

# DECOMPOSITION OF CELLULOSE XANTHATE IN A VISCOSE SPINNING PROCESS

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## INTRODUCTION

In the present communication some representative results obtained in a study of viscose spinning in spin baths of low acid and salt contents will be briefly discussed. The rate of regeneration and the composition of the filaments have been studied during spinning in zinc-free spin baths and in spin baths containing small amounts of zinc. The experimental technique used in the investigation will be briefly outlined. A detailed presentation of the experimental technique and the entire experimental material will be given in a paper to be published elsewhere.

## EXPERIMENTAL

The spinning experiments were carried out in a small laboratory type spinning machine. Spinnerets of commercial types were used. The filament bundle was withdrawn from the spin bath by a small, positively driven, bakelite roller. Samples of spinning filaments were taken by use of special sampling devices mounted right behind the withdrawal roller. By a continuous feed of the circulating spin bath to the roller the spinning conditions were kept constant up to the sampling point. The distance between the spinneret and the sampling point, measured along the filament path, will be referred to as the spinning distance. The velocity of the filament bundle at the end of the spinning distance in all experiments was almost the same as the calculated flow rate of viscose through the spinneret holes.

The dexanthation process was studied by determining the  $\gamma$ -number at different spinning distances. The determinations were made according to a previously described method<sup>1</sup>, in which the dexanthation reaction is quenched by immersion of the filaments in cold 2M sodium hydroxide. The filaments are dissolved in the strongly alkaline solution, and the  $\gamma$ -number is determined spectrophotometrically after purification and appropriate dilution of the solution.

The compositions of the spinning xanthate filaments and the deswelling process were studied in parallel runs. With the aid of a special sampling device the filament bundle was continuously sucked free from adhering spin bath, and subsequently rolled up and collected on small vertically rotating sampling rollers. The lower end of the sampling rollers was cup-shaped, so that the solution squeezed out from the filaments due to the continued regeneration was recovered. The sample collection time was generally one minute.

The total sample size was determined by weighing the rollers before and after the samples were taken. Before analysis the regeneration was completed by boiling the acid samples with water. The amounts of cellulose, sulphuric acid, total sulphate and zinc in the regenerated samples were determined by conventional analytical methods. The amount of sulphuric acid found in the completely regenerated samples is a measure of the amount of sulphuric acid present in excess over the amount required for complete regeneration of the xanthate. This quantity will be referred to as excess sulphuric acid. The true amount of sulphuric acid in the filaments at the instant of sampling will be referred to as the actual amount of sulphuric acid.

The spinning experiments were carried out with spin baths which had the general composition: sulphuric acid 25–33 g/l., sodium sulphate 0–55 g/l., and zinc sulphate 0–0.8 g/l.

The viscose used in the investigation contained 5 per cent cellulose and 2.5 per cent total alkali. In the different runs within a certain series viscose from the same preparation was used. The viscose properties could be kept constant by low temperature storage. After the deaeration step the viscose was divided into spin batches. The spin batches were frozen and stored at  $-20^{\circ}$ . Before being spun the frozen viscose was thawed in a standardized manner. In the experiments presented in this communication the viscose was spun without further ripening.

## RESULTS AND DISCUSSION

### Spinning in zinc-free baths

The dexanthation process in zinc-free spin baths was studied under different spinning conditions. In practically all cases the logarithm of the  $\gamma$ -number, when plotted against the spinning distance, was found to give linear relationships. If the velocity of the filaments is assumed to be constant throughout the spinning distance, the dexanthation process can apparently be described as a first-order reaction. Typical results from dexanthation studies are illustrated in *Figure 1*. In this figure the spinning distance has been recalculated to the time of immersion in the spin bath. The results are from experiments with spinnerets having hole diameters 50  $\mu$  and 100  $\mu$ . As can be seen from the slopes of the lines, the apparent rate constant of the dexanthation process is independent of filament diameter. This observation indicates that the regeneration rate is determined primarily by the rate of the chemical reaction. Diffusion processes seem to be of importance in the first stage of the process only. The displacement between the parallel lines in *Figure 1* can be explained by the difference in time required for the acidification of the fine and coarse filaments spun. In this case the time difference can be estimated as 0.5 seconds.

