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C. 52

DEPARTMENT OF COMMERCE

CIRCULAR
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 52

REGULATION OF ELECTROTYPING SOLUTIONS

[1st Edition]

Issued January 25, 1915



WASHINGTON
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1915



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51. Measurement of Time and Tests of Timepieces.
52. Regulation of Electrotyping Solutions.

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REGULATION OF ELECTROTYPING SOLUTIONS

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I. INTRODUCTION

Observations made at various electrotyping establishments indicate that there is a need for accurate information regarding the composition and operation of electrotyping baths. This conclusion was confirmed by conference with members of the International Association of Electrotypers, who, at a meeting held in New York on October 7, 1914, appointed a committee to cooperate with the Bureau of Standards in a study of the problems of electrotyping.

II. PROBABLE SCOPE OF PROPOSED INVESTIGATION

As the first step in such a study, arrangements have been made for analyzing at regular intervals samples of solutions, etc., from a few representative electrotyping establishments, in order to learn not only the composition of the solutions used but also the changes taking place in them and the effectiveness of the present methods of regulation. In addition this Bureau will test gratis for a limited time, and so far as our facilities permit, such samples as may be sent in by electrotypers in general; and will give advice whenever possible. Such analyses will be made simply in order to further the investigation and in no sense in competition with commercial chemists.

The detailed plans for any exhaustive investigation of these problems will depend upon the needs of the work as determined from the preliminary studies now being conducted, and upon the desire for such work manifested by those engaged in the electrotyping industry. Such an investigation will no doubt require the active services of a number of men for a considerable period, and will involve chemical, electrical, and metallurgical studies. In general, such work will have two objects: (1) To determine the best, or at least the limiting, conditions (composition of solutions and anodes, temperature, electrical arrangement, etc.) whereby metallic deposits having the desired properties (hardness, tenacity, flexibility, etc.) may be obtained with the greatest economy of attention, time, and electrical energy; (2) to select or devise methods for testing and adjusting such solutions, preferably such methods as can be applied by those directly engaged in the industry.

III. SCOPE OF PRESENT CIRCULAR

The results of the above-mentioned studies will be incorporated in Bureau of Standards Circular No. 52, of which this is the first printed edition. This Bureau is not yet able to make definite recommendations regarding the best composition of solutions to be employed for any given method of operation for either copper or nickel electrotyping. However, in response to numerous requests for available information the Bureau has prepared this circular, which indicates merely the nature and object of its work in this field, and describes simple methods for determining and adjusting the composition of the ordinary acid copper sulphate electrotyping baths. This edition of the circular is essentially the same as and supersedes the preliminary circular, of which a limited number of mimeographed copies were issued.

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IV. METHODS OF EXPRESSING RESULTS

1. METHODS OF EXPRESSING DENSITY OF SOLUTIONS

For testing the density of these solutions either a Baumé (Bé) or a 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 a definitely stated temperature. Most of the hydrometers used for commercial work in this country are graduated for a temperature of 60° Fahrenheit (F) for both the liquid and water. Therefore if a certain solution has a specific gravity of 1.15 at 60° F, any definite volume of that solution at 60° F weighs 1.15 times as much as does the same volume of water at 60° F. The specific-gravity hydrometer is almost exclusively used in scientific work, but since the Baumé scale is so generally used in this country in commercial work, and since it is possible to make the necessary simple calculations from it with sufficient accuracy, no objection is made to the use of the United States Baumé scale.¹

Degrees Baumé may be converted to specific gravity and vice versa by means of the following tables, which are given in more complete form in Circular No. 19 of the Bureau of Standards.

TABLE 1.—Conversion of Degrees Baumé to Specific Gravity

Deg. Bé.	Sp. gr.	Deg. Bé.	Sp. gr.	Deg. Bé.	Sp. gr.
0	1.000	9	1.066	18	1.142
1	1.007	10	1.074	19	1.151
2	1.014	11	1.082	20	1.160
3	1.021	12	1.090	21	1.169
4	1.028	13	1.098	22	1.179
5	1.036	14	1.107	23	1.189
6	1.043	15	1.115	24	1.198
7	1.051	16	1.124	25	1.208
8	1.058	17	1.133		

¹This scale for liquids heavier than water is defined by the formula: Degrees Baumé = $145 - \frac{145}{\text{Sp. gr. } \frac{60^\circ}{60^\circ \text{F}}}$, where

Sp. gr. $\frac{60^\circ}{60^\circ \text{F}}$ represents the specific gravity of the solution at 60° F, referred to water at 60° F.

