THE JOURNAL OF THE
TEXTILE INSTITUTE

TRANSACTIONS

5—FLUIDITY DETERMINATIONS ON FLAX CELLULOSE

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INTRODUCTION AND SUMMARY

Determination of the fluidity of solutions of cotton cellulose in cuprammonium hydroxide by the simple procedure standardised by Clibbens and his collaborators[1, 2, 3] has become the principal method of estimating the amount of chemical degradation of cotton materials. It has the merit of sensitivity to slight amounts of degradation as well as giving fairly close co-ordination with tensile strength over a wide range of tendering. This agreement with tensile strength holds good for all types of chemical attack provided that the material is previously scoured in alkali in order to reveal the latent tendering induced by certain oxidising agents such as acid dichromate.

Application of the fluidity estimation to flax cellulose has been complicated by the fact that, even after thorough scouring, linen materials contain a small proportion of adhering lignified tissue and epidermis which is insoluble in cuprammonium. Working with medium-grade unbleached linen damask, Butterworth and Elkin[4] found that the insoluble matter amounted to 5·68 per cent., and that this could be reduced to 1·71 per cent. if the cloth was boiled in a 2 per cent. solution of sodium hydroxide before dissolution in cuprammonium. The presence of this insoluble portion might be considered objectionable from three aspects, namely :—

(*a*) The correct concentration of cellulose in the solution is not attained.
(*b*) The viscometer capillary is liable to become choked.
(*c*) The presence of insoluble particles in the solution might affect the observed fluidity even if they were too small to choke the capillary or even if a falling sphere viscometer was used.

For these reasons it has so far been the practice to filter flax solutions before measuring the fluidity and, by weighing the insoluble portion, to apply a correction for cellulose concentration. The sensitivity of cuprammonium solutions to light and air necessitated filtration under an atmosphere of hydrogen and hence the whole estimation became considerably more involved than is the case with cotton. As a result the fluidity determination has not become the accepted routine method of measuring chemical degradation in linen and, instead, the cellulose solubility number described by Nodder[5] is in general use.

The cellulose solubility number involves rather more labour than the fluidity test as applied to cotton, but the apparatus is simple and the procedure is suitable for works use. It has the disadvantage of being insensitive during the initial stages of acid attack and an appreciable strength reduction can be produced without any accompanying increase in the cellulose solubility. Much better correlation with tensile strength is obtained in the

case of oxidative attack and hence its greatest value is for the detection of over-bleaching. However, there seems to be little doubt that for general purposes a fluidity measurement is to be preferred because of the good agreement with tensile strength for all types of chemical tendering and because of the sensitivity during the initial stages of cellulose degradation.

The present paper shows that the disadvantages associated with the insoluble matter in flax do not constitute an insuperable obstacle towards the development of a simple form of fluidity estimation. As far as the concentration correction is concerned, the material may be purified by a 6-hour boil in 2 per cent. sodium hydroxide solution and then assumed to contain .say, 2 per cent. of insoluble non-cellulosic matter. The small error involved in not actually determining the percentage of insoluble matter would be without practical significance, in the same way as it is sufficient to assume a moisture content of 6 per cent. when weighing cotton materials during the fluidity determination. A further justification of this procedure lies in the fact that in determining cellulose solubility it is permissible to assume constancy in the amount of non-cellulosic matter contained in the alkali-scoured material. Most bleached materials would contain even less than 2 per cent. of insoluble matter and the correction need not then be applied. The possible effect of undissolved particles in interfering with viscous flow must be considered, probably not so much on account of the danger of choking the capillary as by the possibility that in a swollen condition they might increase the apparent viscosity of the solution. This effect would be of greatest importance in the case of degraded samples where the viscosity of the cellulose itself is low. Assuming then that filtration is necessary, the problem of evolving a simple form of fluidity determination for flax resolves itself into one of simplifying the previous method of filtration. Filtration under an atmosphere of hydrogen, as described by Kinkead[6] has so far been considered necessary because earlier workers had found that exposure to light and air rapidly increased the fluidity of cellulose solutions in cuprammonium.