The conclusions drawn from the observed course of the dexanthation reaction were confirmed by the results obtained in the study of filament composition during spinning. Some representative results are given in *Figure 2*. In this figure the composition of the filament phase is given as millimoles per unit weight of a solution, the weight of which was calculated as the weight of the wet filaments minus the estimated dry weight of cellulose xanthic acid in the sample. The concentration of excess sulphuric acid and total sulphate calculated in this way is seen to be almost the same for filaments of

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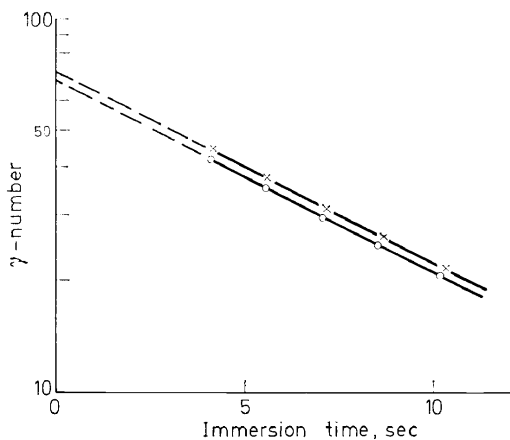


Figure 1. Dexanthation of xanthate filaments spun from spinnerets having hole diameters 100  $\mu$  (x) and 50  $\mu$  (o). [Spin bath; 30 g/l. sulphuric acid, 50 g/l. sodium sulphate, no zinc. temp. 25°.  $\gamma$ -number of viscose = 62.4].

different diameters, and nearly the same as the corresponding concentrations in the spin bath. Despite the large extent of deswelling during spinning, illustrated by the increase in the concentration of cellulose in the filament phase, the estimated concentration of excess sulphuric acid and sulphate is almost constant over the spinning distance examined. It might be concluded that as far as the electrolyte composition is concerned, the filament phase and the spin bath are in equilibrium with each other. A slight decrease in the concentration of excess sulphuric acid and total sulphate is indicated by the

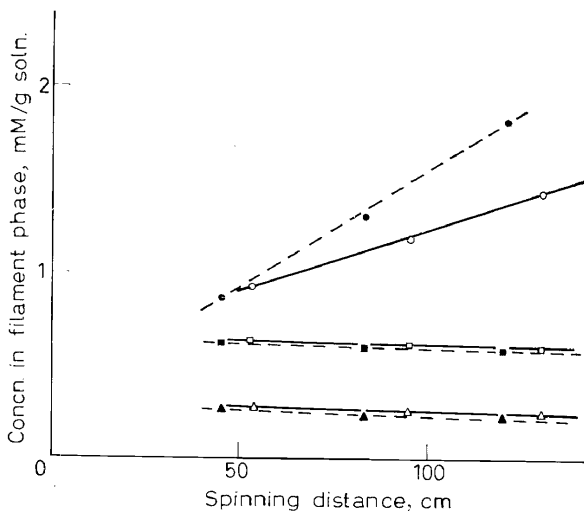


Figure 2. Composition of xanthate filaments when spun in a zinc free spin bath. Spinneret hole diameter 100  $\mu$  (open symbols) and 50  $\mu$  (filled symbols). [ $\Delta$ ,  $\blacktriangle$ , Concn. of excess sulphuric acid;  $\square$ ,  $\blacksquare$ , concn. of sulphate ions;  $\circ$ ,  $\bullet$ , concn. of cellulose, calc. as anhydroglucose units] [Spin bath: sulphuric acid, 0.295 mm/g; total sulphate, 0.650 mm/g; temp. 25° (mm = millimole)]

results. This decrease and the difference between the calculated electrolyte composition of the filament phase and that of the spin bath can be explained by an uneven equilibrium distribution of electrolytes between the filament and the spin bath. It has been shown earlier that the electrolyte concentration inside regenerated cellulose fibres is lower than in the external solution<sup>2</sup>. A calculation of the amount of non-solvent water based upon the amount of sulphate ions in the filament phase gave the result 0.3 g/g cellulose. A similar calculation based upon the concentration of sulphuric acid cannot be made in this case because the actual concentration of sulphuric acid in the filament phase is unknown. It is interesting to note, however, that the given estimate for the amount of non-solvent water compares well with a similar estimate based upon the concentration of excess sulphuric acid in samples taken during spinning in a salt-free spin bath. In this case the sodium ion content of the samples was found to be insignificant. The excess amount of sulphuric acid was thus equal to the actual amount of sulphuric acid. From the results of 11 different determinations made on samples taken at 5 different spinning distances, the amount of non-solvent water was estimated at 0.29 g/g cellulose, with a standard deviation of 0.02.

