 84	46. 25	61. 67	77. 09
14	16. 60	33. 21	49. 81	66. 42	83. 02
15	17. 79	35. 58	53. 37	71. 16	88. 95
16	18. 98	37. 95	56. 93	75. 90	94. 88
17	20. 16	40. 32	60. 48	80. 65	100. 81
18	21. 35	42. 70	64. 04	85. 39	106. 74
19	22. 53	45. 07	67. 60	90. 14	112. 67
20	23. 72	47. 44	71. 16	94. 88	118. 60
21	24. 91	49. 81	74. 72	99. 62	124. 53
22	26. 09	52. 18	78. 27	104. 37	130. 46
23	27. 28	54. 56	81. 83	109. 11	136. 39
24	28. 46	56. 93	85. 39	113. 86	142. 32
25	29. 65	59. 30	88. 95	118. 60	148. 25

[1] 1 ampere-hour deposits 1.186 g copper.

(*b*) IN CUSTOMARY UNITS [2]

Current density used (amp./ft.^{2})	Weight of 1 square foot of deposit (ounces)				
	1 hour	2 hours	3 hours	4 hours	5 hours
10	0. 42	0. 84	1. 26	1. 67	2. 09
20	. 84	1. 67	2. 51	3. 35	4. 18
30	1. 26	2. 51	3. 77	5. 02	6. 28
40	1. 67	3. 35	5. 02	6. 69	8. 37
50	2. 09	4. 18	6. 28	8. 37	10. 46
60	2. 51	5. 02	7. 53	10. 04	12. 55
70	2. 93	5. 86	8. 79	11. 72	14. 64
80	3. 35	6. 69	10. 04	13. 39	16. 74
90	3. 77	7. 53	11. 30	15. 06	18. 83
100	4. 18	8. 37	12. 55	16. 74	20. 92
110	4. 60	9. 20	13. 80	18. 41	23. 01
120	5. 02	10. 04	15. 06	20. 08	25. 10
130	5. 44	10. 88	16. 32	21. 76	27. 20
140	5. 86	11. 72	17. 57	23. 43	29. 29
150	6. 28	12. 55	18. 82	25. 10	31. 38
160	6. 69	13. 39	20. 08	26. 78	33. 47
170	7. 11	14. 23	21. 34	28. 45	35. 56
180	7. 53	15. 06	22. 59	30. 12	37. 66
190	7. 94	15. 90	23. 84	31. 80	39. 75
200	8. 37	16. 74	25. 10	33. 47	41. 84
210	8. 79	17. 57	26. 36	35. 15	43. 93
220	9. 20	18. 41	27. 61	36. 82	46. 02
230	9. 62	19. 25	28. 86	38. 49	48. 12
240	10. 04	20. 08	30. 12	40. 17	50. 21
250	10. 46	20. 92	31. 38	41. 84	52. 30

[2] 1 ampere-hour deposits 0.04184 ounce of copper.

TABLE 10.—*Thickness of copper deposited from acid sulphate solution*

(*a*) IN METRIC UNITS[1]

Current density used (amp./dm.^{2})	Thickness of deposited copper (millimeters)				
	1 hour	2 hours	3 hours	4 hours	5 hours
1	0.013	0.027	0.040	0.053	0.067
2	.027	.053	.080	.107	.133
3	.040	.080	.120	.160	.200
4	.053	.107	.160	.213	.267
5	.067	.133	.200	.267	.333
6	.080	.160	.240	.320	.400
7	.093	.187	.280	.373	.466
8	.107	.213	.320	.427	.533
9	.120	.240	.360	.480	.600
10	.133	.267	.400	.533	.666
11	.147	.293	.440	.587	.733
12	.160	.320	.480	.640	.800
13	.173	.347	.520	.693	.867
14	.187	.373	.560	.746	.933
15	.200	.400	.600	.800	1.000
16	.213	.427	.640	.853	1.067
17	.227	.453	.680	.906	1.133
18	.240	.480	.720	.960	1.200
19	.253	.507	.760	1.113	1.267
20	.267	.533	.800	1.066	1.333
21	.280	.560	.840	1.120	1.400
22	.293	.587	.880	1.173	1.467
23	.307	.614	.920	1.226	1.533
24	.320	.640	.960	1.280	1.600
25	.333	.667	1.000	1.333	1.667

[1] Based upon the following data: One ampere-hour deposits 1.186 g copper. Specific gravity of copper =8.9. 1 ampere per square decimeter, therefore, deposits 0.01333 mm copper in 1 hour.

