

A STUDY OF CUPRAMMONIUM HYDROXIDE
AND ITS APPLICATION TO THE CELLULOSE
VISCOSITY TEST
OF THE PULP AND PAPER INDUSTRY

by

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INTRODUCTION

Schweizer (39), in 1857, published the first paper dealing with the discovery that an ammoniacal solution of cupric oxide would dissolve cellulose. This solution is commonly known in the literature as Schweitzer's reagent, Schweizer's name being incorrectly spelled (38). E. A. Parnell, in "Life and Labors of John Mercer", London, (1886), p. 214, states: "Mercer appears to have been the first to notice the remarkable action which the ammoniacal solution of cupric oxide exerts on cotton fibre" (38).

The solubility of cellulose in cuprammonium was first utilized by the Bereinigte Glanzstoff-Fabriken A. G. of Elberfeld, for the production of rayon (28). This was one of the earliest methods of producing rayon and cellulose films. There are a number of cuprammonium mills in operation in Europe and at least one mill in the United States (35).

The value of this so-called solvent as a test for cellulose quality was not discovered until the experiments of Ost (32) in 1911, who was the first to use viscosity

measurements in connection with cellulose. By availing himself of the previous work of Gibson and Jacobs (14), Gibson, Spencer, and McCall (15), and Puntner (33), Joyner (21) in 1922 for the first time demonstrated the utility of viscosity measurements for characterizing a sample of cellulose.

Clibbens and Geake (6) produced a simplified method of viscosity measurement in 1928 suitable for industrial use which was adopted as a standard by the British Cotton Industry Research Committee of the Department of Scientific and Industrial Research (28). The work originated in connection with cellulose intended for the manufacture of explosives. The viscosity of a solution of cellulose in cuprammonium is extensively used as a routine test in textile laboratories for estimating the effect of technical process on the strength of cotton goods.

In 1929, the Cellulose Section of the American Chemical Society published their description of recommendations for the determination of the viscosity of cellulose in cuprammonium (4).

The first application of the viscosity test as a technical test in the wood-pulp industry was proposed by Brauns (2) in 1930. In 1932, the T. A. P. P. I. tentative standard for the determination of the viscosities of pulp was published. Since then, it has been revised and cor-

rected several times. The main use of the viscosity measurement in the pulp and paper industry is to determine the change in fiber structure, and the amount of degradation that takes place in the different processes to bring about this change.

Many workers in the mills making viscosity measurements have reported great difficulty in the preparation and maintenance of stable cuprammonium solutions, especially the preparation of solutions containing more than 30 grams per liter of copper, such as are used in falling sphere viscosity measurements.

With this difficulty in mind, a study was undertaken in order to determine possible means of improving viscosity testing procedure particularly in regard to the preparation of the solution.

PREPARATION OF CUPRAMMONIUM HYDROXIDE

There have been several methods proposed for the preparation of cuprammonium hydroxide solution, although, in general, the methods of preparation involve the production of cupric oxide and the subsequent solution of this in concentrated ammonium hydroxide. Some of these have not been satisfactory due to the large amount of nitrite which is formed along with the cuprammonium. According to Ishii (19), the nitrite forms a double salt with the copper and this salt will not dissolve cellulose. Another disadvantage of most of the methods is the time required to make the solution.

The cuprammonium solution used by Ost (32) was made by treating a solution containing 5.9 grams of copper sulfate with ammonium hydroxide. The basic copper sulfate thus obtained was then dissolved in ammonium hydroxide (density 0.900) to form one liter of solution.

Gibson, Spencer and McCall (15) on examining Ost's method found that the solution contained tetrammine copper sulfate and gave varying results. They prepared pure cupric oxide from copper sulfate and dissolved it in concentrated ammonium hydroxide but reported great difficulty in obtaining stable solutions.

Joyner (21) prepared the reagent by bubbling air through a mixture of copper turnings in concentrated ammonium hydroxide which contained a small amount of sucrose to hasten the solution of the copper. He stated that preparation of solutions containing as high as 30 g. per liter of copper could be obtained by bubbling air for a long period of time.

Joyner also found it necessary to cool the solution with ice during the preparation to prevent excessive formation of nitrite and loss of ammonia. The cooling has a great effect on the loss of ammonia since at 0° C. the solubility of ammonia is about twice that at 20° C.

Several modifications of Joyner's method have been suggested by different investigators. Oxygen has been substituted for air thus making possible more rapid solution, but this method proved worthless due to the fact that solutions of high nitrite content are formed which interfere with viscosity measurements and stability of the solution.

Scheller (37) reports that grape sugar stabilizes cuprammonium solutions very well and used it in his research on cellulose-cuprammonium solutions. Glycerol, mannitol, and other poly alcohols have been used to stabilize cuprammonium solutions (43).

Farrow and Neale (11) report an electrolysis method for the preparation of cuprammonium by the electrolysis of

pure electrolytic copper in concentrated ammonia. The method requires over twenty four hours and involves low temperatures and nitrite formation of over two grams per liter.

Rich (35) and Mease (29) have developed methods for the preparation of cuprammonium hydroxide which consist of passing air through a solution of ammonium hydroxide containing copper turnings in a refrigerator. They report very good results.

The T. A. P. P. I., tentative standard, recommends the following method of preparation:

"Freshly prepare the cuprammonium solution at least every two months as follows: Place clean copper turnings in a glass tube 24 inches long and 4 inches in diameter, surrounded with ice. (The turnings must be previously cleaned by washing in dilute HCl). Pour in concentrated ammonium hydroxide (26-28 per cent) containing 2 grams of cane sugar per liter until the tube is nearly full. Bubble air, which is passed through a wash-bottle containing concentrated ammonium hydroxide, through the solution for several hours, until the desired copper concentration is reached. Analyze the solution for copper and ammonia and make the proper adjustments, so that the final solution will contain $15.0 \pm .2$ g. of copper and 200 ± 10 g. of ammonia per liter."