As can be seen from the estimated concentration of cellulose in the filament phase plotted against the spinning distance in *Figure 2*, the rate of deswelling in the spin bath is dependent upon the filament diameter. This influence cannot be explained by experimental errors caused by an incomplete removal of adhering spin bath in the sampling device. An incomplete removal of adhering spin bath would give rise to too low values for the estimated cellulose concentration. The error, moreover, should be proportional to the specific surface of the filaments and thus be largest for filaments of the smallest diameter. From the results given in *Figure 2*, it can be concluded that the deswelling of the cellulose xanthate or cellulose xanthic acid gel is hindered by a resistance to the transport of solution out from the filament phase. Whether or not the restricted mass transfer out from the filament phase influences the swelling properties of the final fibres has not yet been investigated.

### Spinning in presence of small amounts of zinc

The addition of small amounts of zinc to the spin bath, less than 1 g/l. zinc sulphate, was found to affect the rate of dexanthation to an unexpectedly high extent. The effect is illustrated in *Figure 3*. It can be seen that in a spin bath containing 0.5 g/l. zinc sulphate, the rate of dexanthation is much lower than in a zinc-free spin bath of the same sulphuric acid concentration. The retarding effect of zinc upon the rate of dexanthation is largest for the filaments of the smallest diameter. This indicates that in presence of zinc the rate of dexanthation is determined in part by the rate of diffusion processes. At the shortest spinning distance the  $\gamma$ -numbers are seen to be almost the same, irrespective of whether zinc is present or not. The initial rate of dexanthation is thus largely independent of the presence of zinc.

The electrolyte composition of the spinning filaments was studied in parallel runs. As can be seen from *Table 1*, the filament phase was found to contain considerable amounts of zinc. The values given correspond to an enrichment of zinc in the filament phase between 4.8 and 17.5 times. An

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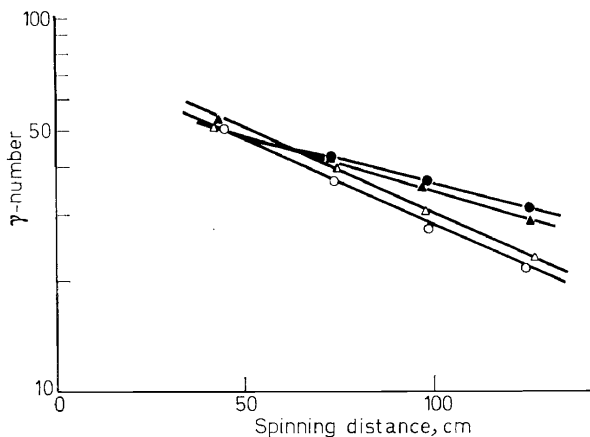


Figure 3. Effect of zinc on dexanthation of xanthate filaments of different diameters. Spinning speed 7.8 m/min; Temperature 25° (from ref. 3). [○, Spinneret hole diam. 50 μ; △, Spinneret hole diam. 100 μ. Spin bath: 30 g/l. sulphuric acid. No zinc.] [●, Spinneret hole diam. 50 μ; ▲ Spinneret hole diam. 100 μ. Spin bath: 30 g/l. sulphuric acid. 0.5 g/l. zinc sulphate.]

incomplete removal of adhering spin bath during sampling would thus make only a small contribution to the total zinc content in the sample. It can be seen that the zinc content increases with the spinning distance. The zinc content in the filaments of the smallest diameter is higher throughout the spinning distance. These observations clearly show the influence of the rate of diffusion, which was indicated by the result obtained in the dexanthation rate studies.

