ACTION OF SULPHUROUS ACID AND BISULPHITES ON CELLULOSE

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By

Leonard Patrick Moore,

B.Ch.E. University of Minnesota,

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OUTLINE.

THE ACTION OF SULPHUROUS ACID AND BISULPHITES ON CELLULOSE.

INTRODUCTION.

It is well known that acids, alkalies, and reagents of various kinds, react with cellulose in different ways and to varying degrees. However the action, in many cases, is one of "degradation". By the term"degradation" is meant a decrease in the polymerized or associated state of the cellulose aggregate as indicated, among other factors, by a decrease in the viscosity of a solution of the cellulose in cuprammonium hydroxide. A change in properties of the cellulosic material always accompanies this degradation and the extent of the change is dependent upon the extent to which the cellulose aggregate is depolymerized.

The present investigation on the action of sulphurous acid and bisulphites on cellulose was outlined with a view to determining the extent of the degradation of the aggregate and, if possible, to obtain an insight into the mechanism of the sulphite pulping process. Mechanically, the latter has been developed to a high degree of proficiency, while chemically, a knowledge of the reaction or reactions taking place is still lacking. This knowledge will probably be obtained through investigations along several lines, of which, the ideas presented in this thesis are but one.

One of the most extensive technical contributions on the chemistry of the sulphite process was carried out by R.N.Miller and W.H.Swanson[1] and a brief review of this work will be given. Their idea was to duplicate plant conditions on a small scale so that accurate control could be kept on all of the variable factors encountered such as, temperature, pressure, composition of acid, and wood used. In addition to these factors they determined, by sampling from time to time, the nature and amount of materials that had been removed from the wood at different stages of the cook and from these facts certain conclusions were drawn as to what took place in the digester.

One of the results of their preliminary work indicated that, while sulphonation may be an essential part of the reaction or reactions leading to the production of pulp by the sulphite process, it is of greater importance, from the standpoint of the commercial value of the pulp, to maintain at the end, conditions favorable to so-called "hydrolytic reactions", namely, a high concentration of free sulphurous acid. On the whole, in mill practice, the aim has been to complete a cook with the liquor containing little or no free SO_2 and, under industrial conditions, this hardly ever exceeds 1% and in general is below 0.5%. From their experimental results, Miller and Swanson outlined a procedure for an ideal cook which, in their estimation, should yield a pulp comparing very favorably with a high grade commercial sulphite pulp (Cellulose 96.05% and lignin 1.62%.) and actually found this to be the case. The free SO_2 at the end of this cook was 1.75%. The fact, on the one hand, that a high grade pulp could be obtained, on a laboratory scale, under conditions involving such a high final free SO_2 concentration and, onthe other, the position taken by many prominent pulp specialists that such conditions lead to marked degradation of the resulting product pointed to the necessity of obtaining a clearer insight into the actual effect exerted by sulphurous acid on cellulose under different conditions of concentration and temperature.

It is the purpose of this research, of which the present thesis is but a preliminary contribution, to determine experimentally the effect of sulphurous acid firstly on pure cotton cellulose, secondly on pulps of various kinds, and finally to extend the work to the more complicated system of a sulphite cooking liquor on the same substances, progressing eventually to a small scale industrial cook. By confining the initial experiments to the more or less easily controlled system of cellulose, sulphur dioxide, and water, it seemed reasonable to expect that from the knowledge obtained progress could be made towards a thorough study of the more complicated system of calcium and magnesium bisulphites, sulphur dioxide and water on the one hand and the very complex substance "wood", on the other.

Work of a somewhat similar nature, under the direction of Professor Hibbert, was commenced by W. H. Birchard[2] using a digester similar to the one employed in this work. As the conclusions, drawn and published independently by this author, do not appear to have been definitely established it seemed desirable to check and extend this work.

He found, among other things, that the purer the original cellulose used the more it was degraded by the action of sulphite cooking liquor. The measure of the degradation was obtained from the decrease in the alpha cellulose content of the substance used. For example; a commercial alpha pulp whose alpha cellulose content was 86% was degraded to only 84% alpha cellulose; whereas a surgical cotton, whose original alpha cellulose content was 99.1%, or higher, was degraded to about 70%, using a commercial acid and a heating cycle comparable to an industrial sulphite cook.

GENERAL OUTLINE.

In order to determine the degradation of the cellulose brought about by the action of the chemical reagents during the cooking process, it seemed desirable to first investigate the action of sulphurous acid on pure cotton cellulose; then on a series of pulps and to follow these by a later investigation dealing with the much more complicated conditions involved in the action of the chemical reagents on the cellulose during the actual "cooking process".

In the work as outlined it was decided to use, as the initial raw material, a standard grade of surgical cotton that could be easily duplicated, the alpha cellulose content of such a substance being always over 99% and averaging about 99.2%. To further standardize the work it seemed advisable to carry out a series of experiments with the raw material (surgical cotton) at temperatures of 100°, 115°, and 145°, and to employ, at each of these selected temperatures, a range of SO_2 concentrations. Succeeding these experiments the degradation of cotton, occurring during a temperature cycle corresponding to that used in the manufacture of sulphite pulp, could be investigated. A determination of the alpha cellulose content before and after each cook and also of the viscosity of a solution of the resulting cotton in cuprammonium hydroxide were selected as control methods to indicate the extent of the degradation of the original cotton cellulose.

The so-called alpha cellulose content of different vari-

varieties of cellulose has been shown to be a purely empirical factor. That is to say, its value depends entirely upon the procedure used. Recognizing this, the Cellulose Division of the American Chemical Society[3] appointed a committee to investigate the various methods then in use. They correlated all the facts concerning this matter from the literature and, after extensive experimental work, developed a method which they recommended as a standard procedure.

As a preliminary to this investigation, the above procedure was first checked against the standard method of the Forest Products Laboratories of Canada[4]. The two were found to vary by a constant amount (2%) for an extended series of analyses. The explanationfor this was found in the somewhat different procedures employed, actually occurringin one stage of the method of The American Chemical Society. By recognizing this fact it was possible to alter the technique at this stage and then to obtain duplicate results from the two methods. This work is covered in detail in the experimental section of this paper.

While providing some indication of the extent of degradation, the alpha cellulose determination is really of very little value as a criterion of whatever change is taking place in the size or physical properties of the cellulose aggregate. Perhaps its weakest point lies in the fact that the least change in any of the steps, the time element for example, exerts a more or less pronounced effect on the final analytical results. Another difficulty made itself evident after the problem had been started. It was practically impossible to filter the mercerized samples of the degraded celluloses without loss of solid due to the colloidal nature of the suspension. If the washing is carried out in a centrifuge fairly good results are obtained but even then it is difficult to obtain duplicate analyses.

From these statements the necessity is obvious for a second criterion for the degradation of the cellulose.

<u>Viscosity of solutions of cellulose in cuprammonium hydroxide as a control factor</u>.

The viscosity of cellulose in cuprammonium hydroxide solutions has been applied in research and control methods in many branches of the cellulose industry. Thus it has been used as a measure of the "tendering" in cotton by chemical agency[5].

A simple relationship has been shown to exist between the viscosity of the original cellulose in cuprammonium hydroxide solution and the viscosity of nitrated cellulose in suitable solvents[6]. Clibbens and Ridge[7] have also shown that the fluidity (reciprocal of viscosity) of cotton in cuprammonium hydroxide increases uniformly with decrease in tensile strength when the cotton is subjected to various forms of chemical attack such as bleaching in alkaline and neutral solutions.

One of the first applications of the viscosity value of solutions of cellulose in cuprammonium hydroxide was described by H. Ost[8]. He used it to follow the course of the oxidation by bleaching agents; the effect of heat on cellulose and its mercerization with alkalies.

Investigations made by W.H.Gibson, L. Spencer, and R. McCall[9] and also work carried out in the Royal Arsenal at Woolwich[10] England, indicate that the value of viscosities of cuprammonium solutions of cellulose only yield satisfactory and comparable results when carried out in an atmosphere free of oxygen and when the solution is kept in the dark. They also reported that H. Ost's method for the preparation of cuprammonium hydroxide from copper sulphate is unsatisfactory.

Somewhat later a new apparatus was described by R. A. Joyner[11] for the preparation of the solution of cotton cellulose. Further investigations on the same subject have been carried out by F. D. Farrow and S. M. Neale[12] and S. M. Neale[13], The Research Department, Woolwich[10], and L. Rys[14].

The actual experimental procedure adopted in this thesis is an adaptation of the method developed by L. Rys[14] and was communicated to us privately through the kindness of Dr. O. S. Pokorny. It will be described in detail in the experimental part of the paper.

From a theoretical standpoint, the work of Joyner[11] is interesting in that he established the fact that if the logarithms of the viscosities of various solutions of cellulose are plotted against the concentrations of cellulose in grams per 100 c.c's. of solution, a straight line results. In other words the relationship of the viscosities to the cellulose concentrations may be expressed by an equation of the form of the exponential law:-

$$y = be^{ax} + c$$

This fact was also verified by Hahn and Bradshaw[15], by most of the other workers in this field, and also in the experimental part of this work.

Joyner(loc.cit.) also investigated the effect of varying the concentration of both the copper and the ammonia. The effect of exposure to light and air on cuprammonium solutions of cellulose was pointed out by H. Ost, Gibson, Spencer, and McCall, Joyner, and Woolwich Arsenal, (loc.cit.).

Pokorny has indicated some of the sources of analytical error in the procedure for measuring the viscosity of a cellulose solution and these will now be discussed. The velocity of a sphere falling vertically in a viscous liquid is given by the "Stokes Equation":-

$$v = 2/9\ g\ r^2 \left(\frac{\rho_1 - \rho_2}{\eta}\right)$$

where
v = velocity of fall.
g = gravitational constant.
r = radius of shere.
ρ_1 = density of sphere.
ρ_2 = density of medium.
η = viscosity of medium.

This equation applies only to a sphere falling through an infinite extent of liquid. According to R. Ladenburg[16] two corrections must be applied to this equation when observing the velocity of fall in a viscometer tube:-

(a) Acorrection for wall effect.

(b) A correction for end effect.

W.H. Gibson and L. M. Jacobs[17] investigated the accuracy of the falling sphere method for measuring the viscosity of a liquid and found that the time of fall, calculated for an infinitely long column of the medium, becomes constant for wider tubes. However, the visibility through the pulp solutions in large tubes is limited and, chiefly for this reason, the maximum bore of the tube should not exceed 2 cm. By the use of a correction factor,(i.e. the tube constant obtained by means of a liquid of known viscosity) fairly accurate determinations of apparent or relative viscosities can be obtained.

