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MEASUREMENT OF THE APPARENT FLUIDITY OF DISPERSIONS OF CELLULOSE IN CUPRAMMONIUM SOLUTION

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ABSTRACT

The importance of the cuprammonium fluidity test for the indication of fundamental change in cellulose, particularly in the earlier stages of degradation, is quite generally recognized. Without special equipment and technique, however, the test is difficult to perform. It is the object of this paper to describe relatively simple equipment and technique found practical for measurement of the apparent fluidity of dispersions of cellulose in cuprammonium solution.

Directions are given for the preparation and storage of the cuprammonium solution; for the construction and calibration of viscometers; for the dispersion of cellulose in the cuprammonium solution; and for the measurement of the fluidity of the dispersion. Some of the difficulties which arise in precise measurements are indicated, and data illustrating the duplicability of results are presented.

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I. INTRODUCTION

It has been observed that the quality of cellulose is indicated by its tensile strength, copper number, methylene blue absorption, and the apparent fluidity of its dispersions in standard cuprammonium solution.¹ The apparent fluidity of such dispersions has been found to be a much more sensitive and precise measure of the changes in the quality of cellulose brought about by the action of light, heat, laundering, and chemicals, particularly in the early stages, than is afforded by the other methods.

Although cellulose can be dispersed in certain salt solutions^{2 3 4} and in concentrated mineral acids,^{5 6} considerable hydrolysis of the

¹ Charles Dorée, *Methods of Cellulose Chemistry* (Chapman & Hall, Ltd., London 1933).

² H. E. Williams, *The action of thiocyanates on cellulose*, *J. Soc. Chem. Ind.* **40**, 221T (1921).

³ P. P. von Weimarn, *Bemerkungen über meine Methode der Dispersion von Zellulose in konzentrierten wässrigen Lösungen neutraler Salze*, *Kolloid-Z.* **29**, 197 (1921).

⁴ P. P. von Weimarn, *Ueber die Eigenschaften der "reinen" Zellulose als Kolloid*, *Kolloid-Z.* **44**, 212 (1928).

⁵ C. E. Guignet, *Cellulose colloids, soluble et insoluble: Constitution du Papier Parchemin*, *Compt. rend.* **108**, 1258 (1883).

⁶ R. Willstätter and L. Zechmeister, *Zur Kenntnis der Hydrolyse von Cellulose*, *Ber. deut. chem. Ges.* **46**, 2401 (1913).

cellulose may take place. Cuprammonium solution, however, appears to come closer than any other known dispersing agent to being a true physical solvent for cellulose.⁷ Although cellulose regenerated from cuprammonium solution is in the hydrated form, there is evidence which indicates that it has undergone less change in the process of solution and regeneration than when other available dispersing agents are used. Cuprammonium solution is therefore regarded by many as the best medium for the examination of cellulose in a highly dispersed state.

The principles upon which fluidity measurements of cellulose solutions are based are adequately described elsewhere.⁸ Considerable difficulty, however, is met in duplicating fluidity measurements. The preparation, preservation, and handling of the unstable cuprammonium solution; the construction and calibration of viscometers; the dispersion of high-grade cellulose; and the adequate control of temperature while the measurements are made, require special equipment and technique. The reliability of the results obtained is determined by the precautions taken in the experimental details, the omission of any of which may lead to erroneous results or complete failure.

It is the purpose of this paper to describe simple laboratory manipulations; convenient and inexpensive equipment which is readily constructed and is suitable for the measurements; and to present data obtained under practical working conditions to illustrate the precision obtained.

II. CUPRAMMONIUM SOLUTION

Cuprammonium solutions of different concentrations of copper and ammonia have been used for the dispersion of cellulosic materials.⁹ The ability to disperse cellulose and the flow characteristics of the resulting dispersions depend upon these concentrations. Solutions relatively high in ammonia content are better dispersing media than similar solutions of lower ammonia concentration.¹⁰

A solution containing 240 ± 5 g of ammonia (NH_3) and 15 ± 0.1 g of copper per 1,000 ml is satisfactory for the dispersion of cellulose of different forms, including cotton fibers which have not been subjected to any drastic chemical processing. Dispersions of high-grade cotton have fluidities as low as 1 to 2 rhes¹¹ in a 0.5-percent solution and are relatively difficult to disperse. The regenerated celluloses, and celluloses modified by bleaching, heating, laundering, or industrial processing are more readily dispersed. A solution of lower ammonia concentration could be used to disperse these materials.

Figure 1 is a diagram of the equipment for the preparation of the cuprammonium solution. The Pyrex-glass cylinder, 13, approximately

⁷ Alfred J. Stamm, *Colloid Chemistry of Cellulosic Materials*, U. S. Dept. of Agriculture, Misc. Pub. 240, p. 26 (1936).

⁸ D. A. Clibbens and A. Geake, *The measurement of the fluidity of cotton in cuprammonium solution*, *J. Textile Inst.* **19**, T77 (1928).

⁹ E. K. Carver and Harold Folts, *The plasticity of cellulose in cuprammonium hydroxide*, *J. Am. Chem. Soc.* **47**, 1430 (1925).

¹⁰ The Effect of Variations in Ammonia Concentration on the Fluidity of 0.5-Percent Cellulose Solutions. Appendix III. *The Viscosity of Cellulose Solutions*. Dept. Sci. Ind. Research (Brit.) Comm. Repts. (1932).

