*The Formation of Cellulose IV in the Viscose Spinning**

By Yoshizo TSUDA and Sadataka MUKOYAMA

(Received April 17, 1957)

It has been generally acknowledged that the crystal form of the cellulose in viscose rayon may be designated as cellulose II. However, as pointed out by Ingersol[1] and Howsmon[2] a small amount of cellulose IV may also be formed during the spinning of viscose rayon under special conditions, although those conditions have not been elucidated. Thus the mechanism of the cellulose IV formation in the spinning of viscose rayon is still unknown.

One will be able to find the presence of cellulose IV in the X-ray diagram of tire cord rayon, while none can be found in that of textile rayon. This fact suggests that the formation of cellulose IV may be facilitated by the spinning process characteristic of the spinning of tire cord rayon. It has been the purpose of this work to investigate the mechanism of the formation of cellulose IV in the spinning of tire cord rayon.

It has been suggested[2] that cellulcse IV may be formed by the direct decomposition of cellulose xanthates. If this is true, the zinc cellulose xanthate formed temporarily in the viscose spinning process may play an important role in the formation of cellulose IV. According to this suggestion the present work was started with the investigation of the regeneration of zinc cellulose xanthate model filament and it was shown that high temperature of regeneration is the necessary condition to form cellulose IV in this case. The mechanism of the formation of the cellulose IV in the viscose spinning process was investigated with the experimental rayon spun by the stretch spinning method on the basis of the conclusion obtained above.

The Crystal Structure of Cellulose IV

It has been confirmed by a number of investigations[3] that cellulose I is stable at higher temperatures and can be formed by transforming cellulose IV at higher temperatures by various methods. The unit cell of cellulose is described as rhombic with the dimension $a=8.11$ Å, $b=10.3$ Å, $c=7.9$ Å and the angle β approximately 90°. The principal X-ray evidence for the existence of cellulose IV lies in the fact that only one equatorial interference occurs in place of the 101, 101 doublet of cellulose I. As pointed out by Howsmon[2] cellulose IV may be regarded as a disordered form of cellulose I.

Experimental

(a) **Cellulose Samples.**—Ammonium cellulose xanthate model filament was prepared according to the procedure employed by Hermans[4]. Zinc cellulose xanthate model filament was obtained by immersing ammonium cellulose xanthate model filament in a cold saturated zinc sulfate solution for half an hour,, stretching to twice its original length and then regenerating. Dilute sulfuric acid solutions at various temperatures (40°C, 60°C, 80°C, 100°C) as well as boiling water and glycerine at 150°C were employed for the regeneration.

Experimental rayon was spun in Müller-type baths of various compositions followed by a second bath either at a higher temperature (95°C) or at a lower temperature (60°C). In the following table the compositions of the Müller-type baths employed and the corresponding temperature of the second bath are shown.

TABLE I
SPINNING CONDITIONS OF EXPERIMENTAL RAYON

No. of Sample	Composition of Müller-type bath wt. %			Temp. of second bath °C
	H_2SO_4	Na_2SO_4	$ZnSO_4$	
I	8	20	1	60
II	8	20	1	95
III	8	20	2	60
IV	8	20	2	95
V	8	20	3	60
VI	8	20	3	95
VII	8	20	4	60
VIII	8	20	4	95

* The main part of this paper was presented at the 10th Annual Meeting of the Chemical Society of Japan, April 1957.

1) H. G. Ingersol, *J. Applied Phys.*, **11**, 924 (1946).

2) J. A. Howsmon, W. A. Sisson, "Cellulose and Cellulose Derivatives" (E. Ott) Part 1. pp. 241-244 (1954).

3) K. Hutino and I. Sakurada, *Naturwissenschaften* 577 (1940); T. Kubo, *Z. phisik. Chem.*, A 49, 297 (1940); K. Hess and H. Kiessig, *Z. phisik. Chem.*, B 49, 235 (1941).

4) P. H. Hermans, "Physics and Chemistry of Cellulose Fibres", p. 439 (1949).

The temperature of the first bath (Müller-type bath) was kept at 50°C, the spinning speed at 25 m. and the first bath travel at 30 cm.