Table 1. Electrolyte composition of spinning xanthate filaments.  
(spin bath: sulphuric acid 0.305 M, zinc sulphate 0.003 M, temperature 25°)

Spinneret hole diameter (μ)	Spinning distance (cm)	Excess H <sub>2</sub> SO <sub>4</sub> ( $\frac{\text{mmole}}{\text{g soln.}}$ )	Total SO <sub>4</sub> <sup>2-</sup> ( $\frac{\text{mmole}}{\text{g soln.}}$ )	Zn in filament	
				(mole % of anhydro-glucose)	(mole % of xanthate groups)
50	38.7	0.267	0.289	2.75	5.2
	63.1	0.249	0.284	4.15	9.3
	94.5	0.229	0.282	5.17	13.6
	121.8	0.218	0.277	5.00	15.6
100	39.5	0.273	0.286	1.72	3.3
	66.5	0.265	0.293	3.33	7.6
	92.1	0.255	0.293	3.92	10.7
	120.5	0.242	0.288	4.37	15.1

The high concentration of total sulphate throughout the spinning distance, and the high concentration of excess sulphuric acid at the shortest spinning distance indicate that zinc has no retarding influence upon the diffusion of these species into the filament.

From the estimated concentration of cellulose in the spinning filaments given in Figure 4, it is seen that small amounts of zinc in the spin bath influence the deswelling process. In the presence of zinc the rate of deswelling

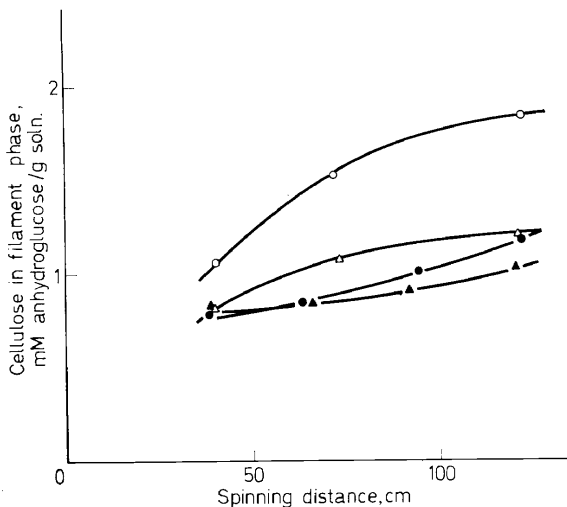


Figure 4. Effect of zinc upon the concentration of cellulose in spinning xanthate filaments of different diameters. Experimental conditions as given in Figure 3. [○, Spinneret hole diam. 50  $\mu$ ; △, Spinneret hole diam. 100  $\mu$ . No zinc] [●, Spinneret hole diam. 50  $\mu$ ; ▲, Spinneret hole diam. 100  $\mu$ . 0.5 g/l. zinc sulphate].

is less rapid than in a zinc free bath. The difference in the rate of deswelling for filaments of different diameters is also reduced. A plot of the cellulose concentration against the  $\gamma$ -number instead of against the spinning distance will show the same general results. The difference in rate of deswelling is thus not caused primarily by the slower decrease in the  $\gamma$ -number. It must instead be concluded that the presence of zinc ions in the filament phase counteracts the tendency of the xanthate gel to deswell and form a dense structure.

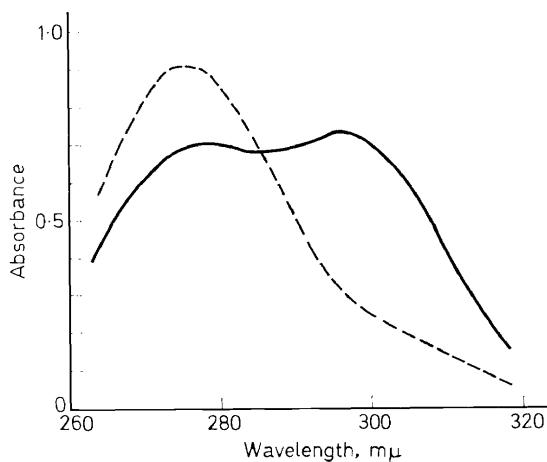
In other spinning processes the presence of zinc in the filament has been partly explained by reactions between zinc ions and viscose byproducts<sup>4-6</sup>. Under the present spinning conditions, however, filaments spun from anion exchanged byproduct free viscose were found to contain almost the same amounts of zinc as filaments spun from ordinary viscose. In this case, evidently, the mechanism must be a different one. The most probable explanation of the high zinc content in the filaments is that complexes between zinc and xanthate groups are formed in the acid filament gel. The retarding effect upon the rate of regeneration accordingly, should be explained by a decrease in the fraction of reactive xanthate groups.