¹¹ According to the definition by the Society of Rheology, a "rhe" is the unit of fluidity in the cgs system. The fluidity of a simple liquid is the reciprocal of the viscosity. It must be recognized that dispersions of cellulose in cuprammonium solution do not behave like simple liquids, since the rate of shear is not proportional to the shearing stress, and that the terms "fluidity" and "rhe" as applied here are not in strict accord with the conventions of rheology. We are concerned here with what may be called "apparent fluidity" as indicated in the title.

29 cm in diameter and 29 cm deep, rests upon the circular brass plate, 12, and is covered by the iron cover, 11. This cover is held in place by the bolts, 15, and a tight seal is obtained with the rubber gasket, 10. The cover is fitted with the iron air-intake tube, 7, a bearing for the iron stirrer shaft, 9, a capillary exhaust tube and rubber stopper, 22, and the siphon, 14. The end of the shorter arm of the siphon is placed 1 to 2 cm above the bottom of the glass cylinder. The upturned end, 16, of the air-intake tube passes through a hole in the hollow crossarm of the stirrer and is fitted with an iron collar serving as a bearing for the rotating stirrer. The cylinder thus fitted is placed in the double-walled sheet-copper container, 5, with rock wool between the walls for thermal insulation. The air-intake tube is connected with the gas-washing bottle, 4, containing concentrated ammonium hydroxide of specific gravity not over 0.90, and with the differential manometer, 3, and the trap containing glass wool through which the air is introduced at 1. The manometer and capillary serve

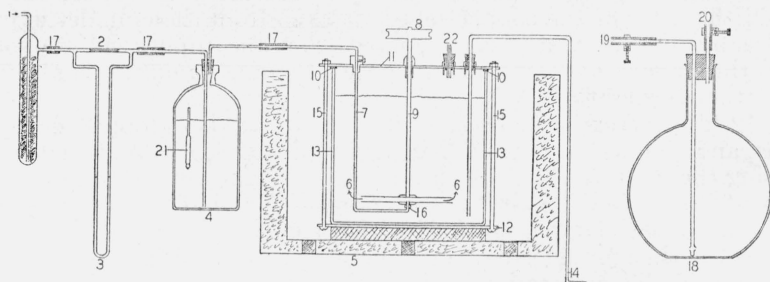


FIGURE 1.—Equipment for preparing standard cuprammonium solution.

1, Air inlet; 2, capillary flow regulator; 3, manometer; 4, reservoir for ammonia; 5, insulated container for ice; 6, hollow arm of stirrer; 7, iron tubing; 8, pulley; 9, shaft; 10, crude-rubber gasket; 11, iron plate; 12, brass plate; 13, Pyrex-glass cylinder, 12 by 12 inches; 14, siphon; 15, iron bolts; 16, bearing for stirrer; 17, rubber connections; 18, 12-liter Pyrex flask; 19 and 20, rubber connections with pinch clamps; and 21, hydrometer.

as a flowmeter to facilitate the regulation of the rate of flow of air. A rate of 10 liters per hour, at the pressure necessary to force it through the system when charged as directed below, is satisfactory.

The length of the capillary convenient for constructing the flowmeter to deliver approximately 10 liters of air per hour at room temperature can be calculated with sufficient accuracy for the purpose by arbitrarily choosing a convenient difference in the level of the water columns in the manometer, and using the equation

$$l = 0.76 hr^4, \quad (1)$$

where h is the difference in the water levels, r the radius, and l the length of the capillary in centimeters.

The space between the glass cylinder and the inner wall of the insulated copper container is packed with ice. The cylinder, 13, is charged with 15 liters of ammonium hydroxide solution of specific gravity 0.88 to 0.90. The stirrer is rotated at about 30 rpm and 15 g of cane sugar followed by 900 g of precipitated copper powder are added. The opening in the cover is then closed with the rubber stopper and capillary tube, 22. The wash bottle, 4, is charged with 2 liters of ammonium hydroxide of the same concentration as that used to charge

the cylinder. The flow of air is then started. If, during the operation the ammonium hydroxide solution in the wash bottle changes so that its specific gravity becomes greater than 0.90, it should be replaced or some gaseous ammonia added. The change in concentration of this solution can conveniently be observed by temporarily stopping the air flow and observing the reading on the hydrometer, 21. The stirring and the flow of air are continued until tests show that the concentration of copper is a little more than 15 g per liter.

For the purpose of observing the change in concentration of dissolved copper, the stirring is stopped and the undissolved powdered copper permitted to settle for a few minutes. A portion of the solution is drawn out by means of a pipette fitted with a rubber bulb and 5 ml of it is placed in a 50-ml Nessler tube and diluted to the mark with water. Five ml of a copper sulfate solution containing 15 g of copper (59 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) per liter is placed in a second Nessler tube, 10 ml of concentrated ammonium hydroxide is added, and the mixture diluted with sufficient water to fill the tube to the mark. When the color of the copper solution taken from the cylinder is just noticeably deeper than that prepared from the copper sulfate solution, the stirring and air flow are stopped and the mixture is allowed to settle overnight.