Carver and Folts[18] point out that solutions of cellulose in cuprammonium hydroxide do not flow as viscous liquids but rather as plastic solids. Measurements, made at different rates of shear with a Bingham and Green plastometer indicate that Joyner's Law, as mentioned above, holds for the rates of shear studied.

On the basis of accumulated evidence it can be seen that the method for the estimation of viscosities of solutions of cellulose in cuprammonium hydroxide ranks as an exact one if the important factors, as mentioned above, effecting a change in the viscosity are avoided. Nevertheless other workers still believe that the method is not entirely free from serious objection. Thus Clibbens and Geake[5] of the Shirley Institute Manchester, England, after doing a large amount of work on this subject come to the following conclusion: " The use of the falling sphere viscometer introduces a large number of unnecessary difficulties and waste of time." Consequently all of their work has been carried out by means of a capillary viscometer of their own design using lower concentrations of cotton in cuprammonium hydroxide.

Their conclusions, while being justifiable in part, are not entirely so. A capillary viscometer, such as they describe, is applicable only to viscosities of less than one poise due to the length of time of flow required. Many times, when working with cellulose, it is desirable to determine viscosities much higher than this and to do so the falling ball method must be employed.

EXPERIMENTAL PART.

I.- DESCRIPTION OF APPARATUS AND METHODS OF PROCEDURE.

(a). Digester.* The "cooks" were carried out in a digester of pyrex glass, in the shape of a long cylindrical tube of 500 c.c's capacity.(15 inches in length and 2 inches in diameter.) A bronze flange was cemented to this, and a cap, fitted with two relief valves, a thermometer, and a pressure gauge could be bolted to this flange as illustrated in the diagram (A). The digester was heated in an oil bath whose temperature was controlled by means of a resistance coil and a lamp bank. The bath was well stirred to ensure uniform heating and was easily controlled over the temperature ranges(100°-145°) desired.

A "cook" lasted a period of nine hours, each experiment being carried out at a constant temperature of 100°. About two hours was required for the digester to reach this temperature which was then held constant for a further 7 hours. At the end of this time the pressure was released through one of the relief valves and the apparatus allowed to cool in the bath.

For each "cook", 30 grams of air dry cotton were used and 400 c.c's of sulphurous acid. These quantities were employed in each run regardless of the strength of the acid and are merely arbitrary figures based on the capacity of the digester. The procedure followed for all "cooks" was the same. When the digester had cooled sufficiently to allow of its removal from the oil bath, the cotton was taken out and thoroughly washed with water in a large beaker to remove the acid, further washed on a Büchner filter, and finally the excess water was removed by suction. The cotton was dried at

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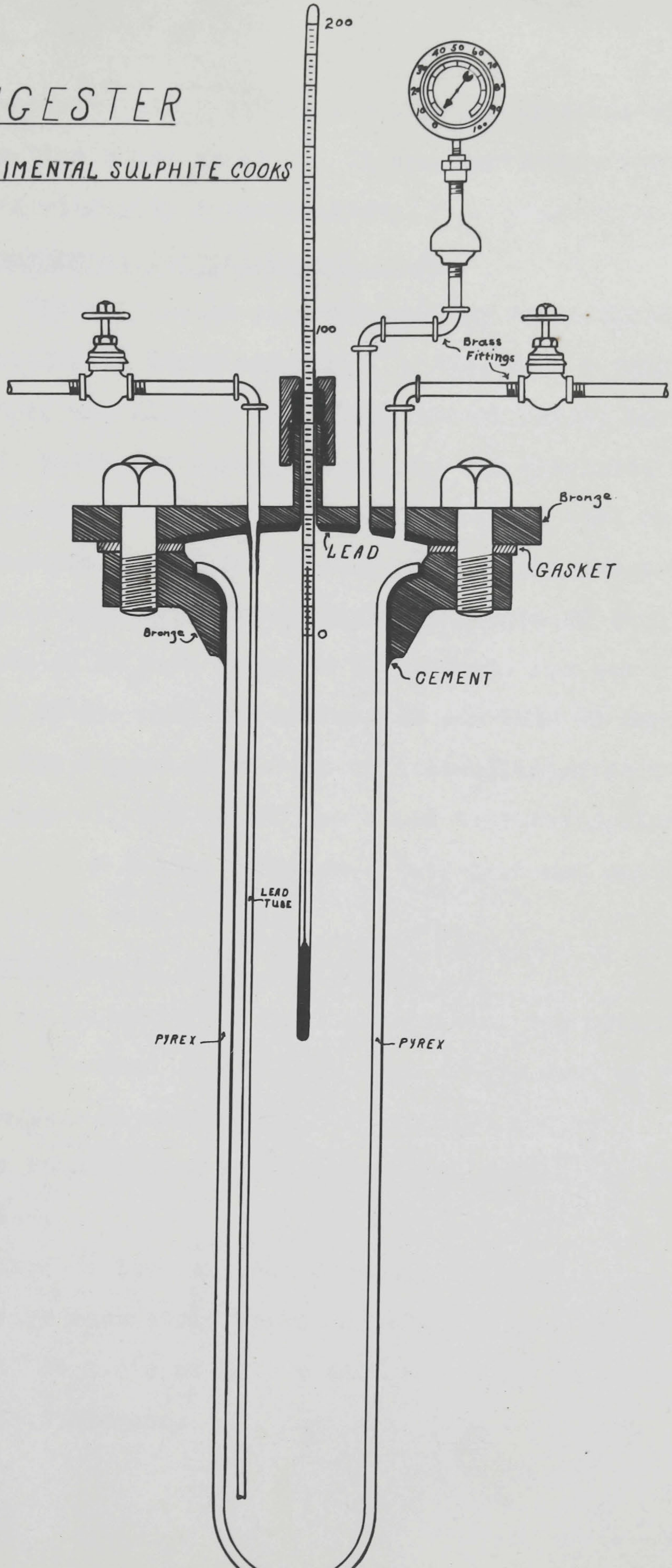
* Originally designed by E.P.Cameron of the Canadian Forest Products Laboratories.

DIGESTER

FOR EXPERIMENTAL SULPHITE COOKS



60° in a vacuum oven for thirty hours, the average moisture content at the end of this time being about 2%. It was then ready for the alpha cellulose and viscosity determinations.

(b). Preparation of the Sulphurous Acid.

The sulphurous acid was made up and titrated according to the method of Maass and Maass[19]. SO_2, from a tank of the liquid substance, was allowed to bubble through water, in a brown glass bottle, until the strength desired was obtained. The acid was made up fresh for each run since it was found that very little or no SO_3 was present in the freshly made solution but that if it were allowed to stand for any appreciable length of time considerable amounts of SO_3 were found to be present. For the titration, 25 c.c's of the acid was allowed to run into an excess of 2 N NaOH containing 2 gms. of sucrose as a stabilizing agent. This solution was then diluted to 250 c.c's and titrated against 25 c.c's of standard .1 N iodine solution. Very good and uniform results were obtained by this method.

(c). Determination of alpha cellulose.

As indicated in the introduction, two methods, that of the American Chemical Society and that of Dr. Ross of the Canadian Forest Products Laboratories, were checked against each other in order to determine a procedure best suited for the present investigation.

Method # 1. (procedure of the American Chemical Society).

1. Weigh accurately approximately a 3 gram sample.
2. Add 35 c.c's of 17.5 % NaOH and allow to stand for 5 minutes.

3. Macerate for 10 minutes, adding 40 c.c's of 17.5 % NaOH in 10 c.c. portions. If the determination is being made on a pulp, it is essential that the sample be thoroughly broken up at this point.
4. Cover with a watch glass and allow to stand for 30 minutes.
5. Add 75 c.c's of distilled water, stir thoroughly and filter immediately.
6. Wash with 750 c.c's of distilled water.
7. Add 40 c.c's of 10 % acetic acid, on the filter, allow to soak for 5 minutes, and then apply suction.
8. Wash until acid free and then dry at 105°C. for at least 6 hours. Weigh and then dry to constant weight.

<u>Method # 2.</u> (Forest Products Laboratories Procedure).

1. Weigh accurately approximately a 3.5 gram sample.
2. Add 70 c.c's of 17.5 % NaOH, macerate thoroughly and allow to stand for 2 hours.
3. Filter on a Buchner being careful that none of the fibres pass through.
4. Suspend in 100 c.c's of 17.5 % NaOH for 30 secs., stirring well, and filter as before.
5. Suspend the residue in 200 c.c's of 25 % acetic acid, bring up to the boiling point, and again filter.

6. Wash the residue with at least 1 litre of boiling distilled water until the final washings are neutral.

7. Dry at 105° C. to constant weight.

Comparison of the two methods. It will be noted that the two methods differ radically as regards : (a) temperature, (b) length of time of maceration, (c) dilution of the liquor after maceration. It was found that of these three factors the only one causing a marked difference in the value of alpha cellulose found was that arising from the dilution of the liquor after maceration (c). Allowing for this check values, within 1%, were obtained by both procedures.

Pulps I & II. These were different samples of the same pulp, namely, a bleached sulphite pulp made by the Brown Company, Berlin, N.H.

Pulps T-500, T-600; Cotton C -100, C-200. These were samples supplied by Dr. Ritter of the U.S. Forest Products Laboratories, Madison, Wis., and represent the check samples used for control work on the standard alpha cellulose determination of pulps (method 1).

Pulps III & IV. These were a Soda and a Kraft pulp respectively, and were supplied by the Howard Smith Company.

Analysis of various pulps for alpha cellulose content.

Table I.

	Pulp I. (sulphite)	Pulp II. (sulphite)	Pulp III. (soda)	Pulp IV. (kraft)
% alpha cellulose by method # 1.				
	94.98		72.44	85.65
	94.80		73.26	85.48
	94.90		73.50	85.51
	94.85			
	94.84			
	95.12			
Mean value.	94.915		73.067	85.55
% alpha cellulose by method # 2.				
	94.97	95.62	81.82	86.39
	95.57	95.82	80.96	86.53
	96.28		81.13	86.58
	95.76		81.54	
	95.85			
	96.00			
Mean value.	95.73	95.72	81.36	86.50

Analyses were made using the procedure of method # 1. but omitting step 5. (dilution after maceration).