(*b*) IN CUSTOMARY UNITS[2]

Current density used (amp./ft.^{2})	Thickness of deposited copper (inches)				
	1 hour	2 hours	3 hours	4 hours	5 hours
10	0.0006	0.0011	0.0017	0.0023	0.0028
20	.0011	.0023	.0034	.0045	.0056
30	.0017	.0034	.0051	.0068	.0085
40	.0023	.0045	.0068	.0090	.0113
50	.0028	.0056	.0085	.0113	.0141
60	.0034	.0068	.0102	.0136	.0170
70	.0040	.0079	.0119	.0158	.0198
80	.0045	.0090	.0136	.0181	.0226
90	.0051	.0102	.0153	.0203	.0254
100	.0056	.0113	.0170	.0226	.0282
110	.0062	.0124	.0186	.0249	.0311
120	.0068	.0136	.0203	.0271	.0339
130	.0073	.0147	.0220	.0294	.0367
140	.0079	.0158	.0237	.0316	.0396
150	.0085	.0170	.0254	.0339	.0424
160	.0090	.0181	.0271	.0362	.0452
170	.0096	.0192	.0288	.0384	.0480
180	.0102	.0203	.0305	.0407	.0508
190	.0107	.0215	.0322	.0429	.0537
200	.0113	.0226	.0339	.0452	.0565
210	.0119	.0237	.0356	.0475	.0593
220	.0124	.0249	.0373	.0497	.0622
230	.0130	.0260	.0390	.0520	.0650
240	.0136	.0271	.0407	.0542	.0678
250	.0141	.0282	.0424	.0565	.0706

[2] 1 ampere per square foot deposits 0.0000565 inch of copper in 1 hour.

TABLE 11.—*Time required for copper deposition from acid sulphate solution*

(*a*) IN METRIC UNITS[1]

Current density used (amp./dm²)	Time required to produce deposit of specified thickness (millimeters)																			
	0.1		0.2		0.3		0.4		0.5		0.6		0.7		0.8		0.9		1.0	
	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes
1	7	30	15	----	22	31	30	1	37	31	45	1	52	32	60	2	67	32	75	2
2	3	45	7	30	11	15	15	----	18	46	22	31	26	15	30	1	33	46	37	31
3	2	30	5	----	7	30	10	----	12	30	15	----	17	31	20	1	22	31	25	1
4	1	53	3	45	5	38	7	30	9	23	11	15	13	8	15	----	16	53	18	46
5	1	30	3	----	4	30	6	----	7	30	9	----	10	30	12	----	13	30	15	----
6	1	15	2	30	3	45	5	----	6	15	7	30	8	45	10	----	11	15	12	30
7	1	4	2	9	3	13	4	17	5	22	6	26	7	30	8	35	9	39	10	43
8	----	56	1	53	2	49	3	45	4	41	5	38	6	34	7	30	8	26	9	23
9	----	50	1	40	2	30	3	20	4	10	5	----	5	50	6	40	7	30	8	20
10	----	45	1	30	2	15	3	----	3	45	4	30	5	15	6	----	6	45	7	30
11	----	41	1	22	2	3	2	44	3	25	4	6	4	47	5	27	6	8	6	49
12	----	38	1	15	1	53	2	30	3	8	3	45	4	23	5	----	5	38	6	15
13	----	35	1	9	1	44	2	19	2	53	3	28	4	3	4	37	5	12	5	46
14	----	32	1	4	1	37	2	9	2	41	3	13	3	45	4	17	4	49	5	22
15	----	30	1	----	1	30	2	----	2	30	3	----	3	30	4	----	4	30	5	----
16	----	28	----	56	1	25	1	53	2	21	2	49	3	17	3	45	4	13	4	41
17	----	26	----	53	1	20	1	47	2	12	2	39	3	5	3	32	3	58	4	25
18	----	25	----	50	1	15	1	40	2	5	2	30	2	55	3	20	3	45	4	10
19	----	24	----	47	1	11	1	35	1	58	2	22	2	46	3	10	3	34	3	57
20	----	23	----	45	1	8	1	30	1	53	2	15	2	38	3	----	3	23	3	45
21	----	21	----	43	1	4	1	26	1	47	2	9	2	30	2	52	3	13	3	34
22	----	20	----	41	1	1	1	22	1	42	2	3	2	23	2	44	3	6	3	25
23	----	20	----	39	----	59	1	19	1	38	1	57	2	17	2	37	3	57	3	16
24	----	19	----	38	----	56	1	15	1	34	1	53	2	12	2	30	2	49	3	8
25	----	18	----	36	----	54	1	13	1	30	1	48	2	6	2	24	2	42	3	----