A 12-liter Pyrex flask, 18, is provided with rubber stopper, connections, and clamps as shown. The air in it is displaced by nitrogen by passing the gas into the flask through the opening, 20, and exhausting through 19. After the air has been displaced, the openings are closed by means of the clamps and the flask is weighed. The cuprammonium solution is then transferred from the cylinder in which it is prepared to the flask by connecting it with the siphon at 14. The flow is started by air pressure applied through the tube, 22, after opening the clamps, 19 and 20, and continued until the flask has been filled within about 10 cm of the stopper, when the flow is stopped by closing the clamp at 19. The clamp at 20 is also closed to prevent air from entering the flask, which is packed in ice or placed in a refrigerator and allowed to stand overnight to permit any undissolved copper to settle. The solution must be kept cool and in a closed container at all times to prevent the escape of ammonia and reaction with air.

About 100 ml of the solution is removed from the flask for analysis by attaching a glass tube to the rubber tube at 19 and one at 20, through which a stream of nitrogen can be forced when the clamps are released. This portion is also kept on ice. The clamps are closed and the flask and its contents weighed.

A 5-ml specimen of the ice-cold solution is pipetted into a 300-ml Erlenmeyer flask containing at least 50 ml of standard approximately 2 *N* sulfuric acid. The solution is added slowly with the tip of the pipette touching the bottom of the flask, which is cooled in ice water. A few drops of methyl red indicator are added and the sulfuric acid not neutralized by the cuprammonium solution is titrated with standard approximately normal sodium hydroxide solution. A second 5-ml portion of the cuprammonium solution is placed in a 250-ml beaker, diluted with about 20 ml of distilled water, acidified with sulfuric acid, and the copper determined by electrodeposition.¹²

¹²W. F. Hillebrand and G. E. F. Lundell: *Applied Inorganic Analysis; with Special Reference to the Analysis of Metals, Minerals, and Rocks*, p. 197 (J. Wiley & Sons, New York, N. Y., 1929).

The cuprammonium solution prepared in the manner described contains a little more copper and ammonia than required for use and needs to be diluted with ammonium hydroxide of the required concentration. The volume of the cuprammonium solution to be removed and replaced by an equal volume of ammonium hydroxide may be calculated by the formula:

$$V = \frac{(Cu_p - 15)(W_p - W_e)}{\rho Cu_p} \quad (2)$$

and the concentration of the ammonia solution to be added is:

$$C_{NH_3} = \frac{248 Cu_p - 51 (V_{H_2SO_4} \cdot N_{H_2SO_4} - V_{NaOH} \cdot N_{NaOH})}{Cu_p - 15}, \quad (3)$$

where

Cu_p = the number of grams of copper in 1 liter of the solution as prepared.

W_e = weight in grams of the flask filled with nitrogen.

W_p = weight in grams of the flask filled with the solution as prepared.

ρ = density of the solution in grams per ml. If the directions for preparing the solution are followed, this may be taken as 0.93, or the density of the solution adjusted to the proper concentration for use.

$N_{H_2SO_4}$ = normality of the standard sulfuric acid solution.

N_{NaOH} = normality of the standard sodium hydroxide solution.

V_{NaOH} = volume in milliliters of the standard sodium hydroxide required for the titration.

$V_{H_2SO_4}$ = volume in milliliters of the standard sulfuric acid used.

V = volume in milliliters of the prepared cuprammonium solution to be removed from the flask and replaced by an equal volume of ammonium hydroxide solution of concentration C_{NH_3} g of ammonia (NH_3) per liter.

The solution to be added is prepared from concentrated ammonium hydroxide (sp gr 0.88 or less). Five ml of the concentrated ammonia solution is analyzed for ammonia content in the same manner described for the titration of ammonia in the prepared cuprammonium solution. A measured volume, V_m , in milliliters equal to or greater than V (formula 2) is taken to adjust to the concentration C_{NH_3} (formula 3). The volume of water, V_{H_2O} , in milliliters to add to this volume is:

$$V_{H_2O} = \frac{3.4 V_m (T_{H_2SO_4} \cdot N_{H_2SO_4} - T_{NaOH} \cdot N_{NaOH} - V_m)}{C_{NH_3}} \quad (4)$$

where $T_{H_2SO_4}$ and T_{NaOH} are the number of milliliters of standard sulfuric acid and standard sodium hydroxide solutions, respectively, used in the titration. The calculated volume of water is added to the ammonia solution and well mixed in a stoppered bottle.

The volume of solution, V , is removed from the flask in the manner previously described and an equal volume of the ammonia solution prepared is added to that in the flask through opening 19 (fig. 1), care being taken to minimize the loss of ammonia by keeping the

solutions cold. The contents of the flask are well mixed by shaking and permitted to stand, preferably overnight, to permit any powdered copper which may possibly be present to settle. The solution is then transferred to the flask 1 (fig. 2).

Figure 2 is a diagram of equipment designed for storing the supply of cuprammonium solution in an accessible manner. It consists of the 12-liter Pyrex flask, 1, in the cold chamber of a refrigerator, 2, and the Kipp's generator, 3, with the connections shown. A copper tank, 4, in which the flask containing the solution is fastened, may be packed with ice as a precaution against failure of the mechanical refrigeration.