Apparatus

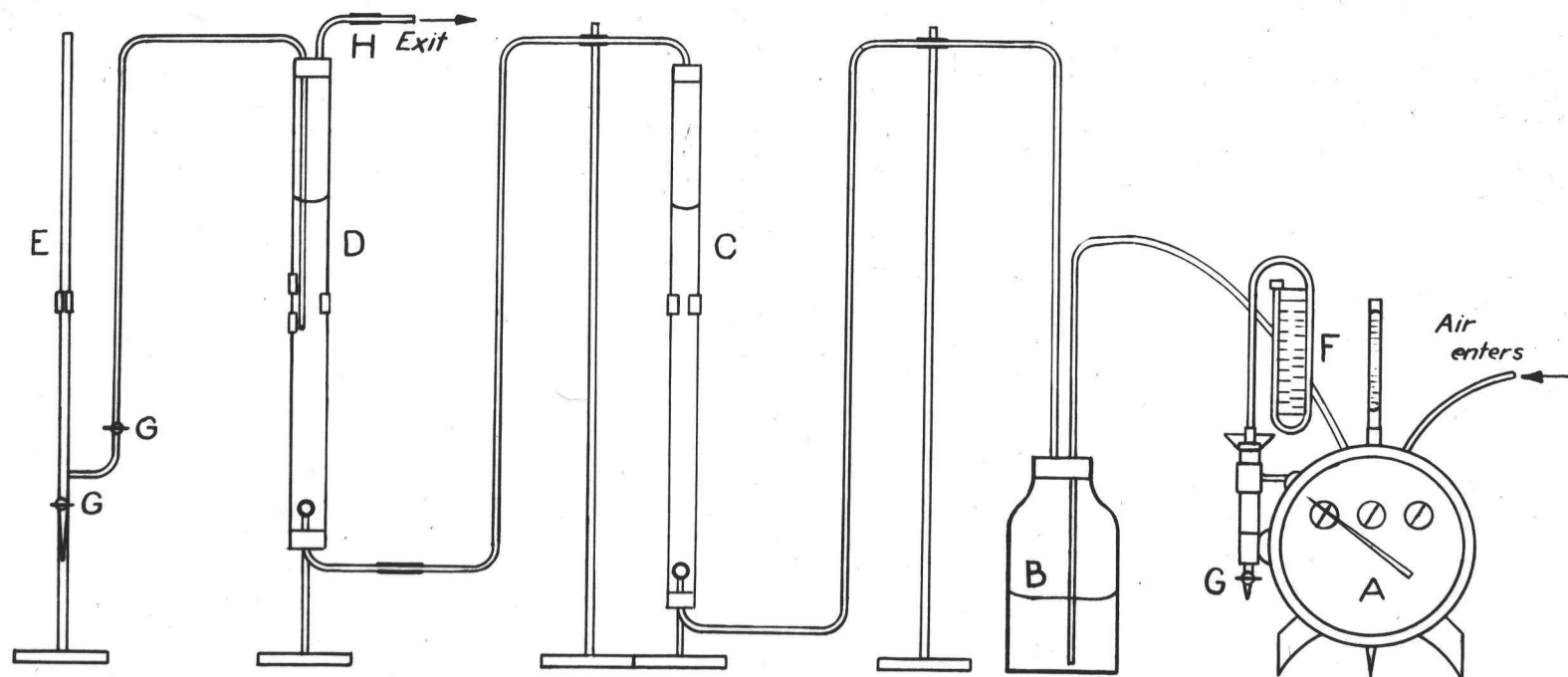
In the laboratory, it was our desire to construct an apparatus for the preparation of cuprammonium hydroxide at room temperatures and be able to obtain solutions of high copper and ammonia content, yet keeping the nitrite content of the solution as low as possible. The final working design of our cuprammonium preparation apparatus is shown diagrammatically in Figure 1 and consists of the following:

- A. Sargent Wet Test Meter (Precision Scientific Co., Chicago, Illinois).
- B. Sodium hydroxide container consisting of a two and one-half liter bottle fitted with a rubber stopper.
- C. Ammonia tower. This consists of a glass tube, 1 inch in diameter and 28 inches long fitted with rubber stoppers at both ends. At the entrance into the tower, there is an air disperser to afford adequate dispersion of air through the ammonium hydroxide.
- D. Reaction tower. This is a 2 inch copper pipe, 24 inches in length fitted at both ends with rubber stoppers. An air disperser is also placed in the bottom of the reaction tower to cause adequate air dispersion.
- E. Burette for sampling.

Fig. 1.
*DIAGRAM OF APPARATUS FOR PREPARATION OF CUPRAMMONIUM
 HYDROXIDE*

A Wet-test meter
 B 2½ liter bottle
 C Ammonium tower
 D Cuprammonium tower

E Burette
 F Mannometer
 G Stopcocks
 H Clamps



Materials

1. Copper. In these experiments, copper turnings were used.
2. Ammonium hydroxide. Twenty eight per cent ammonium hydroxide was used in all of the experiments.
3. Air. The source of air was from a compressed air line fitted with a needle valve to facilitate control of the air supply.
4. Sodium hydroxide (approximately 10%).
5. Stabilizing agents. Chemically pure dextrose, sucrose, and ammonium citrate were used. Ordinary table sugar was also used.

Experimental Procedure

In preparing a cuprammonium solution, 45 g. of copper turnings were weighed out. They were first cleaned with benzene to remove any grease, and then washed with 3 N hydrochloric acid to remove any metal oxide. The copper turnings were then thoroughly washed with water and placed in the reaction chamber.

Five hundred ml. of cold concentrated ammonium hydroxide were placed in the ammonium hydroxide tower, and 850 ml. of cold concentrated ammonium hydroxide containing the desired amount of stabilizing agent were placed in the reaction chamber.

Air was then passed through the wet test meter, the desired amount of air being controlled by the needle valve. The air leaves the wet test meter and bubbles down through a solution of sodium hydroxide. From here, it passes over to the ammonium hydroxide tower where the air entering is dispersed by an air disperser fitted at the bottom of the tower. Air, saturated with ammonia, then passes up through the reaction chamber where another air disperser controls the dispersion of the air through the solution. Air, stripped of oxygen is then passed out into the hood. Tube 1 goes down into the liquid and is connected to a burette. When samples were desired, by pinching off the outlet tube, the solution was forced over into the burette. Before each sampling, the tube was blown out so a representative sample of cuprammonium could be obtained.

The following analytical tests were used:

Copper: A 5 ml. sample of the cuprammonium solution was pipetted into a 250 ml. Erlenmeyer flask, 20 ml. of 6N sulfuric acid were added and the solution cooled under the tap. Ten ml. of 30% potassium iodide were added, and the solution titrated immediately to a colorless end point with 0.1 N sodium thiosulfate. Starch indicator was added near the end point.

$$\text{g/l. of Cu} = N(\text{Na}_2\text{S}_2\text{O}_3) \times 12.7 \times \text{ml.} (\text{Na}_2\text{S}_2\text{O}_3)$$

Nitrite: A 5 ml. sample of the cuprammonium was pipetted into a 25 ml. volumetric flask and made up to mark by dilution with distilled water. The cuprammonium was then used to titrate 2 ml. of 0.05 N potassium permanganate in 10 ml. of 6 N sulfuric acid. The titration was run to a colorless end point at 50° C.

$$\text{g/l of HNO}_2 = \frac{N(\text{KMnO}_4) \times 235}{\text{c.c. (Cuprammonium)}}$$

Ammonia: 2 ml. of the cuprammonium solution were pipetted into 50 ml. of 1 N sulfuric acid keeping the tip of the pipette beneath the surface of the liquid. The excess acid was titrated with 1 N Sodium hydroxide using methyl red indicator.

$\text{g/l. of NH}_3 = 50 - \text{ml. (NaOH)} \times (8.5 - 0.536 C)$,
where C = copper concentration in grams per liter. The correction factor (0.536 C) is made for the alkalinity of the copper hydroxide.

Results and Discussion

In the arrangement of the apparatus, it was found necessary to substitute the ammonia tower in place of a two and one-half liter bottle due to incomplete saturation of air entering the reaction tower. This change reduced the volume loss in the reaction tower from 32% to 14% and made it possible to maintain high ammonia concentration.

In order to determine the desired air speed to be used in our equipment, a series of runs were carried out

on the preparation of cuprammonium using glucose as the stabilizing agent. The results of this work are expressed graphically in graphs I, II, III, and IV. From the results obtained, the optimum air speed was set at between 4 and 5 cubic feet of air per hour for the preparation of cuprammonium solutions containing 30 g of copper, 165 g of ammonia, and less than 1.5 g of nitrite per liter of solution.