	Pulp II.	Pulp III.
% alpha cellulose by method # 1. (without dilution)		
	95.40	75.19
	94.94	76.32
	95.12	76.55
Mean value.	95.15	76.02

The following analyses were made on samples of the different varieties of cellulose that were used by the committee of the American Chemical Society in arriving at their standard method.

Table II.

	Pulp T-500.	Pulp T-600.	Cotton C-100.	Cotton C-200.
Method #1.	86.97	84.60	99.33	92.14
	87.09	83.41	99.25	91.94
		83.57		
Mean value.	87.03	83.86	99.29	92.04
A.C.S.Comm. Av.	86.36	82.82	99.24	91.47

Table II.(continued).

	Pulp T-500.	Pulp T-600.	Cotton C-100.	Cotton C-200.
Method # 2.				
F.P.Labs.	88.75	85.29	99.16	95.07
	88.56	84.86	99.03	94.97
		84.97		95.23
Mean value.	88.65	85.04	99.09	95.09

A comparison of the results. As seen from Tables I.&II., good checks can be obtained in every case with either method but the values found by method #2 are invariably higher than those of method #1 by about 1-2 %. With this fact in mind, method #1 was further investigated but step (5) was omitted. That is to say, instead of diluting with an equal volume of water after mercerization, the mass was filtered immediately. The results, using this procedure, were uniformly higher, as shown in Table I, and approached more nearly to those obtained using method #2. This increase in alpha cellulose content is to be expected because, in the procedure as given, instead of filtering a suspension of cellulose in 17.5 % NaOH, due to the dilution, the liquor contains only 8-9 % NaOH and it has been shown by determinations carried out by Dr. Ross of the Canadian Forest Products Laboratories that the maximum solubility of cellulose in sodium hydroxide corresponds to a sodium hydroxide content of 8-9 %.

The soda pulp gave the most divergent results of any of the samples tried, the second method showing about 8 % more alpha cellulose than the first method.(TableI). Here again it was found that by omitting step (5) in method #1 higher values were obtained approaching those of method #2. They were still about 5% lower however In both cases, the maceration of the pulp after the addition of the sodium hydroxide, was very difficult and great care had to be taken to insure, as far as possible, a complete separation of the fibers. When following the procedure for method #1, as noted above, the suspension in the caustic soda solution assumed a very gelatinous-like character and was extremely difficult to filter, although, when finally accomplished, the filtrate was free from all fibrous substances. There is a possibilty that enough of the cellulose passes through the filter, in a colloidal state, to cause a decrease in the actual weight of alpha cellulose remaining as a residue. This conclusion is substantiated by the fact that when step (5) is omitted the pulp retained its fibrous nature to a greater degree, the filtration is less difficult, and the increase in alpha cellulose (3%) was greater than the increase which occured for the same omission in the analysis of the other pulps.

No final and specific conclusions can be drawn from the results taken as a whole except the fact that method #2 always gives higher results than method #1, the values of the latter averaging from 1-2 % higher. As indicated, step (5) explains a part of the difference but even with this step omitted the values obtained by the second method are higher than those obtained by the first. Disregarding for the moment any difference that might be laid to experimental error, a possible explanation might be drawn from the procedure itself in method #2. After a definite period of mercerization the pulp is filtered, more caustic is added, and the suspension again filtered. The acetic acid is then added to the pulp without any preliminary washing out of the caustic. Under these conditions a part of the sodium hydroxide will adhere to the fibers and, upon addition of the acetic acid, degraded or so-called beta cellulose, which by its definition would be in solution in the sodium hydroxide, would be precipitated upon the alpha fibers. The subsequent washing with water would not remove this beta cellulose and consequently the value for the alpha cellulose becomes higher. In method #1 the pulp is washed with about a litre of water before the addition of the acetic acid. Complete removal of the soda by water is impossible but the amount remaining can be reduced to a negligible quantity. Therefore no beta cellulose will be precipitated and the final weight of alpha cellulose tends to be lower.

It was therefore decided for the purpose of the following work, to use method #1 with step (5) eliminated. It was also found advisable, when filtering off the alkaline solution after the 30 minute mercerization period, to run the filtrate through the residue on the Büchner three times, to insure complete removal of the fibers. This becomes increasingly necessary for the "cooked" samples due to the very short length of the cotton fibers.

(d). <u>Determination of viscosity of cuprammonium solutions of cellulose.</u>

Description of the process.

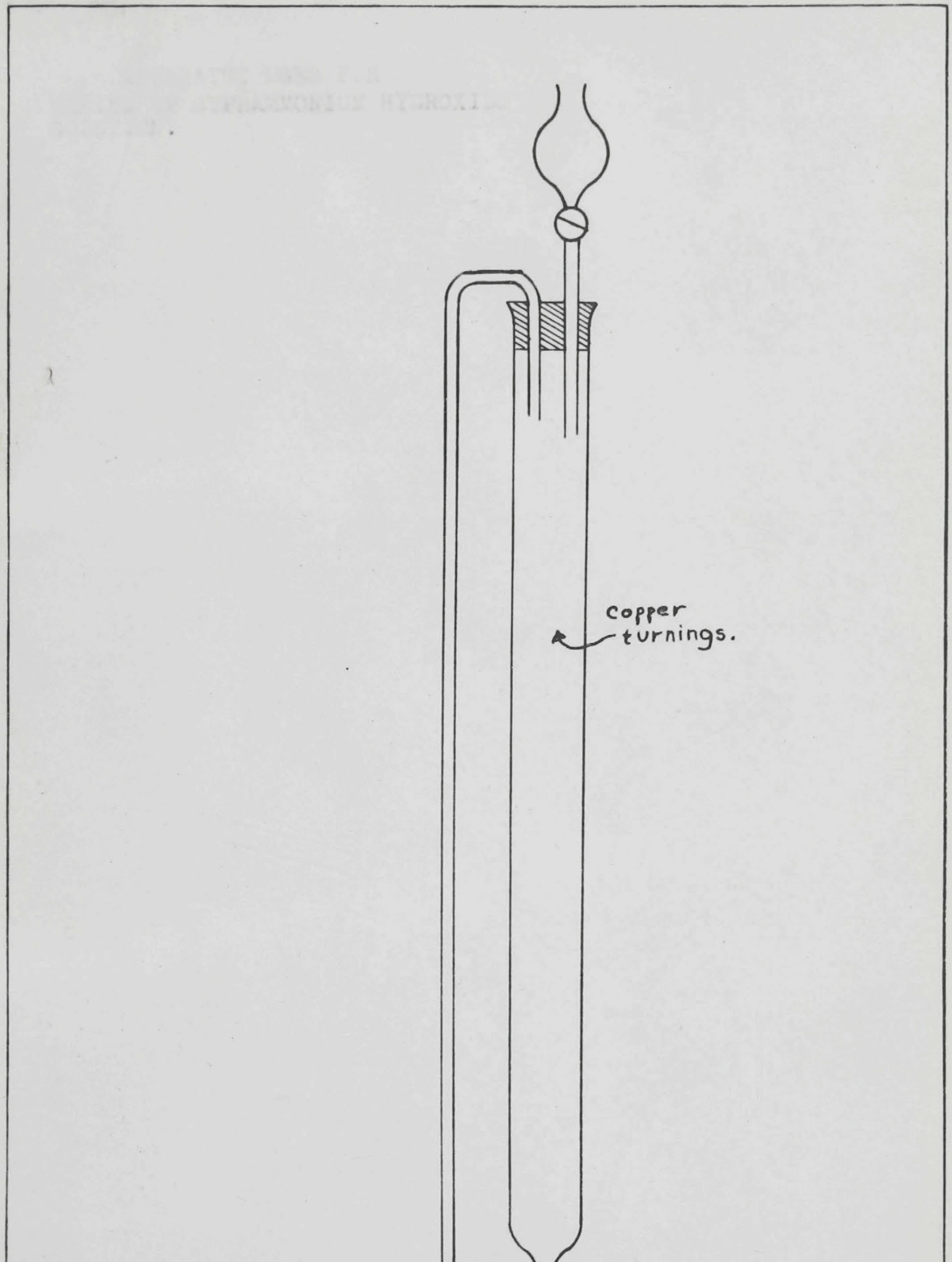
1.- Method used for making up the cuprammonium hydroxide solution.

The formula ordinarily given for this solution is $Cu(NH_4)_2(OH)_4$ or $Cu(OH)_2\cdot 2NH_4OH$. There are several ways in which it can be prepared. H. Ost[8], one of the first workers in this field prepared his solution from copper sulphate and ammonium hydroxide. However this has been shown to be an unsatisfactory method due to the effect of the dissolved salt on the viscosities of the solutions of cellulose made up later. Using freshly precipitated cupric hydroxide and dissolving this in ammonium hydroxide, a satisfactory solution is obtained but with this disadvantage that a copper content of only about 12 grams per litre can be obtained. Since the amount of cellulose, that will dissolve in the solution, is a function of the copper content it is desirable to be able to increase this factor. Joyner[11] found that if air is bubbled through a tower containing clean copper turnings and concentrated ammonium hydroxide a solution is obtained that contains 30-40 grams of copper per litre. Variations of this method have been used by most of the recent workers in this field and is the method employed in the present investigation.

The apparatus used, as illustrated by the diagram, is a long glass tower in which copper turnings are packed. Two liters of concentrated ammonium hydroxide are placed in the tower and air is bubbled through. Sucrose is added to the solution as a stabilizing agent. The exact nature of this stabilizing effect is unknown but solutions containing the sugar will last longer, without precipitation of the copper, than those which do not contain this substance. The amounts, which have been used in the past, vary from 1 up to 15 or 20 grams per litre. The essential factor is that the quantity decided upon must be kept constant, from solution to solution, in all of the work from which comparative results are to be obtained because, as Joyner[11] has shown, the sugar influences the viscosity of the solutions of cellulose in the cuprammonium hydroxide to an appreciable extent. The amount usedin this work was 10 grams per litre of concentrated ammonium hydroxide.

The air was bubbled through a solution of KOH to remove any CO_2 and then passed into the tower, and the gas leaving the tower bubbled through acid wash bottles to collect entrained NH_3 fumes.

APPARATUS USED FOR MAKING UP THE
CUPRAMMONIUM HYDROXIDE SOLUTION.