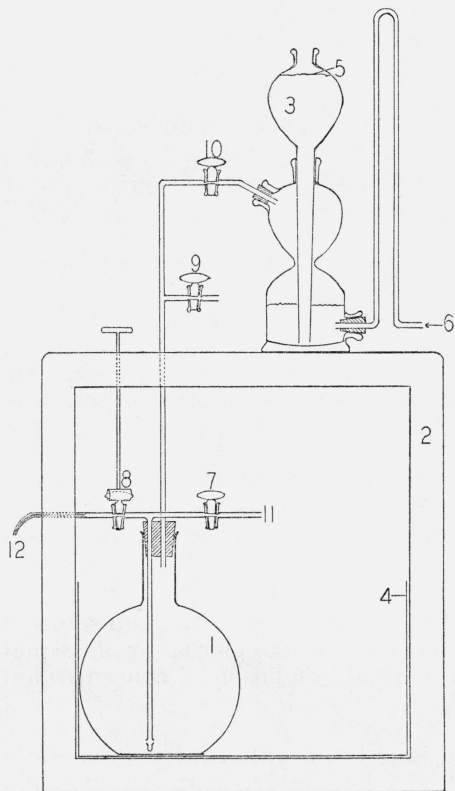


FIGURE 2.—Refrigerator for storing and delivering cuprammonium solution.

1, 12-liter Pyrex flask; 2, refrigerator wall; 3, Kipp's generator; 4, copper tank; 5, level of liquid in charged Kipp's generator; 6, inlet for nitrogen; 7, stopcock for filling; 8, stopcock for tapping; 9, stopcock for releasing pressure in flask when filling; 10, stopcock for controlling flow of nitrogen; and 11, filling tube.

to position 5, when the flow is stopped. To transfer the solution from flask 18, figure 1, to flask 1, figure 2, the tubes 11, figure 2, and 19, figure 1, are connected by means of a rubber tube which is as short as practicable. The clamp at 19 and stopcocks 7 and 9 are opened and the solution is forced into the receiving flask by admitting nitrogen under slight pressure into the first flask through the opening at 20.

¹³ Prepared by dissolving 15 g of pyrogallol in 5 to 10 ml of warm water, which is then added to 100 ml of a solution of potassium hydroxide saturated at room temperature.

After the solution has been transferred, stopcocks 7 and 9 are closed. Stopcocks 10 and 8 are opened to remove the solution as needed through the capillary tube 12, which extends through the wall of the refrigerator. Stopcock 8 is fitted with an extension as shown.

After the solution has been adjusted for concentration, it is analyzed once more for ammonia and copper in the manner previously described. The ammonia content of the cuprammonium solution in grams of ammonia per liter is given by the formula

$$3.4 (V_{\text{H}_2\text{SO}_4} \cdot N_{\text{H}_2\text{SO}_4} - V_{\text{NaOH}} \cdot N_{\text{NaOH}} - 0.157 \text{ Cu}_p) \quad (5)$$

with the symbols used as in the previous formulas.

In addition to the determination of copper and ammonia, the solution is analyzed for nitrogen in the form of nitrates and nitrites¹⁴ with a nitrometer.

If this nitrogen calculated as nitrous acid is more than 0.5 g, or the concentration of ammonia (NH₃) other than 240 ± 5 g, or the copper concentration other than 15 ± 0.1 g per liter of solution, the solution is discarded, or adjusted to the proper concentration, if practicable.

Solutions prepared and stored in the manner described can readily be duplicated and will not change measurably over considerable time. Table 1 gives results of analyses made of a 12-liter lot of solution when first placed in the refrigerator and after approximately 11 months of storage, during which time about 9 liters of the solution was used for making fluidity measurements.

The results of analyses of a second solution prepared to replenish the laboratory supply are also given in table 1, and illustrate the degree of duplicability attainable with ordinary care in the preparation of standard cuprammonium solutions.

TABLE 1.—Results of analyses of standard cuprammonium solutions indicating the permanency on storage and duplicability of solutions prepared at different times by a standard procedure.

	Solution 1		Solution 2
	When first made	After 11 months' storage	When first made
Copper (g/liter).....	14.96	15.01	15.04
Ammonia (g/liter).....	239.8	238.4	240.9
Nitrous acid (g/liter) (nitrometer method).....	<0.5%	<0.5%	<0.5%

III. THE VISCOMETER AND ITS CONSTRUCTION

A viscometer for measuring the fluidity of cuprammonium dispersions of cellulose has been described by Clibbens and Geake. An adaptation of the viscometer with accessories is shown in figure 3. The chamber, A, of the viscometer is constructed from Pyrex tubing

¹⁴ Determination of nitrogen of nitrates (and nitrites) by means of the nitrometer. Standard Methods of Chemical Analysis, third edition, 1, 353, edited by Wilfred W. Scott (D. Van Nostrand Co., Inc., New York, N. Y., 1922).

of inside diameter 10 ± 0.25 mm. The capillary discharge tube, *B*, is also of Pyrex with an outside diameter of 6 ± 2 mm and an inside diameter of 0.88 ± 0.02 mm. The markings, M_1 and M_2 , on the outside of the wall of the body of the viscometer are spaced at the distances indicated in the figure with respect to the capillary opening.