The stability of solutions prepared with glucose as the stabilizing agent proved to be discouraging, especially in copper concentration above 30 g per liter even when kept in the refrigerator at a temperature of below 5° C. After a week or less, cuprous oxide precipitation could be observed on the bottom of the container. This was probably due to the action of glucose which is a reducing sugar. The fact that reducing sugars cause reduction of alkaline cupric solutions is the basis of several biochemical tests for reducing sugars.

Both chemically pure and commercial grade sucrose were used as stabilizing agents in preparation of the solution. Solutions containing 30 g of copper per liter using chemically pure sucrose were maintained in a stable condition for a month, but solution containing 40 g of copper per liter showed reducing action and signs of decomposition in a few days. The use of commercial sucrose in the prepa-

ration of solutions of 30 g per liter of copper gave varying results and were difficult to maintain in a stable state. This is undoubtedly due to impurities in the sucrose. Results of the preparation are given in Table I.

TABLE I
(Sucrose-12g/liter)

Time (minutes)	Copper g/liter		Ammonia g/liter		Nitrite g/liter	
	1	2	1	2	1	2
0	0	0	316.20	----	---	---
30	12.8	11.32	296.95	230.93	---	---
60	18.8	17.10	281.10	219.83	---	0.950
90	25.0	24.80	270.60	198.40	---	1.396
120	29.78	31.50	261.05	175.60	1.104	1.710
150	34.30	36.90	254.20	164.70	1.292	1.870
180	38.15	40.25	240.20	149.00	1.396	2.460
210	41.60	---	235.25	----	1.960	---
240	46.10	---	225.30	----	2.760	---

1 = 4.3 cu. ft. air/hr., 2 = 4.86 cu. ft. air/hr.

The results on the preparation were better than heretofore reported in the literature, but the darkening of the solutions using sucrose and glucose and the care demanded in maintenance of stable solutions demonstrated the desira-

bility of looking for a new stabilizing agent.

The use of sugars as stabilizing agents for this solution was also questioned, as the reaction of sugars in alkaline medium has long been a problem of intensive investigation. Gillman (16) says, "The simple effect of alkali on a sugar is the catalysis of mutarotation, the next is enol formation and epimerization, while more deep seated changes are those of migration of the double bond and cleavage into smaller fragments".

Sodium citrate used in Benedict's solution (1), a biochemical solution used for the detection of reducing sugars, showed promise as a desirable stabilizing agent.

Cuprammonium hydroxide was then prepared using ammonium citrate as the stabilizing agent instead of sodium citrate as a foreign ion would have an effect on viscosity measurements. Results of the preparation of the solution using citrate as the stabilizing agent are given in Table II.

TABLE II
(Citrate-15g/liter)

Time (minutes)	Copper in g/liter		Ammonia in g/liter		Nitrite in g/liter	
	1	2	1	2	1	2
0	0	0	----	----	---	----
30	26.40	20.35	215.65	270.15	---	----
60	35.90	30.90	200.21	244.05	0.606	----
90	41.80	39.0	187.60	----	0.686	0.704
120	49.60	48.7	172.40	230.10	0.980	----
135		51.7		208.25		1.190

The relative stability of cuprammonium solutions prepared using ammonium citrate and sucrose was then studied.

Solutions stabilized by sucrose containing 15 g and 30 g of copper per liter were kept in the refrigerator in dark bottles for a period of thirty days and showed no signs of cuprous oxide precipitation, but showed slight darkening of the solution even when kept in dark colored bottles. Sucrose stabilized solutions left at room temperatures in the presence of light showed darkening overnight, and signs of degradation in the 15 g per liter solution after 28 days and in the 30 g per liter solution in three days. Darkening of the solution is of extreme disadvantage in viscosity determinations using the falling

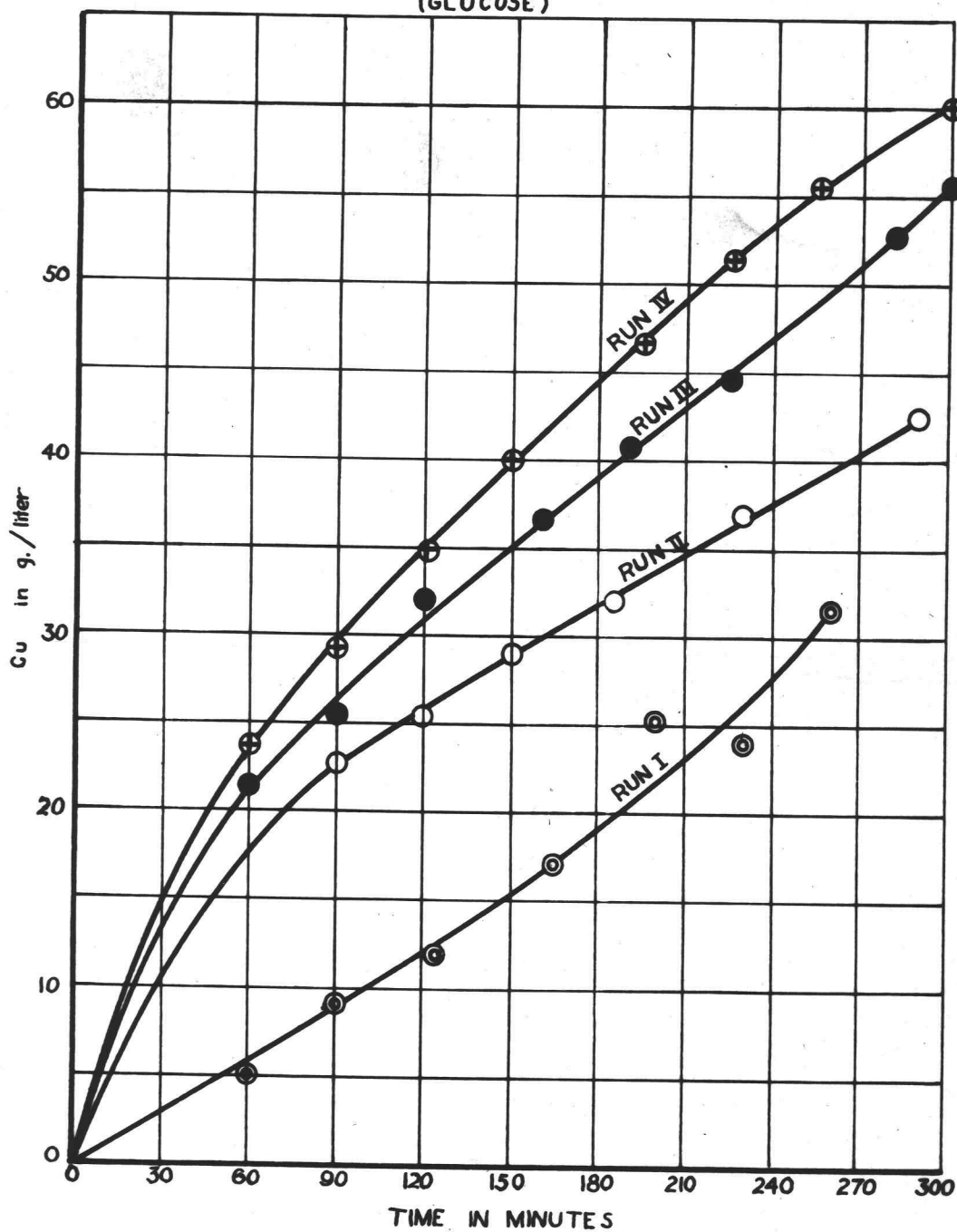
ball technique as the solutions become so dark that it is impossible to see the ball falling through the solution.