The complete set-up was cerected in a cold room at zero degrees in order to decrease the volatility of the NH_3. Some nitrite formation is brought about due to the oxidation of the NH_3, the amounts formed varying according to the length of time required to make up the solution. It was usually found necessary to bubble air through the tower for a period of from 8-12 hours, this length of time giving a copper content of 3-4%, ammonia 15-16%, and nitrite, calculated as nitrous acid, about 1.5%. In order to shorten the length of time required to dissolve the copper, and thus to decrease the nitrite content, it was found adviseble to bubble oxygen through the tower instead of air. It is desirable to dissolve more than 30 grams of copper per litre and then to adjust the various concentrations by dilution, the final solution being as follows:-

Copper.	3%.
Ammonia.	16.5%.
Sucrose.	1%.
Nitrite.	Not greater than 1.5% and preferably less than 1%.

Methods of Analysis.

Copper. The copper can be determined very satisfactorly by electrolytic deposition or volumetrically by use of the potassium iodide-thiosulphate method, the latter being used in this work.

In order to obtain check results it was found necessary to convert all nitrite to nitrate, effecting this by boiling with concentrated H_2SO_4 and adding a small amount of urea.

Experimental procedure. A 5 c.c. sample of cuprammonium hydroxide solution was pipetted into a 250c.c. Erlenmeyer flask containing 25c.c's of distilled water. The excess ammonia is boiled off and the solution acidified with concentrated H_2SO_4 and boiled a few seconds longer. A small crystal of urea is then added to the hot solution to expel any last traces of nitrogen. The solution is cooled and made basic with ammonium hydroxide. It is then acidified with acetic acid and cooled to room temperature. 2.5 grams of KI, dissolved in 10c.c's of water are then added and the precipitated iodine is titrated with .1 N thiosulphate using a freshly made starch indicator. The above method of procedure has been found to give uniform results which can be readily and accurately duplicated.

Ammonia. The ammonia can be determined in the usual way by distillation into standard acid. A 5c.c. sample is pipetted into 150 c.cs of cold distilled water, care being taken to hold the tip of the pipette just under the surface of the water to prevent the escape of any NH_3. 4-5 grams of solid sodium hydroxide are then added and the ammonia distilled through a Kjeldahl bulb into a known excess of standard acid. The excess acid is titrated and the ammonia calculated.

Nitrite. Nitrite content is determined as nitrous acid, the cuprammonium hydroxide solution being used to titrate a given sample of standard permanganate solution until the color just disappears. The nitrite can be calculated from the quanity of cuprammonium solution required.

When the analysis of the solution has been made, it can be diluted to the desired values, namely, those listed above. It is essential that the copper content be exactly 3% in each solution for the sake of comparison. The permissible error in the ammonia content is greater because this factor influences the ultimate viscosities to a minor degree as compared with the copper content.

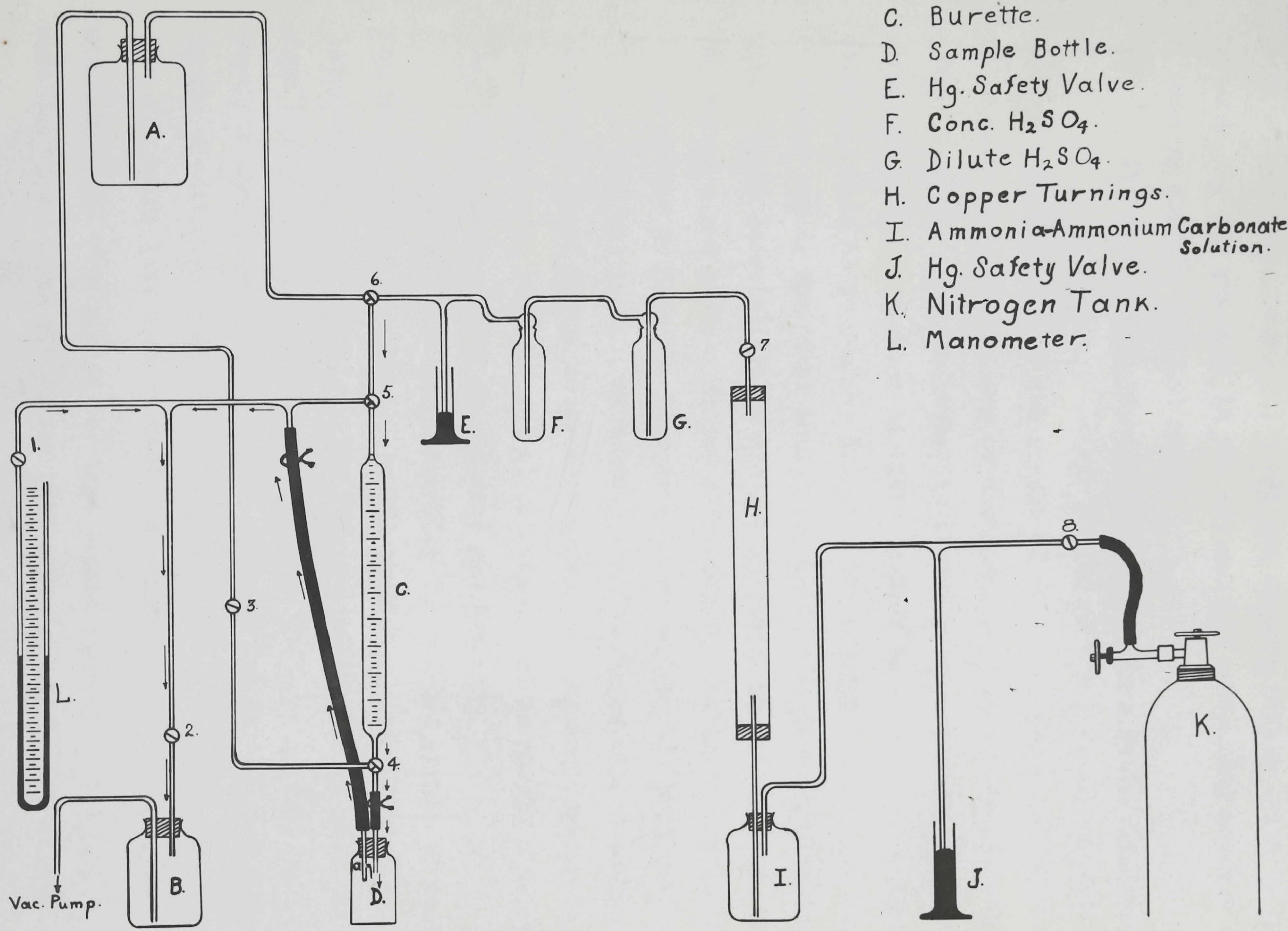
2.- Determination of viscosity.

(a) Description of apparatus used in making up the sample.

At various times throughout the course of the following investigation, different percentage solutions of cotton in cuprammonium hydroxide were employed. In each case, however, the weight of cotton referred to, namely, a 2% solution, 3% solution etc., implies the weight of bone dry cotton per 100 c.c. of solution.

The samples were all prepared in an atmosphere of nitrogen to eliminate any changes in viscosity due to oxidation. Because the commercial nitrogen used always contains a small amount of oxygen, it was necessary to purify the gas by the method described by Van Brunt[21]. The "set-up" for the nitrogen purifier, as illustrated in the attached diagram, consists of a reservoir, I, which is a glass bottle of about a litre and a half capacity, containing diluted ammonia-ammonium carbonate solution, made by adding 1380 c.c's of ammonium hydroxide, sp.g. 0.90, to 2000 c.c's of a saturated solution of ammonium carbonate and diluting to a volume of four litres. (This solution should be renewed after about 100 determinations). When the nitrogen is released through the valve at (K), the solution in (I) is forced into the tower (H) containing copper turnings. Here the oxygen, contained in the nitrogen, unites with the copper forming copper oxide which, in turn, is dissolved by the ammonia-ammonium carbonate solution leaving a fresh surface on the copper to take up more oxygen.

Because of the loss of ammonia from the solution due to volatility, the nitrogen gas, after leaving (H), is passed through two wash bottles, (G) & (F), containing dilute and concentrated sulphuric acid respectively. The dilute acid should be replaced after



A. Storage Bott
B. Safety Trap.
C. Burette.
D. Sample Bottle.
E. Hg. Safety Valve.
F. Conc. H_2SO_4.
G. Dilute H_2SO_4.
H. Copper Turnings.
I. Ammonia-Ammonium Carbonate Solution.
J. Hg. Safety Valve.
K. Nitrogen Tank.
L. Manometer.

L.P. Moore

about 30 determinations. (E) & (J) are mercury safety traps to regulate the gas pressure in the system, (E) containing about 5 cm. of mercury and (J) somewhat more.

(b) Replacement of air in the dissolving bottle by nitrogen.

The sample bottle (D) is of brown glass its size being dependent on the size of the sample of cotton taken,–usually,however, it is about 250 or 400 c.c's capacity,and is fitted with a two-holed rubber stopper. The one outlet is fitted with a straight glass tube connected to a short piece of rubber tubing to which a screw clamp is attached. This is to connect (D) with the burette (C) through the three-way tap 4. The other outlet consists of a piece of glass tubing with a small hole (a) in the side, (the bottom is sealed off), and is used as a gas outlet. Before detaching the rubber tubing the hole (a) is pulled up into the stopper thereby sealing off that outlet.

The bottle (A), containing the reserve supply of cuprammonium hydroxide, is of brown or darkened glass. The complete system is kept filled with nitrogen gas at all times. (B) is merely a safety trap and is large enough to act as a gas cushion.

With (D) in place, containing the weighed sample of cotton, tap (4) is turned to open (C) to (D) thus closing (3),(which is likewise shut,)off from (D). Tap (5) is turned so as to shut off (C) from (2) but so at the same time to leave (C) open to (6). To evacuate the system, (6) is turned to close off (A) and (E) from (5). In the meantime the water pump is started and a vacuum created in (B), (1) being left open so that the pressure will register on the manometer (L). With all of the taps turned correctly, (2) is carefully opened and all of the air or gas is sucked out of the apparatus, being removed as indicated by the arrows. When the maximum vacuum has been established, as shown by (L), (2) is closed. The system is then ready to be filled with nitrogen gas. (6) is now turned so as to close (A) off from (5) and to open (E) to (5), nitrogen immediately passing into the evacuated space. There is usually enough gas in the system to bring the manometer down until it registers only 4 cm. of vacuum. The valve on the nitrogen cylinder (K) is then opened, taps (7) and (8) being open at all times, and nitrogen slowly fills the system. When nitrogen commences to bubble through the mercury in (E) the valve on (K) is closed. Tap (6) is then turned to its former position, i.e. closing the connection to (5) and opening that to (A). The gas pressure forces the ammonia-ammonium carbonate solution out of (I) and up into (H), and on closing the valve at (K) it runs back into (I).