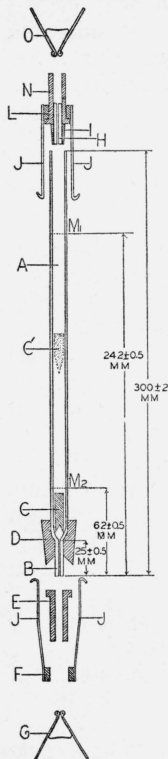


FIGURE 3.—Viscometer and accessories.

A, body of viscometer; B, capillary discharge tube, 0.88 ± 0.02 mm inside diameter; C, steel plunger; C', side view of plunger; D, rubber stopper; E and N, flanged rubber tubes; O and G, clips; H, glass capillary tube; J, rubber stopper; J, metal hooks to take rubber bands; F and L, metal collar; and M_1 and M_2 , calibration markings.

carborundum of about 150 mesh. During the grinding the inside of the capillary should be frequently flushed with water to prevent its becoming clogged. The markings M_1 and M_2 are placed by smoking the portion of the tube to be marked, in a gas flame, first marking

To construct the viscometer, glass tubing of the dimensions specified is chosen. All indicated dimensions of the viscometer, with the exception of the diameter of the capillary discharge tube, can be determined sufficiently closely by an ordinary scale graduated in millimeters. In practice several capillary tubes may be roughly measured by means of a micrometer and glass rod drawn to a taper, the end of which is slightly less than 0.8 mm. By noting the section of the taper having a diameter of approximately 0.88 mm found by measurement with the micrometer, an approximate measurement of the capillaries can be made by inserting the taper in their ends and noting the depth of insertion. A length of capillary tubing found roughly to have an inside diameter of 0.88 mm is well cleaned by drawing a mixture of nitric and sulfuric acids through the tube, rinsing it with water and drying it with a stream of clean dry air. A more accurate measure of the diameter is then made by drawing sufficient clean mercury into the capillary to fill it for about three-fourths of its length. The length of the mercury column is measured and the mercury transferred to a tared glass vessel and weighed. The diameter of the capillary is then found by calculation thus:

$$\text{diameter in mm} = 3.06 \sqrt{\frac{g}{h}}, \quad (6)$$

where g is the weight of mercury in grams, and h is the length of the mercury column in centimeters.

A length of capillary tube of the specified diameter is sealed¹⁵ to the large bore-tubing, working glass into the walls of the sealed portion to give sufficient strength to withstand the action of the steel plunger, shown at C and C' , which strikes this part of the tube when it is used in effecting dispersion of the cellulose. After sealing, the capillary and large tube forming the body of the viscometer are cut to be a little longer than the indicated dimensions, and the excess lengths of glass ground away on a metal plate with water and

¹⁵ H. P. Waran, *Elements of Glass-Blowing*, chap. 3, on joining tubes (G. Bell and Sons, Ltd., London, 1923).

the tube by a scratch through the carbon layer with the end of one leg of a dividing compass, while the other is set at the end of the capillary discharge tube with the dividers spread the required distance. The mark is then impressed in the glass with a diamond, tungsten-carbide pencil, or file, while the tube is slowly turned in a lathe chuck with the portion of the viscometer clamped in the chuck protected with rubber tape.

Accessories for the viscometer are also illustrated in figure 3. The rubber parts, *E*, *D*, *N*, and *I*, are molded from an uncured rubber compound and vulcanized, or buffed and carved into shape from rubber tubing and stoppers of appropriate size. Carving is facilitated by having the rubber and cutting tools wet with water. *H* is a short length of capillary tubing through which the air and excess liquid are discharged when filling the viscometer. A plunger, *C* and *C'*, made from 1/4-inch steel rod with one end wedge-shaped and notched, is provided to agitate the contents when the tubes are filled and rotated end over end. This plunger should weigh 5.6 ± 0.2 g and may be replaced by an equal volume of mercury (see footnote 10) when celluloses are to be tested, which are easily dispersed in the cuprammonium solution. Pinch clamps, *O* and *G*, are provided for closing the rubber fittings on the ends of the charged viscometer.

IV. CALIBRATION OF VISCOMETER

Viscometers for precise work require calibration, since it is impracticable to construct them sufficiently close to specified dimensions. The method of calibration described by Clibbens and Geake, or the graphical method of Higgins^{16 17 18 19} may be used.

The method of Clibbens and Geake consists in the determination of the instrumental constants *C* and *K*, by means of the equation

$$F = \frac{C}{\rho \left(t - \frac{K}{t} \right)}, \quad (7)$$

where *F* is the fluidity, in rhes, of a calibrating liquid of predetermined fluidity, *t* is the time, in seconds, of flow of the volume *V*, of liquid contained between the calibration marks *M*₁ and *M*₂, and ρ is the density, in grams per cubic centimeter, of the calibrating liquid. For the determination of *C* a liquid of low fluidity is chosen so that the kinetic energy of flow is sufficiently small to be neglected, for the degree of accuracy desired in the measurements. For this purpose Clibbens and Geake use a mixture of water and glycerol of density

¹⁶ W. F. Higgins, *On the methods and apparatus used in petroleum testing*. Nat. Phys. Lab. Collected Researches 11, part 2, Viscometry, 3 (1914).

¹⁷ Winslow H. Herschel, *Determination of absolute viscosity by short-tube viscometers*. Tech. Pap. BS 9, (1917) T100.

¹⁸ Winslow H. Herschel, *The standard Saybolt universal viscosimeter*. Proc. Am. Soc. Testing Materials 18, part 2, 366 (1918).