TABLE 2.—Conversion of Specific Gravity to Degrees Baumé

Sp. gr.	Deg. B é	Sp. gr.	Deg. B é	Sp. gr.	Deg. B é
1.00	0.00	1.08	10.74	1.16	20.00
1.01	1.44	1.09	11.97	1.17	21.07
1.02	2.84	1.10	13.18	1.18	22.12
1.03	4.22	1.11	14.37	1.19	23.15
1.04	5.58	1.12	15.54	1.20	24.17
1.05	6.90	1.13	16.68	1.21	25.17
1.06	8.21	1.14	17.81		
1.07	9.49	1.15	18.91		

2. METHODS OF EXPRESSING COMPOSITION OF SOLUTIONS.

In view of the almost universal use of the metric system in chemical analysis and other scientific work, preference will be given in this circular and in reports on this work to the metric system in expressing the composition of the solutions. Since, however, the ordinary United States units are generally employed in electrotyping and similar commercial work, the values will also be expressed in such units. In making such calculations the following values and equivalents will be employed:

One avoirdupois pound=454 grams
 One avoirdupois ounce=28.35 grams
 One United States liquid gallon=231 cubic inches
 One United States liquid gallon=3.785 liters
 One liter=1000 cubic centimeters
 One liter of water weighs 1000 grams

From these values the following simple rules may be derived:

(a) To determine the approximate capacity of the vats in gallons, divide the cubical contents in cubic inches (up to the height of the solution) by 231.

(b) To convert grams per liter (g/l) to ounces per gallon (oz./gal.), multiply by 0.134; or divide by 7.5. Thus, 50 g/l is equal to $50 \times 0.134 = 6.7$ oz./gal.

(c) To convert grams per liter to percentage by weight divide the grams per liter by ten times the specific gravity of the solution. Thus, for a solution with a specific gravity of 1.15, 50 g/l is equal to

$$\frac{50}{10 \times 1.15} = \frac{50}{11.5} = 4.3 \text{ per cent.}$$

V. COPPER SOLUTIONS

1. GENERAL INFORMATION

The solutions usually employed for copper electrotyping contain, in addition to water, only copper sulphate (blue vitrol, blue stone) and sulphuric acid. Since these substances and also the anode copper are usually fairly pure, there is no marked tendency for impurities to accumulate in the solution. The principal changes taking place in the composition of such solutions are due to two causes, (1) mechanical loss of the solution adhering to the "cases" (cathodes) when removed from the vats, and (2) solution of a greater amount of copper from the anodes than is deposited on the cathodes. The first factor would in itself cause a decrease in the density of the solutions, if, as is customary, the level of the latter is maintained approximately constant. (Water should be added to the vats at intervals in order to replace that lost by evaporation.) The second action will cause a decrease in the acidity and an increase in the density of the solutions, owing to a consumption of sulphuric acid with the production of a corresponding amount of copper sulphate. In all cases thus far observed, the latter effect is predominant. The exact causes of this consumption of acid and the best methods of reducing or eliminating it are now the subjects of investigation by this Bureau.

In general, it is necessary at intervals to determine and correct the composition of the solutions. The mere determination of the density of such solutions, whether with a Baumé or specific-gravity hydrometer, is not sufficient to fix their composition. If, however, the density of the solutions and also the amount of free sulphuric acid present are determined, the composition is fixed. Thus, for example, a solution with a specific gravity of 1.16 (20° Baumé) and containing 45 grams per liter (6 ounces per gallon) of free sulphuric acid has a perfectly definite and reproducible composition. The above figures do not, to be sure, indicate the amount of copper sulphate present in such a solution, but this is of no consequence to an electrotyper except when he is preparing a new solution. For such cases tables showing the amount of copper sulphate required to produce solutions of any desired density, with any specified acid content, would be desirable, and will probably be prepared for some future edition of this circular.

The Bureau is not yet able to recommend any composition of the solutions as best adapted to any given conditions of operation. In various commercial solutions thus far tested the specific gravity ranges from 1.12

(15.5° B \acute{e}) to 1.20 (24.2° B \acute{e}) and the acidity from 25 g/l (3.3 oz./gal.) to 90 g/l (12 oz./gal.). In general, the lower the voltage employed the more acid is required to produce a given current strength and rate of deposition, and vice versa. For the present, each operator should find a composition of solution which will give him satisfactory results under his conditions, and maintain it as nearly constant as possible by adjusting the density and acidity of the solutions at regular intervals (e. g., once a week) by the methods described in the following sections.

2. DENSITY

Before testing the solutions they should always be adjusted to the normal level of the vats by the addition of water if necessary, and thoroughly mixed. The hydrometer should always be read 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, 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 60° F.

Having determined the density of the solution (which will usually be found to be higher than is desired), it may be adjusted to the desired density by the following method, based on the assumption that the excess density of the solution (above that of water) is approximately proportional to the content of the dissolved substances.

(a) SPECIFIC GRAVITY.—If a specific-gravity hydrometer is employed, divide the difference between the observed and desired specific gravities by the difference between the observed specific gravity and the specific gravity of water, which is 1.000. The result is the percentage of the solution which should be replaced with water.