The process of evacuation and the subsequent filling with nitrogen is repeated five times. The fifth time, instead of creating the slight pressure in the system as indicated by (E), the gas is allowed to flow through the apparatus and out the water pump. This is accomplished by opening (2) a small amount. A stream of nitrogen is kept flowing through in this manner for two minutes at the end of which time (2) is closed and the pressure created as before. The system is evacuated another three times and another two minute period as before ending with a slight pressure throughout the entire apparatus.

(c) Filling the dissolving bottle with cuprammonium solution.

To fill the burette (C) from (A), tap (4) is turned so as to connect (3) to (C) and to close (D) from (C). Leaving tap (5) in same position, (6) is turned to open (A) to (5) and thus closing (A) from (E). By opening (3) the cuprammonium hydroxide siphons over into (C)and when full (3) is closed. (5) is then turned closing (C) to (6) and connecting (C) with (1), (3), and the rubber connection to (D). Tap (4) is now turned so as to close (3) to (C) and at the same time opening (C) to (D) thus allowing the cuprammonium hydroxide to flow into (D). The burette (C) used had a capacity of 50 c.c's and the quantity of solution desired, for the weight of sample taken in (D), could be supplied by repeating the procedure indicated.

With the required quantity of cuprammonium hydroxide in (D), the screw clamp on the rubber connection is closed. The pressure in the bottle at this time, being about 10 cm. of Hg.,is excessive and should be reduced to 1 cm. The glass tube, with the hole (a) in the side, is then drawn up into the rubber stopper so that (a) is sealed off.

The bottle (D) is then placed in a vertical type shaker* making about 100-150 R.P.M. The time required for complete solution varies with the viscosity characteristics of the material employed. In order to standardize the procedure each sample is shaken for 12 hours. It is advisable, however, to examine the solution prior to its removal from the shaker in order to be quite certain that all all of the material in the bottle has been dissolved. Increase in time of shaking did notseem to alter the viscosities appreciably.

* It was found advisable to wire the stopper into the bottle.

The bottle, containing the sample, is then placed in a constant temperature bath, kept at 20°, until the solution is free of gas bubbles. As with the shaking operation, the time required in this case varies from sample to sample. Here also the time was standardized at 30 hours. The sample is then ready for the viscosity determination.

(d) Measurement of the viscosity.

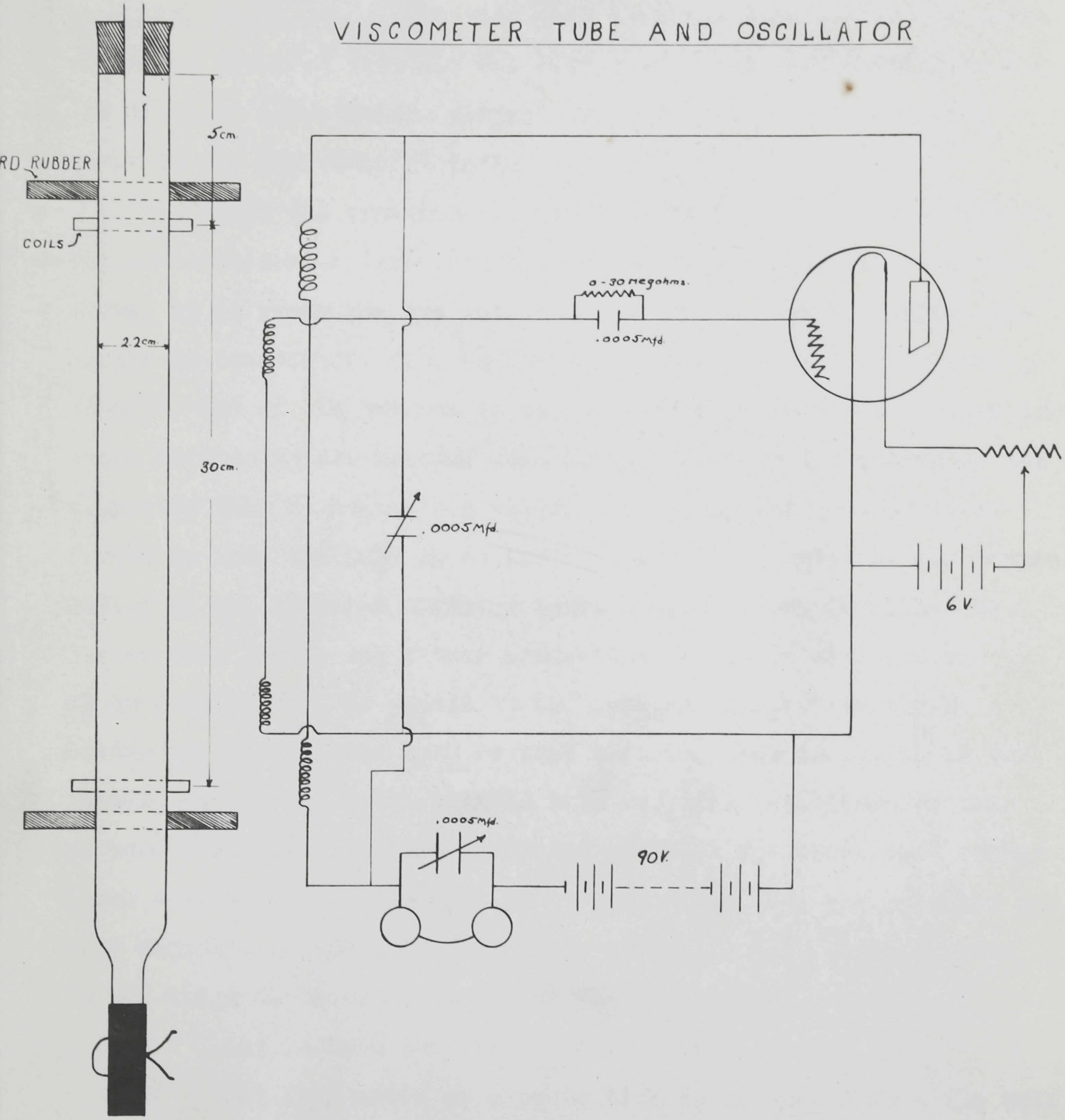
The viscosity was measured by means of the "falling-ball" method as discussed in the introduction. In previous investigations this measurement has been made by determining the time of fall of a ball, (steel, glass, etc.), between two marks on a viscosity tube. It is, however, very difficult to observe accurately the fall of a ball through a solution of cellulose in cuprammonium hydroxide. When the per-cent cellulose is high it is almost impossible unless a very strong light is placed directly in the line of vision. It has been shown by Pokorny (loc.cit.) that a strong light such as this alters the viscosity of the solution a definite amount depending on the length of time exposed.

Description of the viscometer. To remove the necessity for the use of a light it was decided to take advantage of an idea suggested by a publication from the Hercules Powder Co. Laboratories[21]. This consists in the use of a small one-tube oscillator and steel balls. By splitting the grid and plate coils and winding them on the viscosity tube a change in note could be heard as the steel ball passes each coil. The time was determined between these changes in note. Considerable time was spent in trying to apply the method as given but without success.

It was found, however, that by changing the "hook-up" a small amount, as shown in the diagram, a very stable oscillator could be obtained. The capacity across the phones may be either fixed or variable but the latter is preferable. A note, best suited to the ear making the measurement, can be obtained by adjusting the variable grid leak and the capacity across the phones. When this note is finally obtained these adjustments are left permanently in place, the final tuning being done with the capacity across the plate coil. By the use of a vernier the oscillations can be adjusted so that they are just on the verge of stopping. Then as the ball passes a coil the sound ceases altogether and as the ball leaves the coil the oscillation will start up again thus giving a distinct point from which to time the fall. With very viscous solutions, where the rate of fall is extremely slow, the time should be recorded just as the note stops for each coil. The reason for this is that an appreciable length of time (up to 25 secs. for very viscous solutions) is required for the ball to pass through a coil. However by recording the time just as the sound stops, in each case, very good checks can be obtained.

Aluminium balls were employed for the less viscous solutions and can be used, with the tube illustrated, down to 1/8" in diameter. However the results with the 1/8" balls were not consistent, i.e. the set could be adjusted to respond as the ball passed a coil but the adjustment was so critical that the oscillations would often stop of themselves spoiling the measurment. With sizes above 1/8" such as 3/16", 1/4", etc., very good results were obtained. In the cuprammonium hydroxide solutions the aluminium balls were used only once

VISCOMETER TUBE AND OSCILLATOR



L.P. Moore.

being attacked to a slight degree by the strong base. Actually their weights were unchanged if they were allowed to remain in the solution only a short time. However they were never used more than once.

<u>Use of the apparatus in measuring the viscosity of a cuprammonium hydroxide solution.</u> The viscosity tube was standardized by means of an oil obtained from the U.S.Bureau of Standards, Washington D.C. The data and calculations pertaining to the tube constants are given in the experimental part.

After the cuprammonium solution of the sample has stood in the constant temperature bath for the 30 hour period, as mentioned above, it is ready for the actual measurement of its viscosity. The sample is transferred from the bottle to the tube in the following manner:- One of the outlets in the bottle is replaced by a glass tube which extends to its bottom. This is connected to the bottom of the viscosity tube by means of a rubber connection and the sample is forced up into the tube by attaching the other outlet of the sample bottle to the nitrogen pressure tank. When the tube is filled to the correct level, the rubber connection is closed with a screw clamp and the tube is placed in the constant temperature bath. A holder is fixed in the bath so that when the tube is placed in the holder, it is held automatically in a vertical position. For this purpose a standard 4 litre graduated cylinder was used. Hard rubber disks were cut of such a size as to just slide into the cylinder and were cemented to the tube just above and below each coil as shown in the diagram. These disks served three purposes:

(a) To hold the tube in a vertical position.

(b) They acted as a protection to the coils when the tube was being cleaned.

(c) The top disk served for the attachment of the binding posts and the four leads from the coils.