Ammonium citrate stabilized solutions containing 15 g and 30 g per liter of copper did not show signs of degradation or darkening even when left in light colored bottles at room temperature for a period of thirty days.

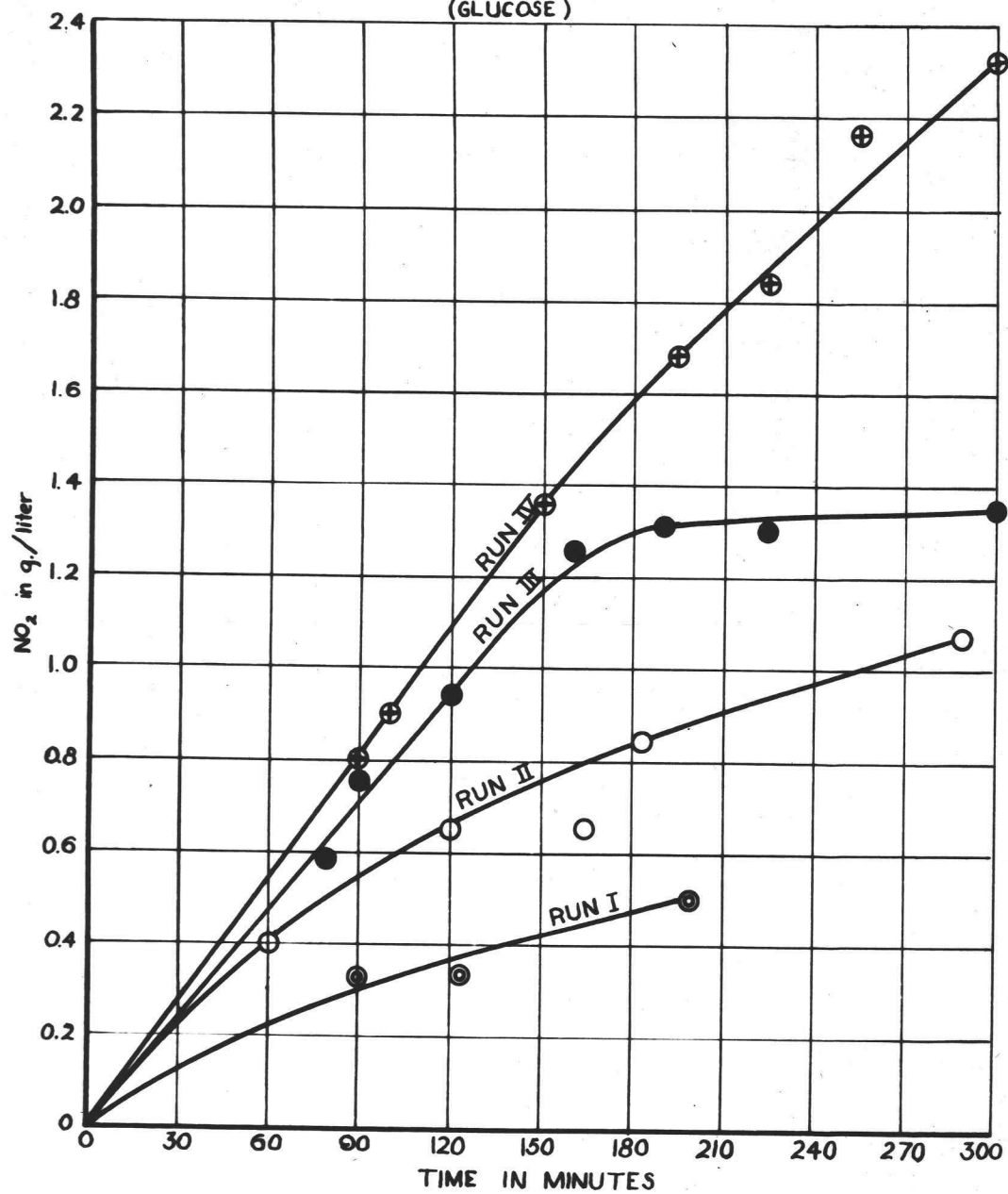
A rise in the nitrite content of the solutions at room temperature in the presence of light was detected with the use of both the citrate and sucrose as stabilizing agents, whereas there was no rise when the solutions were kept in the refrigerator at temperatures below 5° C.

The solutions of cuprammonium should be filtered through asbestos or glass wool before storage and standardizing if stable solutions are desired. The solutions in earlier work were not filtered, and a reduction of the solutions occurred within a few days. This is probably due to the presence of metallic copper which acts as a catalyst in the alkaline solution causing degradation of the stabilizing agent.

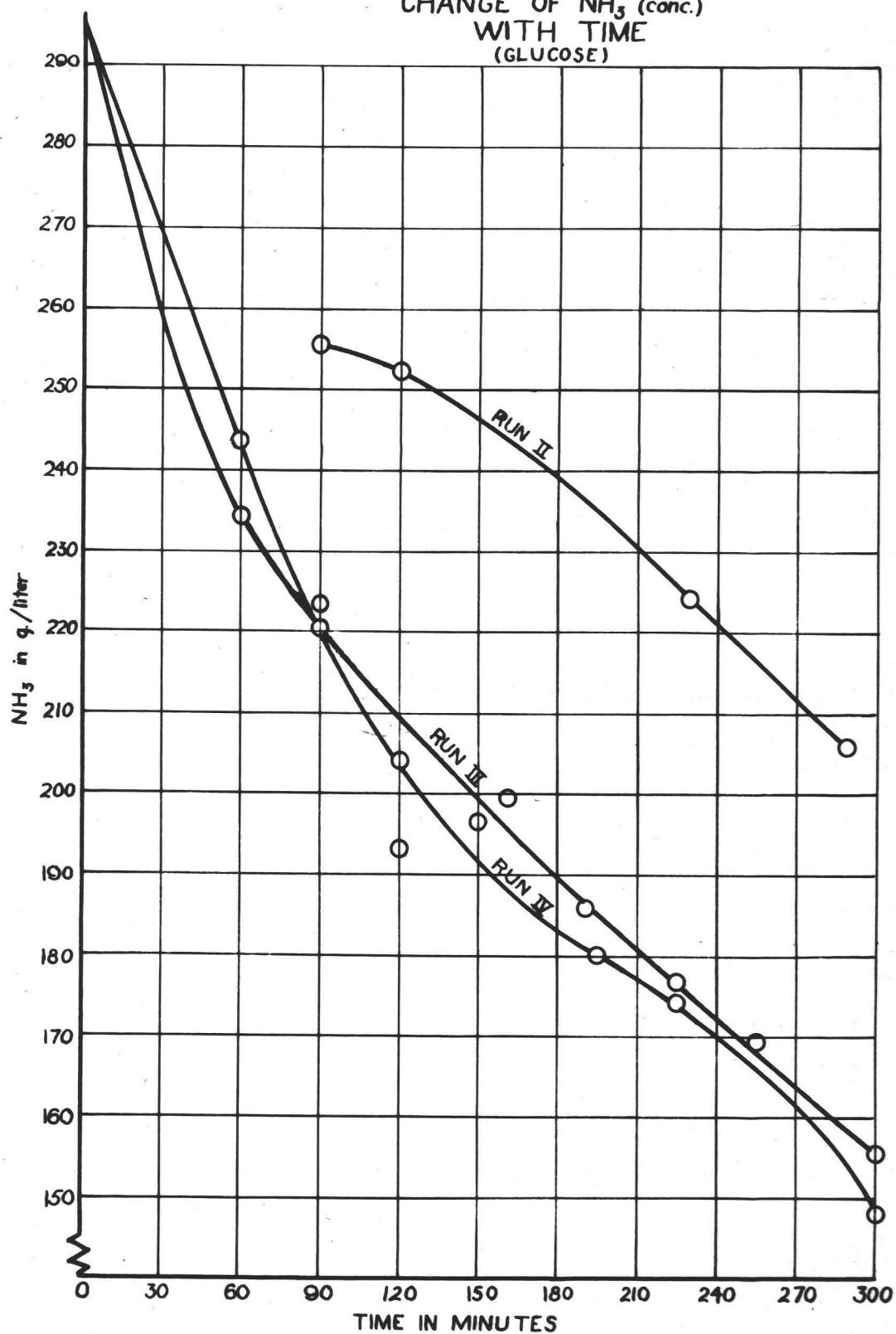
Graph I
CHANGE OF CU.
WITH TIME
(GLUCOSE)