[1] At 1 ampere per square decimeter it requires 7.504 hours to deposit 0.1 mm of copper.

(*b*) IN CUSTOMARY UNITS[2]

Current density used (amp./ft.²)	Time required to produce deposit of specified thickness (inches)																			
	0.001		0.002		0.003		0.004		0.005		0.006		0.007		0.008		0.009		0.010	
	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes	Hours	Minutes
10	1	46	3	32	5	19	7	5	8	51	10	38	12	24	14	10	15	56	17	43
20	----	53	1	46	2	39	3	32	4	26	5	19	6	12	7	5	7	58	8	51
30	----	35	1	11	1	46	2	22	2	57	3	32	4	8	4	43	4	19	5	54
40	----	27	----	53	1	20	1	46	2	13	2	39	3	6	3	32	3	59	4	26
50	----	21	----	42	1	4	1	25	1	46	2	7	2	29	2	50	3	11	3	32
60	----	18	----	35	----	53	1	11	1	29	1	46	2	4	2	22	2	39	2	57
70	----	15	----	30	----	46	1	1	1	16	1	31	1	46	2	1	2	17	2	32
80	----	13	----	27	----	40	----	53	1	6	1	20	1	33	1	46	2	0	2	13
90	----	12	----	24	----	36	----	47	----	59	1	11	1	23	1	34	1	46	1	58
100	----	11	----	21	----	32	----	42	----	53	1	4	1	14	1	25	1	36	1	46
110	----	10	----	19	----	29	----	39	----	48	----	58	1	7	1	17	1	27	1	37
120	----	9	----	18	----	27	----	36	----	44	----	53	1	2	1	11	1	20	1	29
130	----	8	----	16	----	25	----	33	----	41	----	49	----	56	1	5	1	14	1	22
140	----	8	----	15	----	23	----	30	----	38	----	46	----	53	1	1	1	8	1	16
150	----	7	----	14	----	21	----	28	----	35	----	42	----	50	----	57	1	4	1	11
160	----	7	----	13	----	20	----	27	----	33	----	40	----	47	----	53	1	----	1	6
170	----	6	----	12	----	19	----	25	----	31	----	37	----	44	----	50	----	56	1	2
180	----	6	----	12	----	18	----	24	----	30	----	35	----	41	----	47	----	53	----	59
190	----	6	----	11	----	17	----	22	----	28	----	33	----	39	----	45	----	50	----	56
200	----	5	----	11	----	16	----	21	----	27	----	32	----	37	----	42	----	48	----	53
210	----	5	----	10	----	15	----	20	----	26	----	31	----	35	----	40	----	46	----	51
220	----	5	----	10	----	14	----	19	----	24	----	29	----	34	----	39	----	44	----	48
230	----	5	----	9	----	14	----	18	----	23	----	28	----	33	----	37	----	41	----	46
240	----	4	----	9	----	13	----	18	----	22	----	27	----	30	----	35	----	40	----	44
250	----	4	----	8	----	13	----	17	----	21	----	25	----	29	----	34	----	38	----	42

[2] At 1 ampere per square foot it requires 17.7 hours to deposit 0.001 inch of copper.

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