The tube connections to the oscillator were then easily made through the binding posts. After filling, the tube was allowed to stand (stoppered) for two hours to bring the temperature back to that of the bath (20°). Values for several balls were obtained in each case and the mean value was used to calculate the relative viscosity.

EXPERIMENTAL.

A.- Standardization of Viscosity Tube.

The oil used as a standard was a pale yellow oil, presumably castor oil, supplied by the U. S. Bureau of Standards.

Density of the oil at	20°	0.960	
Viscosity " "	20°	9.60	poises.
Viscosity " "	25°	6.54	"

Times of fall, in seconds, of the various balls was as follows:-

Steel Balls.			Aluminium Balls.		
1/4"	3/16"	1/8"	1/4"	3/16"	1/8"
7.0	5.5	12.4	18.5	27.0	37 (?)
7.0	5.5	12.0	18.5	27.0	
7.0	5.5	12.4	18.5	26.8	

Calculation of Tube Constants.

(a) $k = \dfrac{\eta}{(\rho_1 - \rho_2)t}$

(b) $K = k(\rho_1 - \rho_3)$

η = Viscosity of Standard.
ρ_1 = Density of Ball.
ρ_2 = Density of Standard.
t = Time of fall in seconds.
ρ_3 = Density of Water.

(c) "K" multiplied by the time of fall, in seconds, of the ball through the solution, whose viscosity is being measured, gives the relative viscosity of that solution.

Values for "K" as follows:-

	Steel.	Aluminium.
1/8" Ball.	0.772	------
3/16" "	1.365	0.348
1/4" "	1.735	0.508

B.- Summary of "Experimental Cooks".

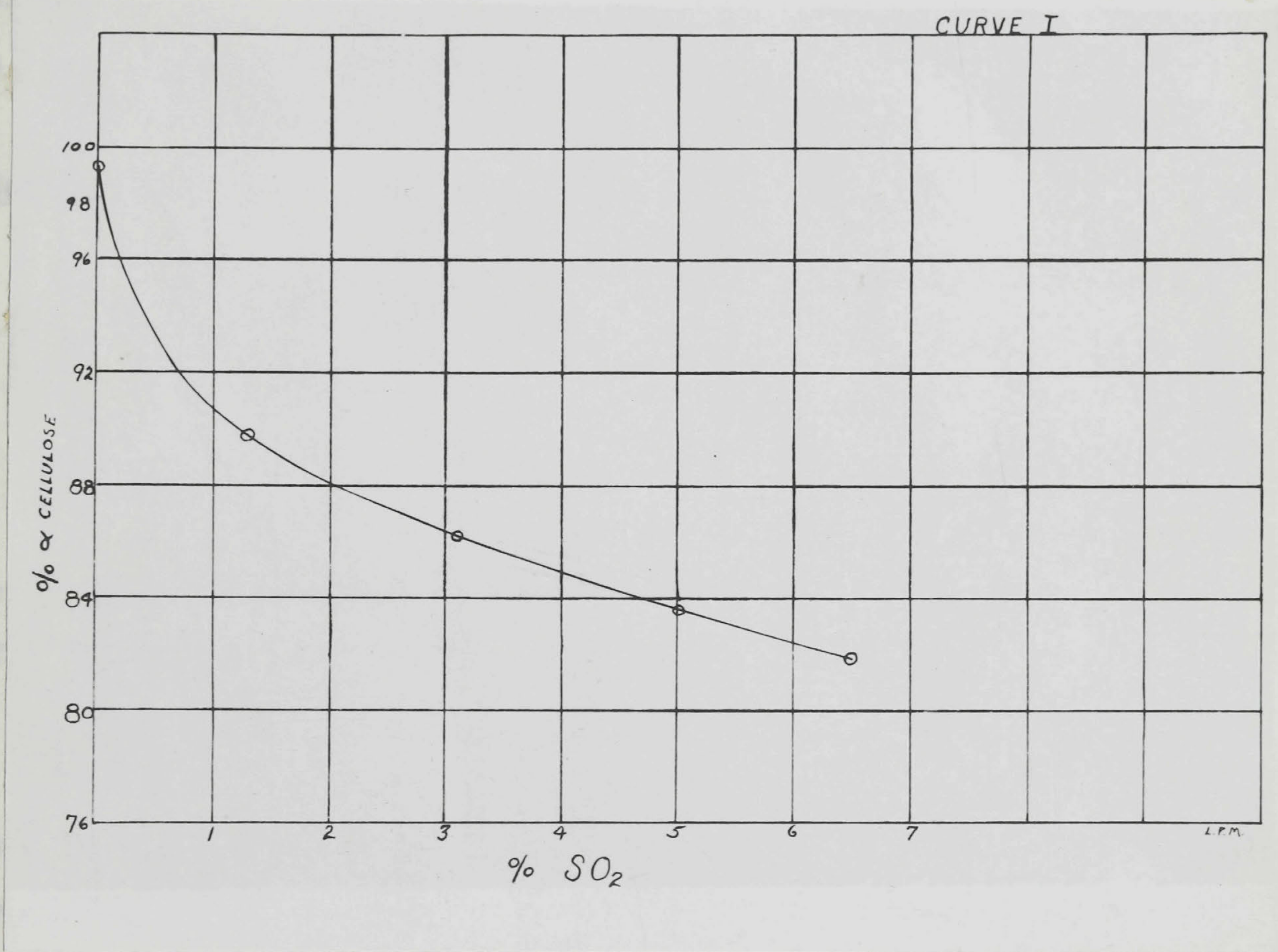
These experiments were all carried out in the glass digester as described above, using a standard grade surgical cotton as the raw material.

Time required to raise the temperature to 100°.	2 hours.
Time, temperature is held at 100°.	7 "
Total time of heating.	9 "
Weight of cotton used per cook.	25-30 grams.
Volume of sulphurous acid used per cook.	400 c.c's.

Alpha Cellulose Results.

Cook No.	% SO_2	% Alpha Cellulose.
13G.	0.48	93.4; 93.3
12G.	0.50	93.2; 93.6
10G.	1.275	89.4; 90.0
19G.	3.10	86.2; 86.9
8G.	5.00	84.0; 83.2
5G.	5.00	83.3; 84.1; 83.5
20G.	6.50	81.9

The variation in alpha cellulose content with the change in the concentration of the acid is shown by graph I.


CURVE I
% α CELLULOSE
100
98
96
92
88
84
80
76
1
2
3
4
5
6
7
% SO_2
L.P.M.

Viscosity Determinations.

(a) Determinations made on the original cotton to check Joyner's Law. The solutions were made in the manner described above, using the standard grade cotton. These samples received no preliminary treatment(i.e. the cotton was not "cooked" with sulphurous acid). The viscosities were determined merely with a view to checking Joyner's Law.

Sample No.	% Cellulose in the Solution.	Viscosity. (poises)	Log $\frac{\eta}{\eta'}$
8.	2%.	8.40	2.8176
6.	3%.	65.60	3.7030
7.	4%.	463.00	4.5517
14.	1.5%.	3.41	2.4176

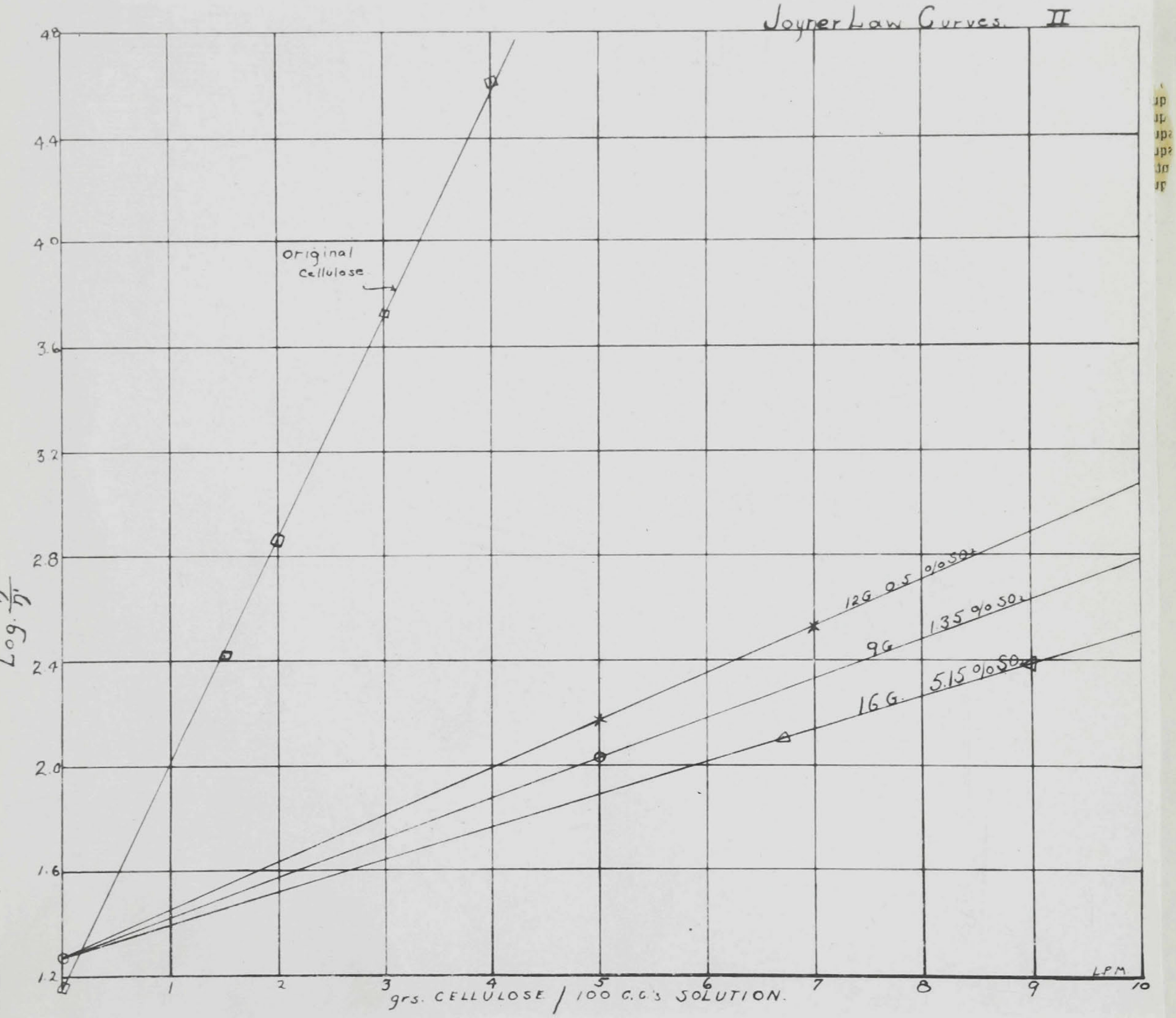
These values are average figures from several runs, with the exception of Sample No. 14 which was run to check the curve. The values are shown plotted on graph II.