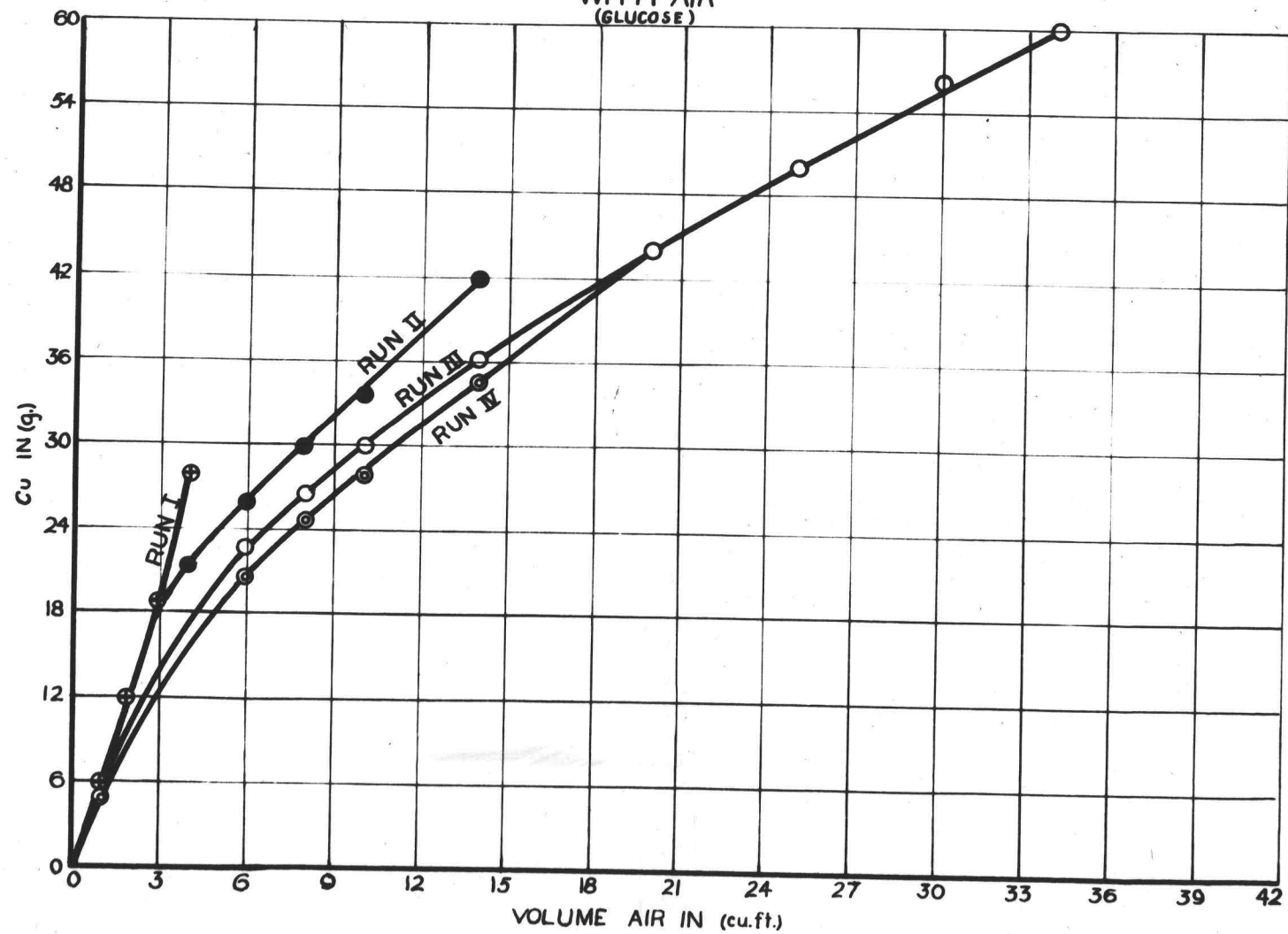
Graph II
CHANGE OF NO_2 (conc.)
WITH TIME
(GLUCOSE)



Graph III
CHANGE OF NH_3 (conc.)
WITH TIME
(GLUCOSE)



Graph IV
CHANGE OF C_u
WITH AIR
(GLUCOSE)



THEORY OF SOLVENT ACTION OF CUPRAMMONIUM HYDROXIDE ON CELLULOSE

Cuprammonium hydroxide is not a true solvent for cellulose. While it is often called a solution, the result of the addition of cellulose to cuprammonium hydroxide is a dispersion of colloidal particles of the cellulose which shows the Tyndall phenomenon, and according to Sisson (41) the particles show Brownian movement, possess a negative charge and are flocculated by electrolysis.

"Explanation of the nature of the solutions has been based upon two theories of cellulose fiber structure. One of these is the macromolecular or continuous theory, and the other is the micellar or discontinuous theory." (12) Staudinger (42) developed the macromolecular theory on the basis of viscosity measurements. The colloidal behavior of the solutions in this theory depends upon the length and form of macromolecules.

The micellar theory of cellulose is based upon the fact that cellulose particles are formed by union, or bundling of many molecules of the elementary cellulose substance. Lieser (27) states that qualitative examination of cuprammonium solutions of cellulose with an ultramicroscope reveals the presence of apparently unchanged cellulose particles designating micellar solutions.

The two theories of cellulose structure, however, are only contradictory in regard to the state of the colloidal particles since it is thought that the micelles are composed of macromolecules.