The use of a less sensitive solvent than cuprammonium would offer a possible solution to the problem and in this connection Russell and Hood[7] have shown that solutions of cellulose in a 2N aqueous solution of dimethyl dibenzyl ammonium hydroxide are much less sensitive to air and in the present paper this observation is confirmed and it is shown that, using this solvent in place of cuprammonium, flax cellulose solutions can be filtered in presence of air through glass wool in the same manner as the filtration is performed during determination of cellulose solubility number. If dimethyl dibenzyl ammonium hydroxide was less expensive and less tedious to prepare, it might prove to be suitable for routine fluidity measurements on linen but at present its employment seems to be out of the question. Accordingly, experiments were made to explore the possibility of stabilising cuprammonium solutions sufficiently to enable them to be filtered in presence of air without undergoing any significant change in the fluidity.

In the first instance it was established that any changes in fluidity likely to occur during short exposures to light and air, such as would be experienced during the operation of filtering, could for all practical purposes be regarded as due to degradation of the dissolved cellulose rather than to changes in the composition of the cuprammonium. Exposure tests and filtration tests were then carried out on cellulose solutions containing antioxidants and as a result it was shown that pyrogallol is very effective in reducing the sensitivity to light and air. Addition of 0·02 per cent. pyrogallol enables the cuprammonium solution of cellulose to be filtered in presence of air without appreciable change in the fluidity. It is therefore possible to suggest a simplified form of fluidity test for linen which, although slightly more involved than the procedure for cotton, is not any more complicated than the

cellulose solubility number. The material is boiled in 2 per cent. sodium hydroxide solution for six hours and then powdered finely and dissolved in standard cuprammonium in a stoppered test tube. The powder is assumed to contain 2 per cent. insoluble matter and 7 per cent. moisture, and the weight taken is such as to give a $\frac{1}{2}$ per cent. solution of cellulose when the tube is completely filled with cuprammonium. After the cellulose is completely dissolved the requisite amount of pyrogallol, 4 per cent. of the fibre weight, is added and dissolved by shaking the tube for one hour. The solution is then filtered into a B.C.I.R.A. viscometer tube by gentle suction through a glass wool filter. For most purposes it is sufficiently accurate to add the pyrogallol by soaking the boiled and washed material in a 4 per cent. aqueous solution of pyrogallol for 15 minutes, and then air drying without further washing.

EXPERIMENTAL

Dimethyl-dibenzyl ammonium hydroxide

Previous investigators[7, 8, 9, 10], who have studied the cellulose solvent properties of this quaternary base obtained supplies from the Rohm and Haas Co. of Philadelphia, but on enquiry it was learned that the manufacture has now been discontinued. Accordingly, for the present work a small quantity was prepared by the following method:—

A mixture of two molecular proportions of methyl iodide and one of dibenzylamine, the latter prepared from alcoholic ammonia and benzyl chloride, as described by Mason[11], was dissolved in methyl alcohol and allowed to stand at room temperature for five days. At the end of this period the alcohol and any unreacted methyl iodide were distilled off and the residue treated with strong aqueous alkali to liberate unreacted dibenzylamine which was extracted with ether. The residue remaining was impure quaternary iodide and it was purified by re-crystallisation from alcohol and checked for melting point and iodine content. The yield was only 35 per cent. of theoretical but the recovered dibenzylamine, containing some methyl-dibenzylamine, could be reacted with a further amount of methyl iodide. The pure quaternary iodide (M.Pt.191° C.) was shaken with an aqueous suspension of silver oxide at intervals for 48 hours and the mixture filtered through fritted glass and the precipitate washed with warm water. The filtrate was then concentrated to 2N strength by distillation on a water bath at 60° C. under reduced pressure. Using a 20 per cent. excess of silver oxide the yield of quaternary hydroxide was 75 per cent. of the thoeretical amount obtainable from the iodide and this could be improved to 99 per cent. by using a larger excess of silver oxide.

