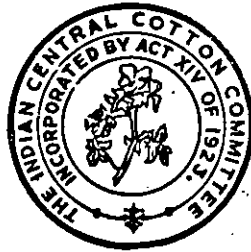


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Ripeness of Viscose Caused by
Addition of Reagents.

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CHANGE IN VISCOSITY AND LOSS OF VISCOSITY CAUSED BY ADDITION OF REAGENTS

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Degradation of the micelle is the only known means of lowering the viscosity of a solution of cellulose or of its compound. Scherer and Leonards, however, reported that small additions of certain reagents lowered the viscosity of viscose solutions without affecting the micellar dimensions. In view of the great industrial advantages that could accrue from such a development, the effect on the viscose solution of 16 different reagents was studied. Of these only 3 viz., pyridine, sodium sulphite and sodium nitrite succeeded in lowering the viscosity of the viscose, others having either no appreciable effect or an adverse one. The lowering of viscosity appeared to be a function of the amount of chemicals added. No attempt was, however, made to explore optimum condition, as it was found in the meanwhile that the viscose solution, whose viscosity was lowered in this manner, did not become ripe in the normally allotted time and had to be ripened longer, during which time the viscosity went on rising. The ultimate result was that what was gained by the lowering of the viscosity, was virtually lost by the reduction in the ripening speed except for a negligible resultant advantage of 2—3% lowering in viscosity under optimum conditions.

The work, conducted under the auspices of the Indian Central Cotton Committee, envisaged the use of chemical cotton as a base for manufacturing rayon by the viscose process. Chemical cotton, particularly when it is purified with care, possesses a much higher viscosity than the ordinary rayon pulp. It is an established fact that rayon, produced from a high viscosity viscose, is stronger than that produced from a low viscosity one, but the high viscosity of viscose presents technical difficulties, particularly with regard to filtration and spinning, which have yet to be surmounted. Thus, although the yarn qualities make the use of high viscosity viscose desirable, the limitations of our present day technique of manufacturing rayon do not permit it. Under the circumstances it appeared as though there was no alternative but to degrade chemical cotton intentionally, in order just to make it fit for viscose manufacture.

At this juncture, a very interesting article by Scherer and Leonards¹ on "Change in viscosity of viscose by addition of reagents" appeared. This apparently was the very first attempt to lower the viscosity of the viscose through a selective absorption by the xanthate particle of the reagent, which would then form part of a colloidal particle aggregate, less lyophilic than the original xanthate particle, without causing any damage to the structure of cellulose. The only reagent, which was found by the authors to thus reduce viscosity, was pyridine. The idea, however, was fascinating and was followed

up in the hope of avoiding the need of degrading the high grade cellulose in order to make it technically fit for rayon manufacture. Unfortunately, however, the hope has been frustrated to a very great extent by the findings reported in this paper, as the degree of ripeness was overlooked by the American workers.

EXPERIMENTAL

Procedure.—A sample of cut chemical cotton was mercerised in 18% caustic soda solution for 2 hours at 18° C. with 1 : 15 bath ratio. The mercerised cellulose was then pressed to three times its dry weight and shredded in a specially constructed disintegrator for 1 hour, to give it the desired fluffiness. These alkali cellulose flakes were then allowed to ripen for 4 days at 18° in a closed bottle.

The ripened alkali cellulose was then xanthated in large glass bottles, which were rotated during the entire period of reaction, keeping the reaction conditions uniform for all the series of xanthations reported in this paper.

The cellulose xanthate, thus obtained, was then dissolved in 3% caustic soda solution, 10 times the weight of dry cellulose. The resulting viscose was each time subdivided into 4 different bottles. To three of these bottles were added measured quantities of the reagents under test, whereas to the fourth was added an equal quantity of distilled water to ensure for a uniform concentration in each bottle. The viscosity, as also the degree of ripening, were then measured as shown in the tables and the change brought about in these characteristics by the reagents calculated on the basis of the viscose containing no reagent.

The viscosity of the viscose was measured by the falling-sphere method and the degree of ripeness by addition of a 10% ammonium chloride solution. As the actual values for viscosity in terms of seconds of the original (to which no reagent is added) xanthate solutions of the various series were not uniform, it appeared more useful and instructive to record the changes not in actual time measured but in the percentage rise or fall in viscosity brought about by the reagent as compared with the original one. Gelling time has also been recorded in case of the first two tables.

The quantity of the reagent added to the viscose has been expressed in terms of percentage on the weight of viscose. Wherever solutions are used, the percentage is expressed in terms of the active reagent itself, excluding water.