Attempts to account for the specific action of cuprammonium on cellulose have been made by many investigators. Traube (43) formulated a theory of solvent action along chemical lines. Hess and Messmer (12) concluded that when cellulose is dissolved in "cuprammonium", a complex copper cellulose ion results, which forms with the cuprammonium cation, the salt.

The hypothesis was based mainly on measurements of rotary power, but Neale (30) pointed out that the solutions belong to the class of colloidal electrolytes, typified by soap solutions. According to this theory, the strong base cuprammonium hydroxide, which is only stable when the quantity of ammonia is greatly in excess of that demanded by the formula, forms with cellulose, which thus behaves as a weak acid, a soluble basic salt of which the cation is crystalloidal and the anion, colloidal. Cellulose neutralizes the cuprammonium to the extent of using completely the hydroxyl arising from the first dissociation of the substance; further action is presumably inhibited on account of the weaker dissociation of the base with respect to its second hydroxyl and by the impossibility of

the existence of the soluble cellulose complex in any but a highly alkaline medium.

The saturation point of the cuprammonium solutions of cellulose as reported by Compton (7) is 4.5% cellulose. At this concentration, a definite equilibrium is established between the dispersed and the undispersed cellulose. Connerada (8) states that the solubility of cellulose in cuprammonium solution is dependent on only the copper concentration provided there is sufficient ammonia present. He also states that the ability of the cuprammonium solution to dissolve cellulose is independent of the viscosity of the solution. Jolley (20) reports that for a constant copper concentration an increase in the ammonia concentration increases the solvent activity of the cuprammonium solution.

THEORY OF VISCOSITY MEASUREMENTS ON CELLULOSE

The exact cause of the viscosity of cellulose in cuprammonium solution is still under discussion. It is, however, an accepted fact that the viscosity depends upon the fiber structure. A. W. Schorger (38) states that "The viscosity of the solution affords a useful means, when stringent precautions are observed, of determining if the cellulose is normal or degraded". L. Lainsney and H. Reclus (26) state that the viscosity of cuprammonium solutions of cellulose depends on the size of the micelles in the solution. This size is strongly affected by the treatment the cellulose has undergone. I. Sakaruda (37) found that there is a definite relation between the solubility of a cellulose preparation in cuprammonium and its physico-chemical properties. He suggests this as a new method of classification. W. Karo (22) in presenting the conception of the cellulose molecule held by various investigators, explains the relation between chain length in the cellulose micelle and the viscosity on the basis of present knowledge. He suggests that viscosity measurements might be used to trace and prevent degradation in commercial processing, evaluating raw materials and determining the relationship between molecular size and chemical activity.

Clibbens and Ridge (6) have pointed out that viscosity and fiber strength are directly proportional. Sakurada (37) attributes some of the viscosity effect to the foreign intermixed membrane elements which are removed more or less by the different purification methods to which the cellulose is subjected. Hilpert and Quan Sut Woo (18) report that while pure cellulose is readily soluble in cuprammonium solution, wood is attacked only slowly. Klingstedt (24) found that hemicellulose was not dissolved by the cuprammonium solution after treatment for several days.

According to Carpenter and Lewis (3) the original and raw cooked fibers are covered with a sheath of lignified material which swells in cuprammonium solution only to a relatively small extent. This then causes a larger colloidal particle and as a result a higher viscosity. As the fibers are slowly degraded, the original sheath is destroyed allowing the micelles to be pulled apart before the molecules are themselves broken down. This causes a lowering but not complete loss of the viscosity of the cuprammonium solution of cellulose. In most cases the viscosity test is not based upon the size of the cellulose molecule, but upon the treatment to which the cellulose has been subjected. The less the fibers are purified, the higher the relative viscosity.

The viscosity test is, therefore, an indication as to the degree of breakdown of the cellulose fibers to micelles and also the breakdown of the micelles. This is true, but it has been pointed out by Reuben (34) that strong West Coast pulps have been found with low viscosities and, conversely, mediocre western pulps with high viscosities. Therefore, even though, in general, fibers of high viscosity have excellent properties, the properties of pulp of cellulosic materials can be evaluated from the results of viscosity tests only if the previous history of the material is known.

Of the other tests of importance in determining the quality of pulp or other cellulosic material, the alpha-cellulose test and the copper number are the most frequently used. The alpha-cellulose test differs from the viscosity test in that it only tells the percentage of the fiber micelles which have reached a certain stage of degradation below which they are soluble in strong sodium hydroxide solutions. The alpha-cellulose test also gives no indication as to the size of the micelles which constitute the alpha cellulose. The copper number is a test for the extent of degradation, but it is not reliable unless all the conditions of pulp treatment are known. According to Ross, Mitchell and Yorsten (36), Okada, Mut-suda and Kayakawa (31) and Coster (9) the alpha-cellulose

content of pulp increases when it is subjected to a dilute alkali treatment at high concentrations, but the viscosity of the pulp decreases. The copper number is not a reliable test for evaluating the strength of cellulosic materials since according to Clibbens and Ridge (6) in the case of cotton a change in the copper number of one point may result in complete loss, a 50% loss, or an insignificant decrease in the strength depending upon the type of chemical action to which the material has been subjected. The copper number can be changed by dilute alkali washes while the viscosity remains the same or decreases slightly. Kress (25) found that when a pulp of high viscosity was recooked in sulphite liquor, the product has practically no strength. The viscosity was lowered 46.6 units, while the alpha-cellulose content decreased by only 6.4 units, and the copper number increased 1.78 units. Coster (9) has found that the same pulp bleached exactly the same way except for the alkalinity will give a lower copper number the higher the alkalinity, while there are no other appreciable differences as far as strength properties or viscosity are concerned.

It is for the above reasons, and also since the viscosity test is quite sensitive to degradation, that workers in the field of pulp and paper have stated that the viscosity test is important in evaluating the properties of

cellulose materials. It is also superior to any other known chemical test for controlling the degradation of cellulose materials.

VISCOSITY MEASUREMENTS

Two general methods have been used in determining the viscosity of the cellulose cuprammonium solutions, namely the efflux and the falling ball methods. Ost (32), in his experiments in 1911, used an apparatus of the efflux type. He found that the viscosity of the solutions decreased with time, and he also recognized the desirability of avoiding contact between the solution and oxygen during the preparation of the cellulose solution. To overcome this latter source of error Gibson (13) in 1920 devised a hydrogen capillary viscometer which permitted preparation of the cellulose solution and the determination of the viscosity in an atmosphere of hydrogen.

The falling ball method was first extensively applied by Joyner (21) in 1922. His apparatus was also so designed as to permit solution of the cellulose and determination of the viscosity in an atmosphere of hydrogen.

Until recently almost everyone who has done any work on the viscosity of the cellulose-cuprammonium solution has used a different method for the determination. Both the falling ball and the efflux methods have been used with a wide variation of cellulose concentration in the solutions. This has hindered the correlation of data from the work of different investigators.

The general purpose of these early developments in methods for viscosity measurements was to prevent contact between the solution and oxygen of the air. Because the solutions required for good accuracy in the falling ball method should have a high viscosity, and their preparation required an unnecessary amount of work and time, Clibbens and Geake (6), in 1928, proposed the use of a rate of flow viscometer in which the solution is made in the measuring instrument itself and there is no danger of exposure to air in transferring the solution from the dissolving vessel to the viscosity measuring device. The method now used as a standard in the pulp and paper industry utilizes a viscometer of this type and is a modification of the Shirley Institute method.