The quaternary base prepared as above was a powerful solvent for cotton and flax and the resulting solutions were very much less affected by light and air than is the case with cuprammonium. Thus it was found that exposure of a 0·5 per cent. solution of grey cotton in cuprammonium for 15 minutes in a K.B.B. fugitometer caused the fluidity to increase from 1·9 to 30·0. With the same yarn dissolved in dimethyl dibenzyl ammonium hydroxide, a 6-hour exposure in the fugitometer was required in order to produce a similar proportional increase in fluidity. Ordinary exposure to air in diffused daylight for short periods had no appreciable effect and filtration could be accomplished without increasing the fluidity by more than 1 per cent. This agrees with the results of Russell and Hood[7], who found that exposure to air for $3\frac{1}{2}$ hours reduced the viscosity by only 4 per cent. There seems, then, to be no objection to the filtering of solutions of flax cellulose in the quaternary base, apart from the fact that the $\frac{1}{2}$ per cent. solutions are extremely viscous when the cellulose is undegraded. When the cellulose concentration is reduced to $\frac{1}{4}$ per cent., the solution can be filtered quite readily through glass wool and this strength was employed to compare the fluidities of the undernoted samples of flax yarn before and after filtering.

A —8½'s lea Pure Flax Tow dry spun, commercially boiled to 10 per cent. alkali solubility.
B —8½'s lea Pure Flax Tow dry spun, bleached ¼ white.
*C*3 —8½'s lea Pure Flax Tow dry spun, acid tendered.
*D*2 —8½'s lea Pure Flax Tow dry spun, hypochlorite tendered.

The acid tendering was carried out by immersing the yarn for 24 hours in 20 per cent. hydrochloric acid at 20° C., and the hypochlorite tendering by treatment with sodium hypochlorite (0·3 per cent. available chlorine and *p*H 11) at 20° C. for 24 hours. Before determining the fluidity all of the samples were boiled for 6 hours in 2 per cent. sodium hydroxide solution and then washed thoroughly and air dried at ordinary temperature. In calculating the weight of powdered yarn necessary to give a ¼ per cent. solution of cellulose it was assumed that the yarn contained 2 per cent. insoluble matter and 7 per cent. moisture.

The fluidity was first determined without filtering and then the same solution was filtered and the fluidity measurement repeated. The results are shown in Table I.

Table I

Sample	Cellulose solubility number	Fluidity of ¼% solution in dimethyl dibenzyl base	
		Unfiltered	Filtered
A	2·2	Too viscous to measure	
B	3·5	1·15	1·19
C3	6·8	2·72	2·79
D2	9·5	2·65	2·51

The results in Table I show that filtration has not caused any marked increase in fluidity and this confirms the stability of the solution to light and air while at the same time it indicates that removal of the insoluble matter may not be necessary if the material has received a preliminary scour. Reduction of the cellulose concentration to ¼ per cent. has been accompanied by an inevitable loss of sensitivity to small amounts of degradation and even at this strength the solutions of undegraded material are too viscous for the standard cotton viscometer.

The difficulty in obtaining supplies of dimethyl dibenzyl ammonium hydroxide coupled with the high viscosity of its cellulose solutions constitute serious practical disadvantages to the use of this solvent for flax and so consideration was given to the problem of improving the stability of cuprammonium solutions to light and air.

Cuprammonium

Effect of light and air. Table II shows the effect of exposing ½ per cent. solutions of undegraded cotton in standard cuprammonium to light and air in various ways. During such exposure the solutions were contained in a standard capillary viscometer tube and the admission of air was brought about by running out some of the solution until the liquid level was ¼ inch above the top mark of the viscometer.