¹⁹ Eugene C. Bingham, *Recent progress in consistency measurement*. Am. Soc. Testing Materials Symposium on Consistency, New York, N. Y., June 29, 1937.

1.1681 and fluidity of 6.83 rhes at 20° C. The constant, C , is then calculated from eq 8, which follows from eq 7 when $K=0$.

$$C = F\rho t. \quad (8)$$

Two methods for finding K are also given. In the first method, the coefficient of the kinetic-energy correction, m , is taken as 1.12, the entire correction being $1.12 \sqrt{V}/(8\pi lt)$. The constant K of eq 7 is $(1.12V/(8\pi l))C$. In the second method, if t_w is the time of flow for water of fluidity F_w and C has been determined,

$$K = \frac{F_w \rho t_w^2 - C t_w}{F_w \rho}, \quad (9)$$

where ρ may be taken as unity.

In the Higgins method of calibration,

$$\eta = \rho \left(At - \frac{B}{t} \right), \quad (10)$$

where A and B are constants, B/t is the kinetic-energy correction, and by definition η is $1/F$, which is also the viscosity in poises. By comparing eq 7 and 10, it may be shown that $C=1/A$ and, provided K is accurately determined, $K=CB$.

Two or more calibrating liquids may be selected so that their fluidities cover the range of apparent fluidities of the cellulose dispersions to be measured. It is satisfactory to use three liquids, one of fluidity 3 to 5 rhes (viscosity 0.33 to 0.20 poise), another of 46 to 48 rhes (0.0217 to 0.0208 poise) and one of intermediate fluidity, 28 to 30 rhes (0.036 to 0.033 poise). From the experimental data a graph is prepared by plotting $\eta/\rho t$ against $1/t^2$. For viscometers constructed in accordance with the specifications given in section III, using calibrating liquids of the fluidities suggested above, the points representing each of the three calibrating liquids should locate a straight line. The instrumental constant, A , is the intercept of this line on the $\eta/\rho t$ axis (where $1/t^2=0$), and B is the slope of the line. The calibration graph, extended, did not pass through a point obtained for water at 20° C, for any one of the viscometers. Therefore, the relation $K=CB$ does not hold when water is used as one of the calibrating liquids.

Advantages of the Higgins method are that it does not necessitate the determination of V ; nor does it involve the dubious assumptions that the kinetic energy correction is negligible for the calibrating liquid of lowest fluidity used; that the coefficient of the kinetic-energy correction has a constant value of 1.12^{20 21 22} for capillaries with a trumpet-shaped entrance, and that, when water is used as a calibrating liquid, there is no danger that it may exhibit turbulence or possess properties which cause annoying flow characteristics. In general, it seems safer to use calibrating liquids which cover approximately the same range of fluidities as the solutions to be tested. It has also been found that the Higgins method is the more convenient of the two, both as regards

²⁰ E. C. Bingham, *Fluidity and Plasticity*, p. 20. (McGraw-Hill Book Co., New York, N. Y., 1922.)

²¹ William Riemann, III, *The value of the Hagenbach factor in the determination of viscosity by the efflux method*, *J. Am. Chem. Soc.* 50, 46 (1928).

²² L. W. Spooner and P. Serex, *A new feature in the calibration of a capillary-tube viscometer*, *Physics* 6, 162 (1935).

calibration, and in calculating F (equal to $1/\eta$) from eq 10 rather than from eq 7. Both methods were used in the present work, however, and the differences were never greater than 2 percent. The values shown in figure 6 were obtained by the Higgins method.

Care must be taken in handling the calibrating liquids not to contaminate them or permit change of temperature while making the measurements. *A*, in figure 5, illustrates a form of vessel suitable for the purpose. It is filled with the calibrating liquid through *B*, which is then closed with a small stopper and is placed in the constant-temperature bath illustrated in figures 4 and 5 to attain the proper temperature and supported in such a position that the delivery tube *C*, figure 5, is directly over the opening of the viscometer in position ready for measurements. The viscometer is filled by applying air pressure at *H*.

The time required for the meniscus of the liquid to travel from the top marking on the viscometer to the bottom one is recorded. From this time of flow, the viscosity of the liquid, the values $1/t^2$ and ηpt previously referred to are calculated.

A thermometer, 1 (fig. 4), with a scale marked in tenths of a degree is provided near the chamber, 2, in which the viscometer, 3, containing the fluid to be measured is shown in position. The chamber, 2, is made from large-bore glass tubing (about 4.5 mm inside diameter), with the lower end consisting of a short section of smaller glass tubing (2.2 mm inside diameter) sealed in the larger and communicating with the exterior of the bath through a large rubber stopper, 4. The upper end of the smaller tube is kept closed when the viscometer is in place by the rubber stopper, *D*, and the chamber is completely filled with water of the proper temperature from the reservoir, 5, by lifting the long-handled stopper, 7. Observations on the position of the meniscus of the liquid flowing from the viscometer, and thermometer readings are made through the glass window, 8. When the viscometer is to be removed, the chamber, 2, is emptied by opening the pinch clamp, 9, with the upper end of tube, 6, closed.