Table I below shows the effect on the viscosity of viscose, caused by 16 different reagents, organic as well as inorganic. The first 5 of these have caused a reduction in viscosity and extended the gelling period. The following 3, namely, Nos. 6-8 have practically no effect on viscosity, but they too extend the gelling period appreciably. The next two *i.e.* Nos. 9 and 10 influence neither the viscosity nor the gelling period. No. 11 registers a small fall in viscosity followed by a small rise but without any effect on the gelling period. The last five reagents, represented by Nos. 12-16, show a definite rise in viscosity accompanied by a shortening of the gelling period except in case of No. 12, which has no effect on the latter property.

TABLE I

Change in viscosity of viscose by addition of reagents

No.	Chemical added.	% Addition on wt. of viscose.	% Lowering in viscosity after		Estension or shortening of gelling period** by number of days.
			5 days.	8 days	
1.	Pyridine	0.53	2	..	1 day more
2.	Na ₂ SO ₃	0.033	2	..	2 days ..
3.	NaNO ₂	0.014	4	8	2
4.	*Tetrachloroethylene	0.4	5	..	1 day ..
5.	Acridine in pyridine (sat.)	1.4	3	10	2 days ..
6.	*Toluol	0.4	Negligible	Negligible	1 day ..
7.	Urea	0.033	2
8.	KH ₂ PO ₄	0.033	2
9.	*CCl ₄	0.4	No change
10.	<i>cyclo</i> Hexanone	0.4	Do.
11.	Acetonitrile	1.0	1	(rise in viscosity)	Do.
12.	Amyl acetate	0.4	6	7	Do.
13.	40% Formaldehyde	0.16	34	..	4 days less
14.	Chloroform	0.4	26	48	2
15.	Ethylene chloride	0.4	87	..	4
16.	Dichlorhydrine (1:2)	1.25	8

* These chemicals are not miscible with viscose.

** The gelling period in case of the viscose to which no reagents were added was generally found to be 11 days.

Table II reproduces the effect of the quantity of the reagent on the reduction in viscosity of viscose in case of the first 3 numbers of Table I, tetrachloroethylene having been discarded as it is not miscible with viscose, and acridine, because the solvent used is pyridine which itself is being tested.

TABLE II

Quantitative effect of certain reagents on the change in viscosity of viscose

No.	% Addition on wt. of viscose.			Extension or shortening of gelling period.	% Addition on wt. of viscose.			Extension or shortening of gelling period.	% Addition on wt. of viscose.			Extension or shortening of gelling period.
	5 days	8 days	10 days		5 days	8 days	10 days		5 days	8 days	10 days	
	A. Pyridine.				B. Sodium sulphite.				C. Sodium nitrite.			
1	0.53	2	—	1 day more	0.033	2	—	2 days more	0.014	4	8	2 days more
2	0.66	2	8	„ „	0.084	4	10	„ „	0.23	5	10	„ „ „
3	1.33	3	10	2 days „	0.42	9	16	3 „	—			

The obvious conclusion from the data presented in Table II would be to carry on these tests with increasing quantities of the reagents concerned as long as the reduction of viscosity continues. But, since the degree of ripening is an important factor in spinning, and in view of the fact that the viscose under normal spinning conditions should have a degree of ripening, as determined by 10% ammonium chloride solution, of the magnitude of 8-10, it was decided at this stage to observe the effect of the degree of ripening of viscose caused by the addition of these three reagents which affect the viscosity favourably. Table III reproduces the change in degree of ripening of viscose brought about by these chemicals added in varying quantities.

TABLE III

Change in the degree of ripening of viscose caused by the addition of varying quantities of certain reagents.

% Addition on wt. of viscose.	Degree of ripening after			% Addition on wt. of viscose.	Degree of ripening after		% Addition on wt. of viscose.	Degree of ripening after	
	4 days	5 days	6 days		4 days	5 days		4 days	5 days
1. Sodium sulphite.				2. Sodium nitrite.			3. Pyridine		
Nil.	16.0	8.0	5.4	Nil.	10.0	6.0	Nil.	10.0	6.5
0.42	27.0	15.5	8.0	0.23	9.0	6.0	0.66	13.0	8.5
0.84	27.0	15.5	8.5	0.46	9.5	6.0	1.32	13.0	8.5
1.22	27.0	15.5	8.0	0.69	8.5	5.5	1.98	10.5	7.0

It is clear from Table III that the degree of ripening does not remain unchanged, the magnitude of the change from the original viscose depending upon the type of reagent, as also upon the amount of the same reagent added to the viscose. In view of this fact it was thought proper to measure both the viscosity as well as the degree

of ripening on the same viscose before drawing any conclusion from data so far obtained. The variations observed in these two properties, as a result of the addition of pyridine and sodium nitrite in different quantities, are reproduced in Table IV. Sodium sulphite was discarded from these experiments as it is clear from Table III that it slows down the process of ripening to such an extent that no advantage could be expected from the reduction in viscosity caused by that reagent. Each number denotes a separate series, in which the same viscose is used for tests.