(b) Viscosity determinations on degraded cellulose.

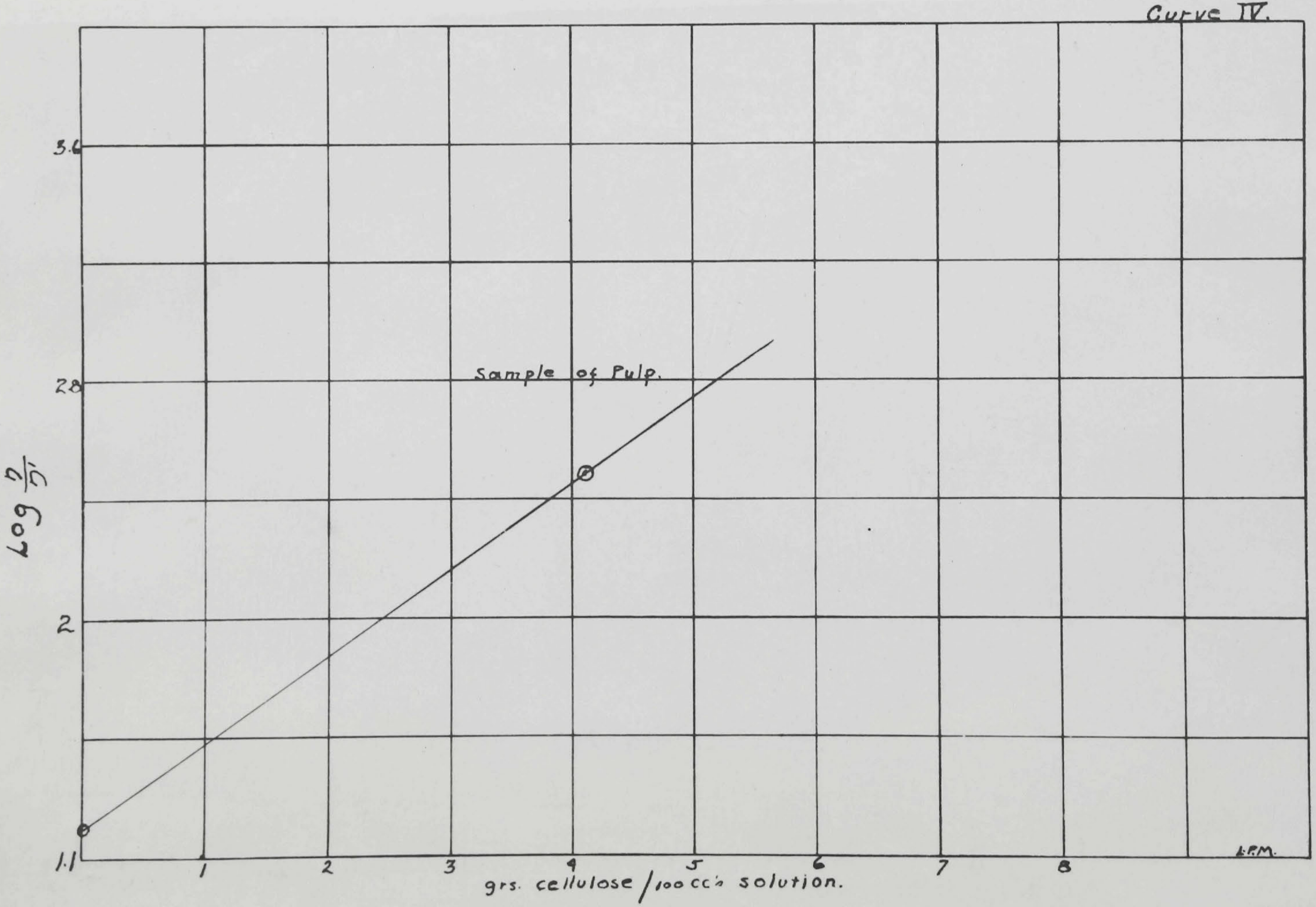
The following table represents the values obtained for the viscosities of the cotton in cuprammonium hydroxide after it had been cooked with various concentrations of sulphurous acid.

Sample No.	Cook No.	% SO_2	% Cell.	Viscosity.	Log $\frac{\eta}{\eta'}$
1.	9G.	1.35	5.0	1.365(poises)	2.0213
2.	12G.	0.50	5.0	1.910 "	2.1671
3.	12G.	0.50	7.0	4.40 "	2.5296
16.	16G.	5.15	6.72	1.64 "	2.1009
17.	16G.	5.15	9.00	3.14 "	2.3830

Joyner Law Curves. II



Curve IV.



Log $\frac{\eta}{\eta'}$
3.6
28
2
1.1
Sample of Pulp.
1
2
3
4
5
6
7
8
grs. cellulose / 100 cc's solution.
L.F.M.

Miscellaneous Results.

The results, listed below, comprise a series of runs, of a more or less miscellaneous nature, made for the sake of comparison with the major portion of the thesis. These runs indicate the lines along which the work, started in this investigation, is to be extended. That is to say, the effect of sulphurous acid on cotton cellulose is to be studied at 110°, 115°, 145°, and later the action of sulphurous acid on pulps of various kinds will be determined as indicated in the introduction to this thesis.

(1). Cook 17G. A sample of surgical cotton was "cooked" with sulphurous acid containing 3.1% SO_2 at 110°. The details of the "cook" were exactly the same as those given above for the work carried out at 100°.

Alpha Cellulose content of the degraded sample:-

77.0%; 78.2%.

Viscosities of this sample were tried as follows:-

An attempt was made to obtain a solution, containing 9% of the degraded cotton, in cuprammonium hydroxide but this was a failure. A 3% solution was then tried and was obtained without any trouble. The viscosity was such, however, that it could not be measured by means of a falling ball.

(2). Cook 14G. A sample of sulphite pulp, (Brown Company's Alpha Pulp.), was digested under the conditions as given above.

Weight of pulp used.	50 grams.
Volume of Sulphurous acid.	400 c.c. (0.566% SO_2)
Temperature.	100 degrees Centigrade.

Alpha Cellulose in original pulp.	95.4%; 95.3%.
Alpha Cellulose after "cooking".	89.5%; 90.8%.

(3). Viscosity determinations.

A solution , of the untreated Brown sulphite pulp, in cuprammonium hydroxide was made containing 2% by weight of pulp. The viscosity of this sample was 4.095 poises.

A 4.1% solution of the"cooked" pulp was made, its viscosity being 9.83 poises.

DISCUSSION AND SUMMARY.

(a). Discussion of alpha cellulose results.

As indicated above, the alpha cellulose determination is a purely arbitrary method of analysis, in that the alpha cellulose content of a given cellulose sample merely represents that part of the material insoluble in 17.5% sodium hydroxide under a certain definite set of conditions. In spite of this empiricism, however, if carefully determined this value represents a factor, on the basis of which, cellulosic materials of various kinds, (cotton, sulphite pulp, etc.), may be compared with each other.

From the experimental work carried out in this investigation, it is to be noted, that the alpha cellulose content of the cotton, used as a raw material, decreases markedly on treatment with sulphurous acid. Under the conditions employed the action of the sulphurous acid liquor is apparently chiefly hydrolytic in character. It would seem therefore that as the hydrolysis proceeds, the original cellulose aggregate is changed into some substance which is soluble in 17.5% caustic, the degree of solubility increasing with the increase in hydrolysis. Accompanying this, a fairly uniform decrease in the length of the cotton fibres was noted and a corresponding decrease in the viscosity characteristics of a solution of the substance in cuprammonium hydroxide. This latter property will be discussed later.

The modification of the cellulose aggregate seems to be of the following type:-

$$(C_6H_{10}O_5)_x \longrightarrow Y(C_6H_{10}O_5)x/Y$$ proceeding ultimately to complete saccharification, glucose being of course the end product. The substance $(C_6H_{10}O_5)_x$ is assumed to represent the compound insoluble in the 17.5% sodium hydroxide. Whether the alpha cellulose values, obtained for the so-called "degraded cellulose", represent the per-cent of unchanged $(C_6H_{10}O_5)_x$ or whether some of the substances of the formula $(C_6H_{10}O_5)x/Y$ are also insoluble, is unknown. It seems hardly correct to assume that some of the cellulose of the form of $(C_6H_{10}O_5)_x$ remains totally unchanged throughout the "cook" but this assumption has to be made unless, on the other hand, it is assumed that cellulose of the formula $(C_6H_{10}O_5)x/Y$ is also insoluble in 17.5% caustic, although, as a matter of fact, certain non-uniformities in the product, as it came from the digester, were noticed. However this is probably due to the method of heating rather than anything else. The length of time of heating and the temperature used are both of such a nature that action must take place on all of the cellulose present. If then this is the case, cellulosic materials of the formula $(C_6H_{10}O_5)x/Y$ are also insoluble in 17.5% sodium hydroxide under the conditions as outlined above and this method of analysis can be used as an indication of the decrease in the state of aggregation of the cellulose molecule. However, at best, it is only a qualitative measure but it certainly indicates some sort of uniform change in the cellulose aggregate.

(b). Effect of Acid Concentration and Temperature.

The effect of changing the concentration of sulphurous acid is indicated on the several graphs. It is to be noted that, relatively, the lower concentrations of acid have more effect than the higher; that is to say the decrease in alpha cellulose content falls off more rapidly at the lower concentrations than it does at the high. The curve,(Graph I.), begins to flatten out at about 3-4% SO_2 but continues steadily downwards over all of the values of acid concentrations investigated.