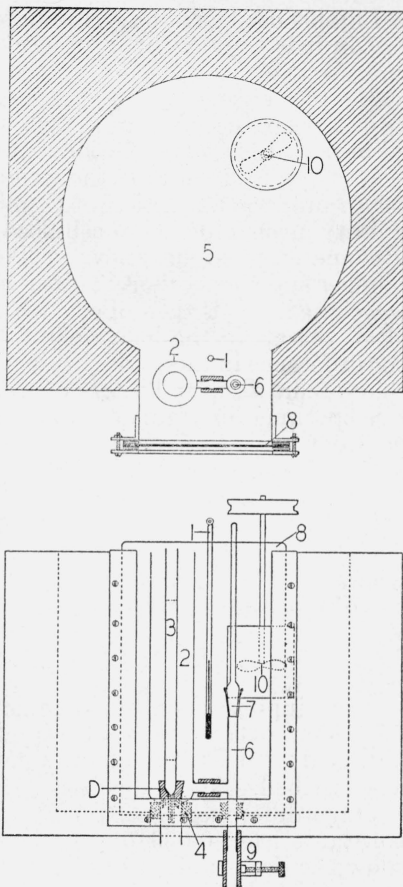


FIGURE 4.—Water bath for controlling temperature while making measurements

1, thermometer; 2, glass-walled water jacket for viscometer; 3, viscometer; 4, large rubber stopper; 5, water reservoir; 6, tube for filling water jacket around viscometer; 7, long-handled stopper; 8, glass window; 9, rubber tube and pinch clamp; 10, stirrer; and *D*, rubber stopper supporting viscometer.

When making fluidity measurements at or near room temperature, the temperature of the water in the reservoir and around the viscometer in place for making observations, can readily be kept constant within $\pm 0.05^\circ \text{C}$ by adding warm or cold water as needed. Sudden changes in temperature are avoided by using a rather large volume of water in the reservoir which is well insulated and provided with a circulating device, 10.

Liquids used as fluidity standards may change on storage. For this reason it is convenient in practice to calibrate a viscometer carefully and use it exclusively for the accurate redetermination of the fluidity of the reference liquid at the time it is to be used for calibration purposes. Samples of oil of known viscosity for calibration purposes can be obtained from the National Bureau of Standards.

In order to determine the weight of cellulose to place in a viscometer to produce a solution of definite and chosen concentration for the fluidity measurements of cellulose dispersions, the total capacity of the viscometer must be known. The empty viscometer with the steel plunger and connections in place as shown in the photograph in figure 3, is weighed. It is then filled with water in such a manner as to displace all of the air in the instrument. It is wiped dry and again weighed; the difference in these weights in grams at room temperature is taken as the volume L , in milliliters of the viscometer. The amount of cellulose specimen in grams required for a chosen concentration in percent on a dry basis is given by the relation

$$\frac{0.93 LP}{100 - M'} \quad (11)$$

where P is the percentage concentration chosen, and M is the percentage of moisture in the cellulose.

V. DUPLICABILITY OF VISCOMETERS

The duplicability of viscometers when made by a laboratory technician of average ability in glass working is illustrated by results obtained with a group of viscometers which were made and calibrated as described. The capacities differed from 19.20 to 20.66 ml with an average difference from the mean value of 1.3 percent and of the A constants from 0.000452 to 0.000593. Figure 6 presents data which show the duplicability of measurements obtainable with one viscometer, or with different viscometers which exhibit these differences in the A constants. The B constants differed from 0.200 to 0.220. The effect of the kinetic-energy correction, B/t on F is small when liquids of low fluidity are measured but amounts to about 14 percent of the value for F for liquids of fluidity of 45 rhes, which is the upper limit of the range of fluidities in which the viscometers are recommended for use.

VI. PROCEDURE FOR THE DETERMINATION OF THE FLUIDITY OF CELLULOSE DISPERSIONS

When the fluidities of cellulose dispersions are to be determined the viscometer serves as the container for the dispersion of the specimen in the cuprammonium solution.

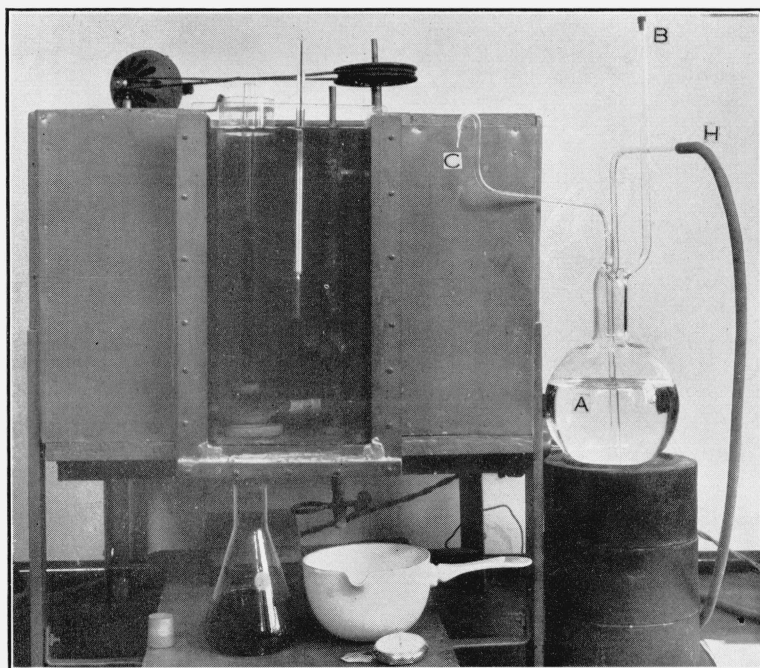


FIGURE 5.—*Constant-temperature bath for controlling the temperature while making flow measurements.*

Special container with calibrating liquid shown at A.