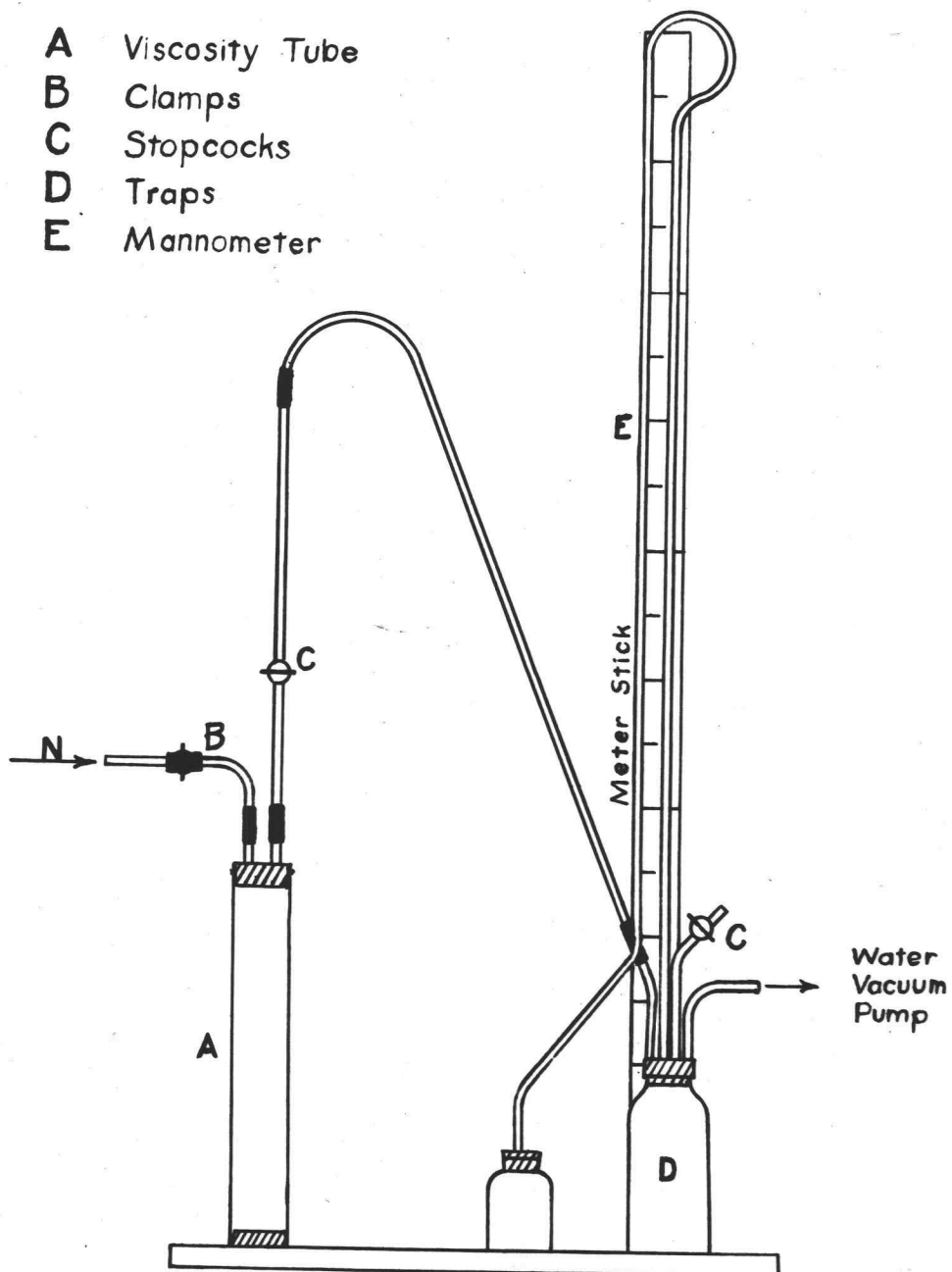
The standard T.A.P.P.I method for the determination of viscosity has several bad features. One of these is that only about 0.2 g of oven-dry pulp is used in each tube. This calls for accurate weighing and transferring of the pulp from the balance to the tube. Due to the finely divided character of the cellulose sample this transfer without small loss is difficult. To overcome this difficulty, Reuben (34) has suggested that the pulp be cut into one-eighth inch squares instead of shredding. Good technique is also required to avoid introduction of air to the tube when filling and adding the pulp samples.

Failure to take the necessary precautions will result in a solution of lower viscosities.

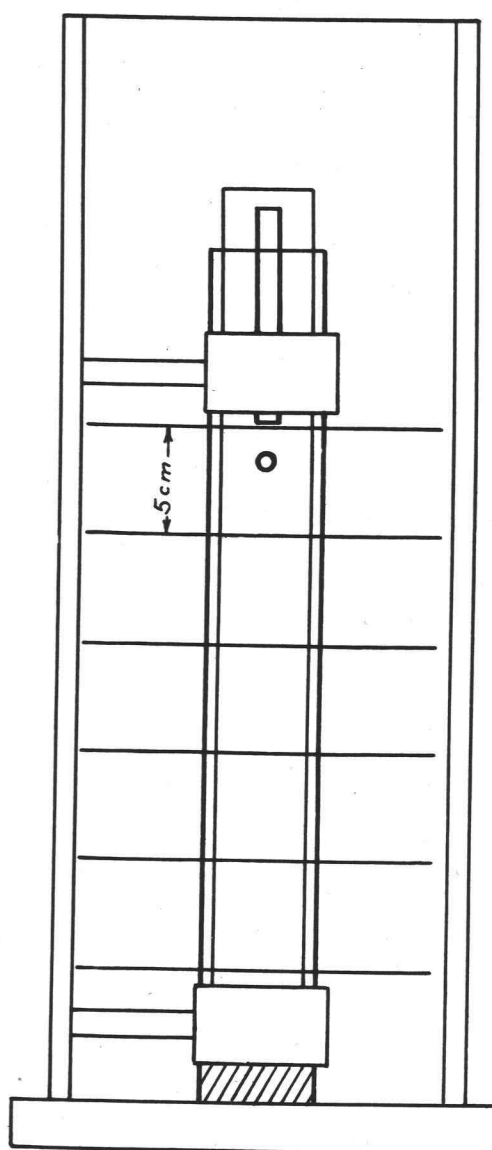
Since the capillary through which the solution must flow is small, a particle of cellulose, representing such a small amount of the sample as to cause a negligible error in viscosity by failure to dissolve, may nevertheless cause extremely large errors by slowing down or actually stopping flow of solution when it passes into the capillary. Other disadvantages of the method are that only one determination can be made on a solution and this determination requires a long time. Fifteen hours is the recommended time for solution of the cellulose.

To determine the dissolving power of the cuprammonium solution stabilized by citrate, the following apparatus was set up. The falling ball method of determining viscosity was used in this study in order to eliminate the numerous difficulties encountered in the efflux method.