The effect of temperature is to be taken up in detail in later work and all that can be said here is that a marked decrease in alpha cellulose content is noted for an increase of only 8-10° above the 100° used for the work in this thesis. One "cook" was made using 3.1% SO_2 and increasing the bath temperature to 110°, all other conditions of the"cook" remaining as given above. The alpha cellulose content of this degraded sample was 77.6% as compared with 86.5% of a corresponding (3.1% SO_2) "cook" at the lower temperature. It is well known,of course, that the temperature of 110° represents a critical phase in the preparation of sulphite pulp and it is hoped that further investigation at this temperature, under the conditions as outlined in this paper, will throw some light on the reason for this critical point in the manufacture of sulphite pulp.

The effect of acid concentration and temperature on cellulose has been investigated by Dr.Pokorny (loc.cit.) using sulphuric acid as his degrading agent. The normalities, of the acid solutions used, and the temperatures employed were somewhat different than those made use of in the present work. He found that with diluted acids at higher temperatures, the attack seemed to be much faster on the surface than completely through the fibres. That is to say, a partial hydrolysis takes place on the surface of the fibres, and the consequent formation of cellulosic dextrins, of some sort or other, prevents further action of the acid, the assumption being that a protective coating is formed. Evidence confirming an idea such as this, may be drawn from the fact that in many of the"cooks", carried out in this investigation, small amounts of a brown stain appeared in spots on the fibres. Washing with water removed parts of this color and it all disappeared during the alpha cellulose determination. The effect of higher temperatures or of a "critical" temperature might be to remove some such protecting as this, thus allowing freer action of the acid to all parts of the cellulosic material.

(c). <u>Discussion of Cuprammonium Viscosities</u>.

1.- <u>Cotton</u>. In attempting to determine the viscosities of solutions of the degraded cellulose in cuprammonium hydroxide, it was found that the concentration (3%) of cotton, arbitrarily chosen as a basis for comparison, gave solutions of extremely low viscosities as compared with 3% solutions of the original cellulose. The maximum solubility of the original material was a 4% solution whereas a 4% solution of the degraded cotton could not be measured with a falling ball. In his work, Joyner[11] found that $\log. \eta = \theta C$, where η = the ratio of the viscosity of the solution to that of the solvent, θ is a constant, and C the concentration of the cellulose in the solution. This fact was checked, as shown by graph II., over the complete range of viscosities that could be measured with the instrument available, i.e. from about 3 poises to 500. These values represented concentrations of 1.5 to 4% of the original cotton. Therefore, by obtaining viscosities of two higher concentrations of the degraded material, a 3% value could be obtained by extrapolating the corresponding Joyner Law curve.

This procedure was carried out for several of the "cooks" and the curves on graph II. were thus obtained. It was noted that all three coincided at a common point on the zero concentration line. This point did not check exactly the one for the original cotton but they came very close together. The mean value does not equal the viscosity of the solvent however, which is .013 poises (slightly higher than that of water). The value from the graph was 0.224 poises. Joyner also noted this same fact and he assumes that it probably would be incorrect to use the Arrhenius formula for extrapolating the value for the viscosity of the solvent, but in this case the value obtained for the zero concentration point was a constant over considerable differences in concentration of the cotton and great differences in the viscosities of the solutions. Joyner obtained a value of 0.08 poises for the viscosity of his solvent which is lower than the value given above. This discrepancy arises from the fact that the zero concentration varies with the copper content of the solvent, Joyner using a 1.5% solution whereas the solvent used in the present work contained 3.0% copper.

The point to be noted however, is the fact that the viscosity obtained, for the solvent, by plotting varying concentrations of cotton against the corresponding log., and extrapolating the curves to the zero concentration line, is the same for the degraded samples as for the original cellulose. This indicates that the values obtained are comparative which, in part, was the object of this work, i.e.

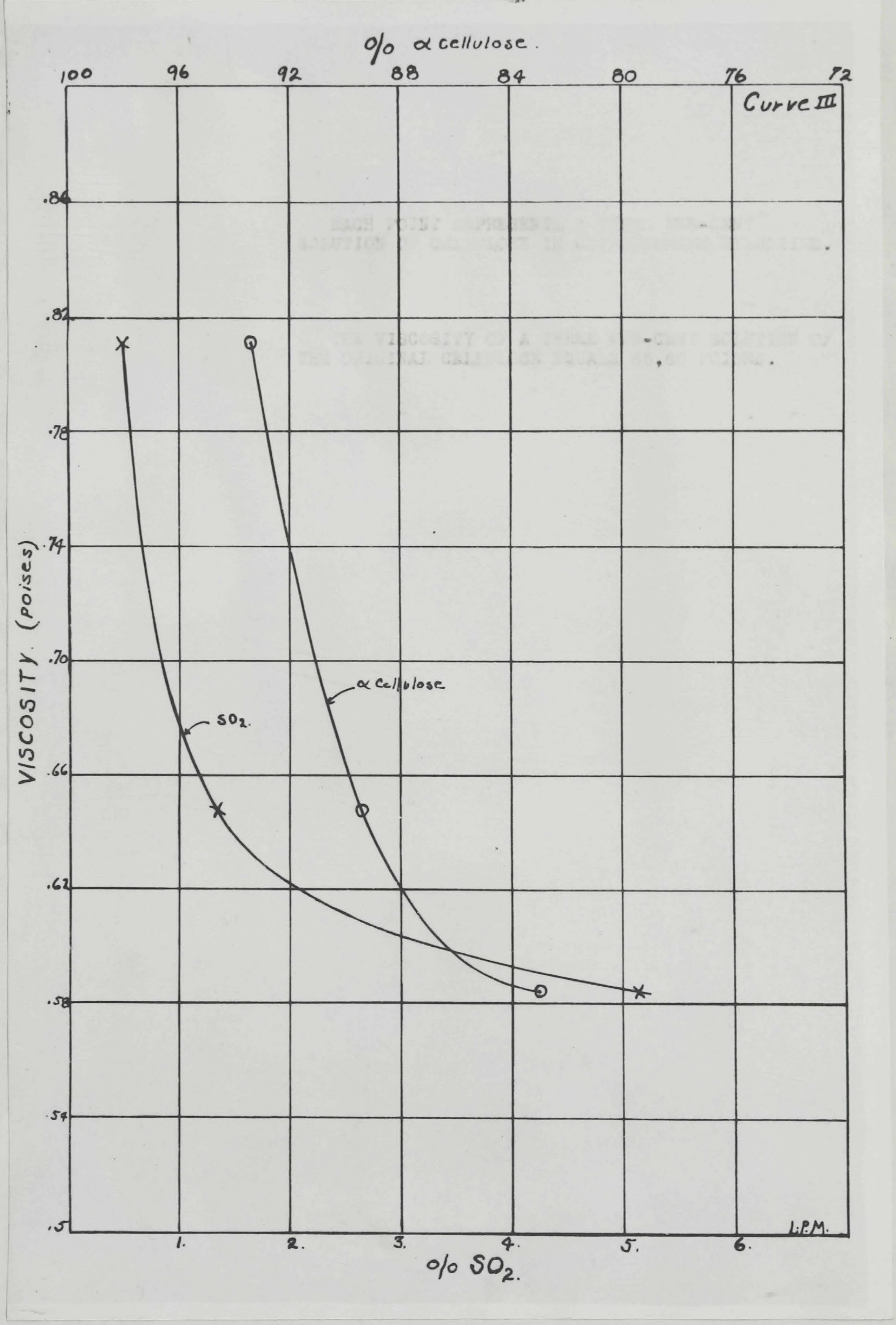
arriving at a method for measuring the degradation of the cellulose and comparing the degraded samples with the original substance.

From graph III., it can be seen that the initial drop in viscosity was extremely great, that is to say, the drop in viscosity of a 3% solution of the original cellulose to that of a 3% solution of the degraded material which had been cooked with 0.5% acid, the latter being the least degraded of any of the samples. After this initial decrease in viscosity, the curve practically parallels the curve showing the lowering of the alpha cellulose content with increased acid concentration.

In attempting to dissolve, or better to disperse, the degraded cellulose in the cuprammonium hydroxide, it was found that above 6-7 grams of cotton per 100 c.c's of solution it was impossible to completely dissolve the sample. At that concentration only a very small quantity, probably a fraction of a per-cent of the total, remained undissolved. At higher concentrations (9%) considerably larger amounts remained undissolved. Values for the viscosities of these suspensions were obtained and they fitted the curves fairly well. Whether or not the values obtained represent true viscosities is of course questionable. Clibbens and Geake[5] report a similar phenomena and they ascribe it to the amount of nitrite in the original cuprammonium hydroxide. While the nitrite, in the solution used, was 1.5% as compared to the 0.5% which they recommend, it is doubtful whether or not this factor was the one responsible for the incomplete solution. For example: Two samples were made up, one a 3% solution and the other a 9% solution both under identical conditions. The 3% went into solution readily and the 9% sample left

Each point represents a 3% solution of cellulose in cuprammonium hydroxide.

The viscosity of a 3% solution of the original cotton equals 65.60 poises.



a residue. An attempt was made to filter the 9% solution with very little success but a part of the undispersed solid was obtained. This, when treated with fresh cuprammonium hydroxide, went into solution without any difficulty. Joyner[11] showed that the amount of cotton dissolving depended on the amount of copper present which is substantiated by the above. That is to say, each gram of copper present will disperse about 2 grams of cotton and no more regardless of the state of polymerization of the cellulose molecule. If then this is the case, and it seems a reasonable conclusion to draw, the viscosities of these solutions, when obtained in a manner that excludes extraneous variables such as the effect of oxygen, light, etc., should provide a measure of the state of polymerization of the cellulose molecule.

(b). Pulp. Viscosity determinations were made on the "cooked" pulp sample 14G. Considering the fact that only one run was made nothing conclusive was shown. The value obtained however indicates that the decrease in viscosity would be less for a pulp than for a cotton sample when treated similarly which is to be expected when the method of preparation of the sulphite pulp is considered.

SUMMARY.

(a). Two standard methods for determining alpha cellulose have been compared and after a suitable modification of one of them this was used as a comparative method of analysis.

(b). A method for determining the viscosity of a solution of cellulose in cuprammonium hydroxide was investigated.

(c). Joyner's Law was checked and applied to the determination of the viscosities of degraded celluloses.

(d). The effect of the action of sulphurous acid at 100° on cotton cellulose was measured by-

1.- The change in alpha cellulose content of the cotton.
2.- The decrease in viscosity of a solution of the cotton in cuprammonium hydroxide.

(e). The inter-relationship of these two factors as a means of evaluating the degradation of pulp is pointed out.

ACKNOWLEDGEMENT.

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