To charge the viscometer with cellulose and cuprammonium solution, the capillary end is closed by means of the clip, collar, and rubber connections *G*, *F*, and *E*, figure 3. The wedge, *C*, is placed in the tube and the tube is nearly half filled with cuprammonium solution. About one-fourth of this solution is permitted to flow out of the capillary by temporarily releasing the clip. Any remaining air which may be entrapped at the lower end of the capillary is displaced by pressing the rubber connection just above the clip several times by hand. The calculated amount of cellulose for producing a solution containing 0.5 percent of cotton or 2 percent of rayon, is introduced into the instrument, which is nearly filled with cuprammonium solution, and the specimen carefully stirred with a fine glass rod to dislodge any entrapped air. The viscometer is completely filled with cuprammonium solution and closed by means of the capillary tube, rubber stopper, flanged rubber tube, and collar, *H*, *J*, *N*, and *L*. In so doing, cuprammonium solution will be forced through the capillary and will partly fill the flanged rubber tube. To insure the displacement of all of the air, the rubber tube is completely filled with solution and then closed with the clip. The parts are kept in place on the ends of the viscometer by rubber bands on the hooks provided for the purpose. The viscometer is then placed on a suitable device, protected from light, and rotated end over end at the rate of about 4 rpm until the specimen is completely dispersed. Rayons, bleached cotton, and degraded celluloses may be completely dispersed in about 4 hours. Cotton celluloses of fluidities less than 3, in a 0.5-percent dispersion, often require a longer time. An effective procedure for such specimens is to rotate them from noon of one day until noon of the next, occasionally stopping the rotation and turning the viscometers about their long axes through an arc of approximately 30° every half hour during the daytime. This is to permit the wedge to slide down the sides of the tubes in different paths and remove the swollen cellulose which tends to adhere to the walls. A device now in use in this laboratory which simultaneously and automatically effects both motions of the viscometer is more convenient and reliable.

After dispersion is complete, the viscometer is immersed in the water in the reservoir (5, fig. 4) and permitted to come to the desired temperature. It is then placed in position, 3, surrounded by water in the jacketed chamber, 2, and the rate of flow determined. The fluidity, η , of the solution is calculated by means of eq 10.

VII. DUPLICABILITY OF FLUIDITY MEASUREMENTS

Dispersions of cellulose that has not been degraded by the action of light, heat, chemicals, or other deteriorative influences have relatively low fluidities, and dispersions of modified celluloses higher fluidities. The first differ most from simple liquids and in consequence the results of fluidity measurements of these are likely to be affected more by differences in viscometers. In order to show the duplicability of the measurements, the fluidities of cotton cellulose in 0.5- and 0.25-percent dispersions and of rayon in 1-percent dispersion were determined. Nine of the viscometers of the group referred to in section V, including the one with the lowest and the one with the highest value for *A* were used. Duplicate measurements were made of the fluidity of the

material in each of the viscometers at 21° C. The results are presented in figure 6.

The average difference in the duplicate results obtained with each viscometer for the 1-percent concentration of rayon is 0.18; for the 0.25-percent cotton, 0.31; and for the 0.5-percent cotton, 0.09 rhes. The average deviations from the mean value for all 18 determinations

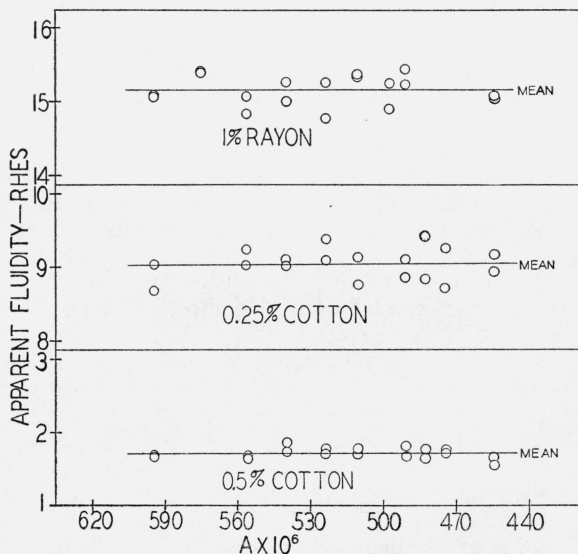


FIGURE 6.—Data showing the duplicability of results of measurements with the same viscometer, and with viscometers of the same type but differing in their characteristic constant, A .

The results for two concentrations of cotton dispersions and one of rayon are given. The straight line represents the mean fluidity of each group.

of the fluidity of the rayon, 0.25-percent cotton, and 0.5-percent cotton are 0.17, 0.18, and 0.05 rhes, respectively. It is concluded, therefore, that the viscometers described are sufficiently alike for ordinary purposes.

Acknowledgment is made of the invaluable suggestions of W. H. Herschel on the calibration of viscometers.

WASHINGTON, December 12, 1938.