TABLE IV

Change in viscosity and degree of ripening of viscose caused by addition of reagent.

No.	Chemical added.	% Addition on wt. of viscose.	4 Days after xanthation		5 Days after xanthation	
			% Lowering in viscosity.	Degree of ripening.	% Lowering in viscosity.	Degree of ripening.
A.						
1	Nil	15.5	..	9.0
	Pyridine	0.5	2	20.0	4	12.0
	Sodium nitrite	0.086	3	15.5	3	9.5
2	Nil	18.0	..	10.5
	Pyridine	1.0	4	22.0	4	12.5
	Sodium nitrite	0.17	3	18.5	3	10.0
3	Nil	14.5	..	8.5
	Pyridine	2.0	3	18.5	4	9.5
	Sodium nitrite	0.34	2	14.0	1	8.0
4	Nil	13.0	..	8.0
	Pyridine	3.0	3	18.0	1	12.0
	Sodium nitrite	0.62	Negligible	12.0	1% Rise	7.5
5	Nil	15.0	..	9.0
	Pyridine	4.0	3	21.0	7	14.0
	Sodium nitrite	0.69	Negligible	15.5	1% Rise	9.0
B.						
1	Nil	7.5	..	5.5
	Pyridine	2.0	3	9.0	3	6.0
	Sodium nitrite	0.17	3	7.5	5	5.5

DISCUSSION

Scherer and Leonards¹ have shown that the addition of pyridine to viscose reduces its viscosity. They have also shown that the reduction in the viscosity of viscose is directly proportional to the quantity of the reagent added, of course, up to a certain limit. This observation has been substantiated by the present work. It has further been found that not only an organic substance like pyridine with its unwelcome odour and with its narrow limit of miscibility, but harmless inorganic substances like sodium sulphite and sodium nitrite, which can be added in any quantity to the viscose, also bring about the desired reduction in the viscosity, as can be seen from Table I.

Moreover, it can safely be deduced from Table I that those chemicals, which reduce the viscosity of viscose, necessarily extend the gelling period, while those which increase the viscosity contribute to the shortening of the gelling period. What is, however, likely to prove valuable to the industry is the observation that certain chemicals, such as urea, bring about an extension of the gelling period although they have practically no influence on viscosity. This point needs close study from the industrial point of view, not only because the extension of the gelling period is a desirable feature, but also because of the possibility of the yarns made from such viscose exhibiting special properties.

Table II represents a quantitative study of the effect of addition of pyridine, sodium sulphite and sodium nitrite on the viscosity of viscose. Whereas pyridine and sodium nitrite bring about approximately the same reduction in viscosity, within the range of experiments, sodium sulphite causes considerably greater reduction in the viscosity than the other two. If reduction in viscosity were the only criterion to evaluate these reagents, sodium sulphite would decidedly be preferable to pyridine, as the same reduction in viscosity can be achieved by a much smaller quantity of the former than of the latter, which can moreover be added to any extent.

But does a mere reduction in the viscosity of viscose by itself mean an advantage from the technical point of view? It is well known that the spinning of rayon is not regulated by the viscosity of the viscose alone. The degree of ripening is a factor which cannot be neglected, as it is in all probability of even greater importance than viscosity in view of the fact that it determines the coagulation velocity of the viscose during the process of spinning. The reduction in viscosity, to be real, must therefore be obtainable to the maximum extent at a point when the viscose has attained the degree of ripen-

ing essential for spinning, say about 8-10. According to Scherer and Leonards¹, addition of 5% pyridine brings about a reduction of 30% in the viscosity of viscose after 316 hours. But this gain is certainly not real, as the degree of ripening does not remain unaffected by the presence of the reagent in the viscose.