Example.

Observed sp. gr.	1.179	Observed sp. gr.	1.179
Desired sp. gr.	1.160	Sp. gr. of water	1.000
Difference019	Difference179

$$\frac{0.019}{0.179} \text{ or } \frac{19}{179} = 10.6 \text{ per cent.}$$

Therefore, replace with water 10.6 per cent of the solution, or 10.6 gallons for every 100 gallons in the vat.

(b) BAUMÉ.—If a Baumé hydrometer is used, the calculations are even simpler, and for practical purposes are sufficiently accurate. In this case we simply divide the difference between the observed and desired density, in degrees Baumé, by the observed degrees Baumé, to obtain the percentage of the solution to be replaced with water.

<i>Example.</i>	Deg.
Observed degrees Baumé.....	22
Desired degrees Baumé.....	20
Difference.....	2

$$\frac{2^{\circ}}{22^{\circ}} = \frac{x}{11} = 9.1 \text{ per cent.}$$

NOTE.—Since 22° Bé=1.179 sp. gr., and 20° Bé=1.160 sp. gr., the results in the above examples by the two methods of calculation should be the same, instead of 10.6 per cent and 9.1 per cent, respectively. The observed difference, which is due to the assumption that the readings of the Baumé scale are proportional to the specific gravity, is negligible in practical work, being equivalent to a difference of only 0.003 in the resultant specific gravity. Whichever instrument is used, there is no advantage in a very accurate adjustment of the density, since this will be somewhat altered by any subsequent addition of sulphuric acid.

3. DETERMINATION OF ACIDITY

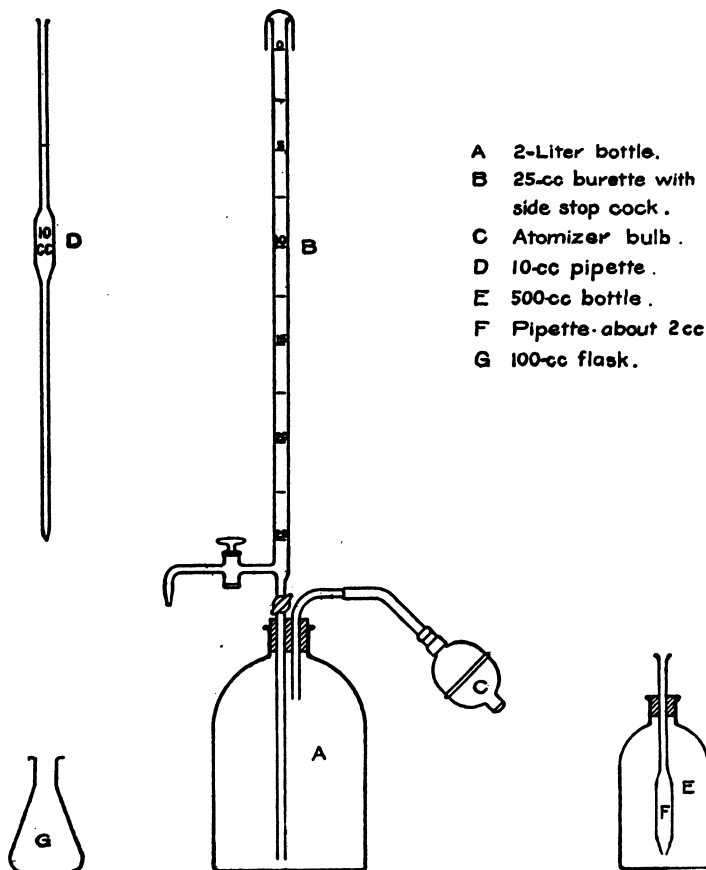
(a) PRINCIPLE.—The amount of free sulphuric acid in the solution is determined by measuring the volume of an alkali solution of known strength which is required to neutralize the acid present in a measured volume of the solution. An indicator (methyl orange) is added to the solution in order to show, by its change in color, when all the acid is neutralized by the alkali. The method as applied to such solutions is not original, having been published by Wogrinz² in 1913. Even before that time it was used in a few electrotyping establishments in this country.³

(b) 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 bottles. Fig. 1 illustrates a form of apparatus that has been found convenient in this work. Doubtless many other forms of reservoir burettes will be found equally suitable. This apparatus and also the necessary solutions can doubtless be secured for a moderate charge from any local chemist or chemical supply house.

² Chem. Ztg., 37, p. 869; 1913.

³ Private communication from Wilson Yerger.