The formation of xanthate complexes offers an explanation also to the observed decrease in the concentration of excess sulphuric acid in the filaments during spinning (cf. Table 1). In this spinning experiment the amount of sodium ions in the filament samples was found to be insignificant at all of the spinning distances examined. On the assumption that each zinc ion at the instant of sampling is bound to at least two xanthate groups, the actual amount of sulphuric acid would correspond to the total amount of sulphate. As can be seen from Table 1 the total concentration of sulphate ions in the filament phase is nearly constant throughout the spinning distance,

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and just slightly lower than that in the spin bath. This is a strong indication that in this case also, an equilibrium distribution of sulphuric acid between the filament phase and the spin bath solution is approached.

The formation of a zinc xanthate complex under the acidity conditions prevailing in the spinning xanthate filaments could be established by spectrophotometric measurements. With use of two motor driven syringes, a dilute xanthate solution and a sulphuric acid solution were fed into a small mixing chamber and then into a flow cell. When a steady state condition was reached in the flow cell the spectrum of the flowing reaction mixture was scanned. The spectra reproduced in *Figure 5* were obtained by measurement of xanthate solutions having the same sulphuric acid and zinc contents as the spin



*Figure 5.* Influence of zinc upon the absorption spectra of acid cellulose xanthate solutions of equal xanthate content. [(---), 30 g/l. sulphuric acid, no zinc; (—), 30 g/l. sulphuric acid, 0.5 g/l.  $ZnSO_4$ ].

baths used in the experiments underlying *Figure 3* and *Table 1*. In the zinc free solution an absorption maximum was found at 276  $m\mu$ . This maximum can be ascribed to the absorption of free cellulose xanthic acid. By addition of zinc the absorbance at 276  $m\mu$  decreases and a new maximum appears at 298  $m\mu$ . According to Phifer<sup>7</sup> the absorption maximum at 298  $m\mu$  can be ascribed to a zinc xanthate complex. From the absorption spectrum obtained in presence of zinc the fraction of complex bound xanthate groups could be estimated as 0.3–0.4. This estimate was obtained with use of molar absorptivities for the zinc xanthate complex taken from Phifer. The decomposition of xanthate in the dilute acid solutions could be studied with use of the same equipment. In this case, when a steady state condition in the flow cell was reached, the flow was suddenly stopped, and the absorbance of the acid solution was recorded during the decomposition. The absorbance time curves obtained in this way clearly showed the retarding influence of the small amount of zinc ions present. In the dilute xanthate solutions, the retarding influence of zinc upon xanthate decomposition can thus be explained by complex formation. Approximate calculations showed that the rate of decomposition was proportional to the fraction of uncomplexed

xanthate groups as estimated from the absorbance of the reaction mixture at 298  $m\mu$  and 276  $m\mu$ .

It is likely that the same mechanism is involved in viscose spinning. With this assumption, an estimate of the fraction of complex bound xanthate groups in the spinning filaments can be obtained from a comparison of the dexanthation rate in presence and absence of zinc. The number of xanthate groups bound to one zinc ion might then be found by comparing the estimated fraction of complex bound xanthate groups and the observed zinc content in the filaments. As can be seen from *Figure 3*, dexanthation during spinning in presence of zinc proceeds almost as a first order reaction. This would indicate that the fraction of complex bound xanthate groups is constant. From *Table 1* it can be seen that the zinc content in the filaments, expressed as mole per cent of the xanthate groups, increases rapidly during the decomposition in the spin bath. According to the suggested reaction mechanism the number of xanthate groups bound to each zinc ion should thus decrease during the decomposition. In the interval between the shortest and the next shortest spinning distances examined (cf. *Figure 3*) the retarding influence of zinc can be explained by complex formation between one zinc ion and almost six xanthate groups. In the interval between the longest and the next longest spinning distances the mechanism requires that each zinc ion on the average is bound to 2.5 xanthate groups. Such a decrease may be explained by an increase in the average distance between xanthate groups during the decomposition, whereby a larger number of zinc ions is necessary to give the same extent of complex formation.

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