Table III reproduces the effect of the three reagents under consideration on the process of ripening. Each of them behaves differently. Sodium sulphite very considerably reduces the speed of ripening, thereby showing clearly that what is gained by way of reduction in viscosity is lost by way of reduction in the speed of ripening, the net gain being that the viscose can be spun a day or two later. It deserves to be noted that the effect on the degree of ripening is independent of the quantity of sodium sulphite added to the viscose, whereas the effect on viscosity is a function of the quantity added. Sodium nitrite has practically no effect on the speed of ripening, while pyridine retards the speed of ripening up to an addition of 2%, at which concentration the speed of ripening remains more or less unaffected. The effects of still higher concentrations of pyridine on the degree of ripening of viscose will be seen from Table IV, which also gives the change in viscosity.

Let us first observe the effect of pyridine on viscosity and speed of ripening the viscose, as depicted by Table IV (A). After a lapse of 5 days, when the blank attains the degree of ripeness necessary for spinning, the viscose containing varying quantities of pyridine is found to be definitely lagging behind in ripeness. Only in case of 2% pyridine, the degree of ripeness is more or less the same as that exhibited by the blank, but on either side, *i.e.* at lower as well as at higher concentration of pyridine, there is a distinct fall in the speed of ripening of viscose. Turning to the effect on viscosity, it will be observed that at this ripening period only 4% reduction in viscosity is achieved except in the case of 4% pyridine, which shows a higher reduction *i.e.* 7% in viscosity, but a degree of ripeness, not sufficiently advanced for spinning. If, however, this viscose is allowed time to attain the required degree of ripeness, the gain in the form of reduction of viscosity would vanish, as the viscosity, which is a function of time, would not stand stationary but go on increasing until gelling takes place. It follows therefore that only that reduction in viscosity, which is obtainable at the technically essential ripeness of viscose, denotes the real gain. The optimum concentration for pyridine therefore is 2% and the reduction in viscosity of viscose brought about by that quantity of pyridine is 4%.

Sodium nitrite has no effect on the speed of ripening, as the degree of ripening, attained by viscose containing varying quantities of this reagent, shows the same degree of ripening as the blank. This being the case, the optimum concentration of sodium nitrite would be what gives the maximum reduction in the viscosity of viscose. It will be seen from Table IV (A) that the maximum reduction in viscosity is attained at 0.17% concentration and its magnitude is only 3%, of course at the time when the viscose is ripe for spinning. A further rise in concentration of the reagent has a reverse effect on viscosity and has therefore to be avoided. The optimum concentration for sodium nitrite is therefore 0.17% and the reduction brought about in the viscosity of viscose at that concentration is only 3%.

In a fresh series, reproduced in Table IV (B), both these reagents, viz. pyridine and sodium nitrite were added in optimum concentration to the same viscose and their effect on the viscosity and degree of ripening observed under identical conditions, when the viscose had attained the technically required degree of ripening. The net gain is the same in both cases, viz. 3% reduction in viscosity of viscose. Apparently this is not an attractive finding for the industry.

SUMMARY

The change in viscosity of viscose brought about by the addition of 16 different reagents was observed. Only the following three were found to reduce the viscosity:—

(a) Pyridine, (b) sodium sulphite and (c) sodium nitrite. The reduction in viscosity was found to be a function of the ripening period as also of the quantity added. The maximum reduction in viscosity was found to lie near 8% in case of pyridine and near 0.23% in that of sodium nitrite. The maximum was not ascertained in case of sodium sulphite, which definitely reduced viscosity to a much greater extent than the other two reagents.

But in view of the fact that the reduction in viscosity does not by itself denote any gain unless it is obtainable at a stage when the viscose is ripe for spinning, the determination of the degree of ripening was brought into the scope of this investigation and the effect on the speed of ripening of viscose due to the addition of pyridine, sodium sulphite and sodium nitrite, was ascertained. Pyridine at 2% concentration had practically no effect on the speed of ripening but at either higher or lower concentrations it did retard the speed of ripening appreciably; sodium sulphite effected a very considerable retardation of the speed of ripening, irrespective of concentration; whereas sodium nitrite had no effect on the ripening of viscose at all.

Both the degree of ripening as well as the viscosity were determined on the same viscose to which varying quantities of pyridine and sodium nitrite were added. It was found that at a stage, when the viscose reached the ripeness required for spinning, the maximum reduction in viscosity, and this was only 3%, was obtained by either 2% pyridine or 0.17% sodium nitrite. In all other cases the reduction in viscosity was smaller or the viscose not ripe enough for spinning.

The magnitude of the reduction in viscosity is apparently too small to attract the attention of the industry, unless a more effective reagent is found out.

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