Table II

Method of exposure	Fluidity of solution at 20° C. after exposure
Unexposed	1·8
Air admitted 2 hours in dark, not shaken	2·8
,, ,, ½ ,, ,, ,, ...	1·8
,, ,, 4 ,, ,, shaken continually	3·5
,, ,, 4 hours in diffused daylight, shaken continually ...	7·0
,, ,, solution exposed 1 hour in KBB fugitometer	47·8
,, ,, ,, ,, ¼ ,, ,, ,, ...	26·1
Air not admitted, solution exposed 1 hour in KBB fugitometer ...	42·1

The extensive change in fluidity produced by exposure to the carbon arc is noteworthy and must be presumed due to the action of ultra-violet light rather than to development of heat in the solution because when a tube of undegraded cellulose solution was covered with a thin black cloth and then exposed in the fugitometer, the fluidity rose to only 2·5 after ¼ hour. Confirmation was obtained by admitting air to another tube of undegraded cellulose solution and heating it in the dark at 30° C., the maximum temperature reached in the fugitometer, for ¼ hour. The fluidity was found to be unaffected at 1·6. The fact that light causes a large increase in fluidity even without admission of air suggests either that the action of light is independent of the presence of air or that sufficient air is contained in solution. From the results recorded it seems that the solution of cellulose in standard cuprammonium is not particularly sensitive to air in the absence of light.

The increase in fluidity which occurs when the cellulose solution is exposed to light and air could be regarded as due to one or more of the following factors :—

(*a*) degradation of the cellulose ;
(*b*) changes in the cuprammonium itself affecting its solvent properties ;
(*c*) changes in the cuprammonium itself affecting its own fluidity.

It can be readily demonstrated by examination of the regenerated cellulose, that extensive degradation of the cellulose does in fact take place when the solution is exposed to ultra-violet light. In one experiment air was admitted to a viscometer tube containing a solution of undegraded cellulose until the liquid level was ¼ in. above the top mark. The tube was then inverted four times, placed in a vertical position just inside the ring of test spaces in a KBB fugitometer and exposed to the light for 15 minutes. At the end of this period the tube was removed, again inverted four times and allowed to cool in the dark for 30 minutes from approximately 30° C. to 20° C. The solution then had a fluidity of 30 and the regenerated cellulose from this solution gave the usual reactions of a degraded cellulose and, in addition, it had a fluidity of 36 when dissolved in fresh cuprammonium and the fluidity determined in the standard manner. In comparison it was found that the cellulose regenerated from an unexposed solution had a fluidity of only 3·5 when re-dissolved.

To determine the effect of factor (*c*), air was admitted to a tube containing cuprammonium itself, without dissolved cellulose, and it was found that exposure to the fugitometer for 15 minutes increased the fluidity from 70·8 to 73·5, which comparatively small change is of little importance.

Factor (*b*) is more likely to have an appreciable effect because it is well-known that changes in the composition of the cuprammonium can affect the cellulose fluidity, quite apart from the possibility of cellulose being precipitated from solution. To determine whether exposure to light and air caused such changes, solutions of undegraded cotton were made from ordinary cuprammonium and from cuprammonium which had previously been exposed. Comparative fluidity measurements were then made and the results are shown in Table III.

Table III

Method of exposure of solvent	Observed fluidity of undegraded cotton
Unexposed	1·6
Exposed 15 minutes in fugitometer	1·7
Shaken with air 4 hours in dark	2·1
,, ,, ,, 4 ,, ,, diffused daylight	2·1
Filtered twice at the pump	1·6

Shaking with air has produced a slight change in the cuprammonium affecting its solvent properties but this change, presumably due to oxidation of some of the ammonia, seems not to be influenced by light. However, the alteration in fluidity resulting from exposure of the solvent is small in comparison with the increase in fluidity caused by exposing the cellulose solution. The latter may therefore be regarded for all practical purposes as being due to degradation of the cellulose. Speculation upon the reason for the lower susceptibility to oxidation when the cellulose is dissolved in dimethyl-dibenzyl ammonium hydroxide suggests that the metal in the copper cellulose complex exerts an acceleration on the degrading action of light.