Fig. 2
EVACUATION APPARATUS



VISCOSITY CASE



VISCOSITY TESTING

Apparatus and Supplies:Large Buchner filter funnel2 liter suction flaskVacuum serviceAcetone (Commercial)

Moder 270 Moisture Teller (Harry W. Dietert Co., 9330
Roselawn Avenue, Detroit, Michigan.

Balance250 ml Erlenmeyer flasks

Glass tubes (1 foot long and 1 inch in diameter, having
stoppers in both ends (Figure 2)

Reading Cabinet (Box containing a fluorescent 15 watt
light backed by a reflector. The light is shielded except
for a slit one-half inch wide and eleven inches high.

Wires are placed in back of the tubes horizontally at 0,
5, 10, and 15 cm. respectively. (See Figure 3)

Standardized Aluminum Balls (0.125 ± 0.001 inch in diameter
and 0.0474 ± 0.005 grams in weight; obtained from Hoover
Ball and Bearing Company, Ann Arbor, Michigan.

Stop WatchThermometer (Range 0° to 50° C.)Evacuation Apparatus: Figure 2.

VISCOSITY TESTING

Experimental Procedure

The pulp used in the experiments was in the form of sheets secured from the Weyerhaeuser Timber Company. These were torn into small strips and placed in a container filled with water. An electric mixer was then used to get the pulp in a finely divided state. After this was accomplished, the pulp solution was poured into a Buchner filter, sucked dry and washed twice with acetone. The pulp was then peeled into thin pieces and placed in a drying pan and dried for four minutes in the Moisture Teller (98% bone dry). The desired weight of sample was then weighed out and placed into the tubes. The tubes were then evacuated three times replacing the vacuum with nitrogen. Cuprammonium was then pipetted into the tubes replacing the nitrogen (Figure 2). The small, filled rubber tubes were closed with a screw clamp, a black rubber tube was placed over the glass viscosity tubes and they were then placed on a rotator and allowed to rotate for a period of twenty-four hours in order to obtain complete solution of the cellulose.

After the rotation period, the tubes were placed upright and allowed to stand for thirty minutes. The rubber stopper at the top of the tube was then removed and

the tube placed in the viscosity case. The time for the ball to pass fifteen centimeters was measured and the room temperature was taken as the temperature of the solution.

Results and Discussion

The purpose of the viscosity measurements was to check the dissolving action of the cuprammonium solution stabilized by the citrate against that stabilized by the sucrose in order to determine whether or not it would give reliable viscosities.

The viscosity test as set up is one in which all of the previous knowledge in regard to other investigators is taken into account. Larger samples are used (2 g. per 100 ml. of solution) to eliminate the error of loss in transfer. The falling ball method is used to eliminate the possible error of plugging of the tubes as takes place in the efflux method, and a fairly large tube is used in order to make Ladenburg's corrections applicable. A simple evacuation apparatus was set up in order to evacuate, removing all air and replacing the vacuum with an inert gas, nitrogen, which is replaced by the cuprammonium in filling. The tubes were covered with black rubber tubing during rotation and the room temperature was not allowed to go over 25° C, in order to keep the error due to light and heat at a minimum. A fluorescent light was used in the viscosity cabinet to eliminate heat

effect heretofore encountered in falling sphere viscosity measurements on cellulose.

Viscosity determinations were made on three pulp samples secured from the Weyerhaeuser Timber Company. Determinations were made on solutions stabilized by ammonium citrate and by sucrose in 2% solutions. The calculated values are given in Table III.

These values were calculated from the Stokes equation applying Ladenburg's corrections. The viscosity is calculated from the formula (10)

$$\eta = \frac{29r^2(S-6)T}{9 \cdot 1(1+2.4 \frac{r}{R})(1+3.3 \frac{r}{h})}$$

where η the viscosity of the solution, $g = 981$, r = the radius of the sphere, $1/16" = 0.159$ cm, S = the density of the sphere, 2.70, 6 = density of cuprammonium solution (0.942 for 2 per cent solution), T = time of fall in seconds, l = distance between wires 15 cm., R = internal radius of tube, 1.1 cm., h = total height of liquid, approximately 27 cm. The results are expressed in poises and are multiplied by 100 to convert to values of centipoise.

The W. T. Co. values were expressed in values for a 1% solution, the values determined by the standard T.A.P. P.I. method, so the results of the 2% solution were calculated to values of 1% solution by means of Kendall's

equation (23)

$$1 + \frac{C}{m_1} = B/\log \eta_1/\eta_B, \quad 1 + \frac{C}{m_2} = B/\log \eta_2/\eta_B$$

where m is the weight of dry cellulose dissolved in 100 ml. of solvent, η the observed viscosity, and η_B the viscosity of the cuprammonium solvent (determined as 0.0152 C.G.S. units), B and C are constants, and $B = 11$. These two equations may be solved algebraically.

The calculated results are given in Table III.

TABLE III

	W.T.C. 1%	Sucrose		Citrate	
		Calc. Val. 1%	Calc. Val. 1%	Calc. Val. 1%	Calc. Val. 2%
Standard Pulp	53.4	58.6	917.5	46.5 cp	636 cp
Book Pulp	38.3	37.2	440	29.0 cp	300 cp
Select Pulp	27.9	17.0	126.5	16.2 cp	112.5 cp

Our calculated values for 1% solutions determined by falling sphere measurements compare very favorably with those made by the W. T. Co. using the T.A.P.P.I. method for the Standard and Book pulps with sucrose stabilized solutions, but the select pulp gave a much lower value.

The calculated values for 1% solutions stabilized by ammonium citrate were somewhat lower (Table III). This is possibly due to the much higher nitrite content of the sucrose stabilized solutions. The nitrite reacts with the cuprammonium causing higher viscosities (44).

Using ammonium citrate stabilized solutions, it was found possible to distinguish between pulps of low and high viscosity. In the pulp and paper industry, actual values mean nothing. The important thing is to be able to detect changes in the viscosity during processing. Ammonium citrate stabilized solutions will readily detect such changes.

SUMMARY

A study of the preparation of cuprammonium solutions stabilized by dextrose, sucrose, and ammonium citrate at room temperature was made. Dextrose proved to be very unsatisfactory for the preparation of stable solutions, whereas solutions stabilized by sucrose and ammonium citrate containing 30 g per 1 of copper, 165 g per 1 of ammonia, and less than 1.5 g per 1 of nitrite, were prepared and maintained in a stable state for thirty days.

Solutions stabilized by ammonium citrate could be prepared much more rapidly giving a lower nitrite content. They were not affected by light and showed much greater stability than solutions stabilized by either glucose or sucrose.

Viscosity determinations were made using sucrose and ammonium citrate stabilized solutions. Calculated values for the ammonium citrate stabilized solutions were lower than those of the sucrose solution, but this was probably due to the larger nitrite content which accompany the preparation of solutions stabilized by sucrose.

Due to the fact that cuprammonium solutions containing ammonium citrate may be prepared very rapidly avoiding high nitrite concentration, show great stability, and give a very good differentiation between low and high

viscosity pulps, the author believes its substitution for sucrose as the stabilizing agent in the viscosity test in the pulp and paper industry would do much to alleviate trouble experienced by chemists in the preparation and maintenance of stable cuprammonium solutions for use in viscosity measurements.

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