(c) SOLUTIONS.—(1) *Alkali*.—A sodium hydroxide (caustic soda) solution of any *known* and convenient strength may be employed. In the preliminary circular a solution prepared of a strength (0.61 normal) equivalent in the titration to 3.0 grams per liter of sulphuric acid was suggested. In view of the greater ease of securing a normal solution of sodium hydroxide



- A 2-Liter bottle.
- B 25-cc burette with side stop cock.
- C Atomizer bulb.
- D 10-cc pipette.
- E 500-cc bottle.
- F Pipette about 2 cc.
- G 100-cc flask.

FIG. 1.—Apparatus for testing acidity

we now recommend the use of a *normal*⁴ solution. One cubic centimeter (1 cc) of such a solution will neutralize 0.049 gram of sulphuric acid. If, therefore, a sample of 10 cc (or 1/100 of a liter) of the copper solution be titrated, each cubic centimeter of the sodium hydroxide required is equivalent to 4.9 grams per liter (or for most practical purposes 5 g/l or 0.67 oz/gal.)

⁴ This should not be confused with a *decinormal* solution, which is often used in scientific and technical work.

of sulphuric acid. Solutions of other strength may be employed, provided the calculations be correspondingly changed. Since the sodium hydroxide may change in strength on standing (owing to its attacking the glass of the container) it should either be renewed, or restandardized by a chemist, at intervals of about six months.

(2) *Methyl orange* solution, containing 1 part of methyl orange in 5000 parts of water, is used as an indicator, i. e., it changes color when all the sulphuric acid is neutralized.

(d) TITRATION.—To carry out the titration, measure with a pipette 10 cc of the copper sulphate solution to be tested (after the bath has been adjusted to the desired specific gravity and thoroughly mixed) and run it into a small flask. Add to it about 2 cc of the methyl orange solution. To adjust the sodium hydroxide solution to the zero mark in the burette, turn the center stopcock so that the burette is connected with the stock bottle, and with the bulb pump the solution until it is above the zero mark, and then shut off this stopcock. Next turn the side stopcock and allow the solution to run into any convenient vessel (for waste) until all air is displaced from the side tube and the lower edge of the curved surface of the liquid is just at the zero mark. Now run the sodium hydroxide solution into the copper sulphate solution slowly, with constant shaking, until the violet 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 position of the lower edge of the curve at the end of the titration. After completing the titrations, allow the burette to empty and put a *little* vaseline on the stopcocks.

(e) CALCULATION.—To find the number of grams per liter of sulphuric acid in the copper solution, multiply by *five* the number of cubic centimeters of alkali used in the above titration. To find the number of pounds of acid to be added for each 100 gallons in the bath, deduct the amount of sulphuric acid thus found from the prescribed content and multiply the result by 0.83, or practically $\frac{5}{6}$. (Since 1 gallon is equal to 3.79 liters, or 100 gallons equal 379 liters, we multiply by 379 the number of grams per liter required; and since there are 454 grams in 1 pound, we divide the last result by 454. For practical purposes, therefore, we multiply by $\frac{379}{454}$ or 0.83.) For any given capacity of vat the correct factor can be readily determined.

Example.—Suppose 10 cc of the copper solution requires 9 cc of the alkali in the titration. Then the solution contains $9 \times 5 = 45$ grams per liter of acid. If, for example, we desire to have present in the solution 60 grams per liter of acid, it is necessary to add $60 - 45$ or 15 grams of acid for each liter of the solution. For a vat holding 100 gallons we must add 15×0.83 (or $15 \times \frac{5}{6}$) = 12.5 pounds of acid. Or, if the vat holds, for instance, 180 gallons, we use the factor $\frac{180}{100} \times 0.83 = 1.49$; i. e., we must add $15 \times 1.49 = 22.4$ pounds of acid.

(f) 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.

VI. NICKEL ELECTROTYPING SOLUTIONS

Owing to the great variations observed in the composition of solutions employed in nickel electrotyping which yield fairly satisfactory results, it is impossible to state at this time the best composition of the baths or the best methods of operation. Obviously, the object of work in this field should be to determine the simplest solution which will give satisfactory results and to devise methods for controlling its composition. Additions of such substances as sodium chloride, ammonium chloride, boric acid, vanadium salts, etc., render the testing and adjustment of the solutions far more complicated, and should not be used except so far as it can be shown that any beneficial effect exerted by them outweighs the above objection. The whole subject of the best composition of nickel solutions and nickel anodes, and of the deposited nickel, is in great need of study, which will be conducted as rapidly as the facilities permit. In the mean time the Bureau will be pleased to furnish any information or advice that it can in this connection.

VII. NOTICE OF NEW EDITIONS

Copies of this circular can be obtained upon request addressed to the "Bureau of Standards, Washington, D. C." Notices of new editions of this circular will be published in the Journal of Industrial and Engineering Chemistry, Brass World, Metal Industry, Inland Printer, Engraver and Electrotyper, Plate Maker's Criterion, and other journals requesting such advance notices.

S. W. STRATTON,
Director.

Approved:

E. F. SWEET,
Acting Secretary.