Addition of antioxidants. Although it has been shown that in the absence of bright light the cellulose solution in cuprammonium is not very greatly affected by short exposures to air, yet it is not sufficiently stable to make reliable fluidity determinations after filtering the ordinary solution in presence of air. The possibility arises that if an antioxidant was added it might be possible to reduce to negligible amount the oxidation occurring during a short exposure. Accordingly fugitometer exposure tests were carried out with solutions of undegraded cotton in cuprammonium containing small proportions of antioxidants. To facilitate dissolution in cuprammonium the various substances were applied in 2 per cent. alcoholic solution to the cotton yarn before powdering the latter and the solutions were then exposed for 15 minutes in the fugitometer as already described. Fluidity measurements were then made and the results are recorded in Table IV.

Table IV

Antioxidant	Fluidity after exposure
(Untreated control)	30·0
Thiourea	16·1
Diphenylthiourea	19·4
Allyl thiourea	19·7
Benzidine	21·3
Diphenylamine	26·0
Carbazole	26·6
Catechol	30·1
Hydroquinone	9·4
Pyrogallol	6·7
Gallic acid	22·4
Protocatechuic acid	29·4

The protection afforded by pyrogallol is very striking, especially in view of the small amount added, i.e., 2 per cent. of the fibre weight or 0·01 per cent. of the solution. Further experiments were then carried out to test its effect during the process of filtration in air and the results are shown in Table V.

Table V

Pyrogallol concentration in solution	Method of exposure	Observed fluidity of undegraded cotton
%		
0·02	Unexposed	1·6
0·01	Air admitted, shaken in dark, 4 hours	2·6
0·02	" " " " 4 "	1·6
0·03	" " " " 4 "	1·9
0·01	" " shaken in daylight, 4 hours ...	3·3
0·02	" " " " 4 "	1·9
0·03	" " " " 4 "	1·9
0·01	Filtered at the pump...	2·3
0·02	" " "	1·7
0·03	" " "	1·7
Nil	" " "	2·3

It is very clear that at and above 0·02 per cent. concentration the presence of pyrogallol enables the solution to receive fairly severe exposure to light and air without concomitant degradation of the dissolved cellulose. That this effect is not merely due to the pyrogallol increasing the viscosity and so masking any degradation is shown by the fact that in Table V the unexposed solution containing pyrogallol gives a normal fluidity. Fluidity tests were also carried out on unexposed solutions of a degraded cellulose, with and without pyrogallol, and the results were 26·6 and 26·1 respectively, thus confirming that pyrogallol has no tendency to lower the fluidity and that its effect during exposure of a solution must constitute protection of the cellulose against oxidation.

It is reasonable to expect that similar protection would be exerted in the case of flax cellulose and that the presence of pyrogallol would enable solutions of linen materials in standard cuprammonium to be filtered without risk of degradation. For confirmation, fluidity determinations were made on samples of $8\frac{1}{2}$'s lea flax tow yarn, dry spun, and the results are shown in Table VI. All samples were boiled for 6 hours in 2 per cent. sodium hydroxide solution and 0·02 per cent. of pyrogallol was added after the cellulose had dissolved. The fluidity was first measured without filtration and for most of the samples the same solution was then filtered and the fluidity again measured.

Table VI

Sample	Cellulose solubility number	Fluidity	
		Before filtering	After filtering
A —boiled	2·2	1·4	1·5
B —$\frac{1}{4}$ white	3·5	3·5	3·4
C1 —acid tendered	2·9	5·0	4·7
C2 — ,, ,, ...	3·9	7·3	—
C3 — ,, ,, ...	6·8	12·1	12·1
D1 —hypochlorite tendered	7·9	7·0	6·5
D2 — ,, ,, ...	9·5	11·9	—
D3 — ,, ,, ...	18·7	23·5	22·6

The close agreement between the fluidities before and after filtration is of great interest and confirms the effect of pyrogallol in inhibiting degradation of dissolved cellulose. Table VII shows that there is no loss of ammonia during filtration and hence there is no possibility of degradation being masked by a decreased fluidity caused by loss of ammonia.

Table VII

Solution	Ammonia content (grams per litre)	
	Unfiltered	Filtered through glass wool
Standard cuprammonium	191	190
Solution containing 0·5% cotton (fluidity 1·8)	191	188
Solution containing 0·5% cotton (fluidity 28·0)	191	193

It is evident that the cuprammonium fluidity of flax cellulose can be determined in a simple and reliable manner by scouring the material in 2 per cent. sodium hydroxide before powdering and by including 0·02 per cent. freshly added pyrogallol in the solution to prevent any change in fluidity of during filtration. For greatest accuracy the pyrogallol should be added after the cellulose is dissolved so that its weight is not included along with the weight of powdered material. However, for most purposes it would suffice to immerse boiled samples in a freshly made 4 per cent. solution of pyrogallol

for 15 minutes and then squeeze off excess and air dry at ordinary temperature without washing.

The powdered material should be dissolved in standard cuprammonium in a completely filled stoppered test tube, the volume of which has previously been accurately determined so that the weight of powder necessary to give a 0·5 per cent. solution may be ascertained. The powder may be assumed to contain 7 per cent. moisture, 2 per cent. insoluble matter and 4 per cent. pyrogallol while, if the material is fully bleached, the correction for insoluble matter could be omitted. The capacity of the tube should be approximately 25 c.c., and a small cylindrical piece of iron is added to mix the contents while the tube is being shaken overnight on a slowly revolving wheel.

The solution is filtered into a B.C.I.R.A. capillary viscometer through a glass wool or coarse fritted glass immersion filter attached to a glass tube leading through a rubber stopper inserted in the wide end of the viscometer and gentle suction applied by means of a vacuum pump connected to the capillary end of the viscometer. Using 0·5 gram of glass wool packed into a suitable tube so as to form a column 2 cms. long by 1 cm. in diameter, it was found that even the most viscous solutions can be filtered in five minutes under gentle suction. The addition of pyrogallol darkens the colour of the cuprammonium and it is rather difficult to observe the clarity of the filtered solutions but judging from the appearance of flax solutions not containing pyrogallol the insoluble matter is effectively removed by glass wool. After filtration the fluidity is determined in the manner standardised by Clibbens and co-workers (*loc. cit.*).

The fluidity method which has been outlined involves slightly more labour than the standard determination applied to cotton but it can be performed just as rapidly as the cellulose solubility number and involves no special apparatus apart from the calibrated viscometer tubes. Its chief practical advantage over the cellulose solubility number lies in the greater sensitivity during the initial stages of degradation while the ability to detect the early stages of acid tendering, clearly shown in Table VI, is of much practical importance in the investigation of faults.

As far as cotton is concerned the present standardised fluidity determination seems to be generally satisfactory although Berl[12] considers that the cuprammonium solution of cellulose is too sensitive to light and air and prefers to estimate the viscosity of the nitrocellulose in acetone. The use of pyrogallol with cotton solutions should be advantageous in special cases, for example, where there is a possibility that the ordinary daylight might be strong enough to cause degradation during the period of flow of the solution through the viscometer.

Acknowledgments are made to the Directors of The Gourock Ropework Co., Ltd., for permission to publish this paper.

REFERENCES

[1] Clibbens and Geake. *J. Text. Inst.*, 1928, **19**, T77.
[2] Clibbens and Ridge. *J. Text. Inst.*, 1928, **19**, T389.
[3] Clibbens and Little. *J. Text. Inst.*, 1936, **27**, T285.
[4] Butterworth and Elkin. *J. Text. Inst.*, 1933, **24**, T10.
[5] Nodder. *J. Text. Inst.*, 1931, **22**, T416.
[6] Kinkead. *J. Text. Inst.*, 1931, **22**, T411.
[7] Russell and Hood. *Ind. Eng. Chem.* (*Anal.*), 1942, **14**, 202.
[8] Russell and Woodberry. *Ind. Eng. Chem.* (*Anal.*), 1940, **12**, 151.
[9] Brownsett and Clibbens. *J. Text. Inst.*, 1941, **32**, T32.
[10] Brownsett and Clibbens. *J. Text. Inst.*, 1941, **32**, T57.
[11] Mason. *J.C.S.*, 1893, **63**, 1311.
[12] Berl. *Ind. Eng. Chem.* (*Anal.*), 1941, **13**, 326.