(b) X-Ray Diffraction.—The Norelco diffractometer of the North American Philips Company, Inc., with auxiliary equipments, consisting of a recording potentiometer and a scaler counting unit, was used in these studies. Nickel-filtered radiation from a copper target operated at 35 kV and 15 mA tube current was used.

In order to obtain pulverous specimens, the cellulose samples were methanolized for a day with one normal hydrochloric acid in absolute methyl alcohol at 40°C. This treatment gave a ninety-five per cent. yield of cellulose.

No change in the crystal form through the methanolysis was confirmed by comparing the X-ray diffraction intensity curve of the methanolized sample with the X-ray diffraction diagram of the fibrous sample.

Results and Discussion

The X-ray diffraction intensity curves of textile rayon and tire cord rayon are shown in Fig. 1. No peak of cellulose IV appears in the diffraction intensity curve of textile rayon. In contrast, a remarkable peak of cellulose IV is observed in the diffraction intensity curve of tire cord rayon. The difference of this nature will be found between any textile and tire cord rayons.

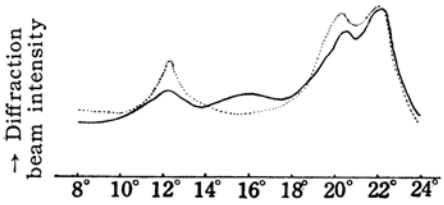

Fig. 1. X-ray diffraction intensity curves of tire cord rayon (full line) and textile rayon (dotted line).

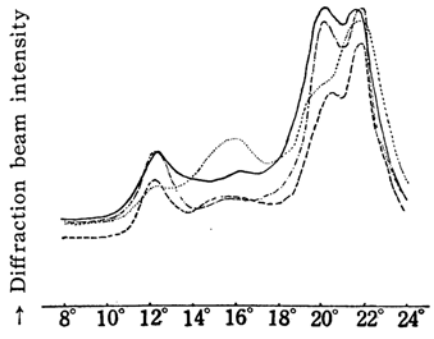

Fig. 2. X-ray diffraction intensity curves of model filaments regenerated at various temperatures: 40°C (full line), 60°C (chain line), 80°C (broken line) and 100°C (dotted line).

The X-ray diffraction intensity curves of the model filaments regenerated with dilute sulfuric acid solutions at various temperatures are shown in Fig. 2. It is seen that the relative intensity of the peak of cellulose IV increases slightly with the increase in the temperature of regeneration from 40°C to 80°C, while a marked increase of cellulose IV is observed with the sample regenerated at 100°C. It should be mentioned that the critical temperature which determines the formation of cellulose IV lies between 80°C and 100°C.

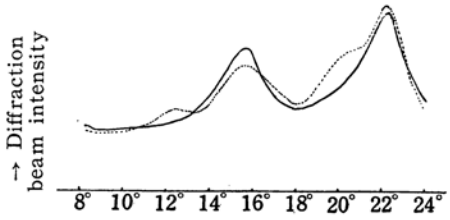

Fig. 3. X-ray diffraction intensity curves of model filaments regenerated with boiling water (dotted line) and regenerated with glycerine at 150°C (full line).

The X-ray diffraction intensity curves of the model filaments regenerated with boiling water and with glycerine at 150°C are shown in Fig. 3. The curve for the sample regenerated with boiling water is identical with that for the sample regenerated with dilute sulfuric acid at 100°C. This fact indicates that the formation of cellulose IV depends solely on the temperature of regeneration.

The curve for the sample regenerated with glycerine at 150°C shows that the crystal form of the sample consists of cellulose IV alone. It may be concluded that the degree of formation of cellulose IV by the decomposition of zinc cellulose xanthate is determined by the temperature and that the regeneration temperature above a critical temperature which is between 80°C and 100°C, is required for the formation of cellulose IV.

The X-ray diffraction intensity curves of the experimental rayon are shown in Fig. 4. It can be seen from those curves that the formation of cellulose IV depends on the temperature of the second bath. Namely the samples which passed through the second bath at 95°C contain the crystal

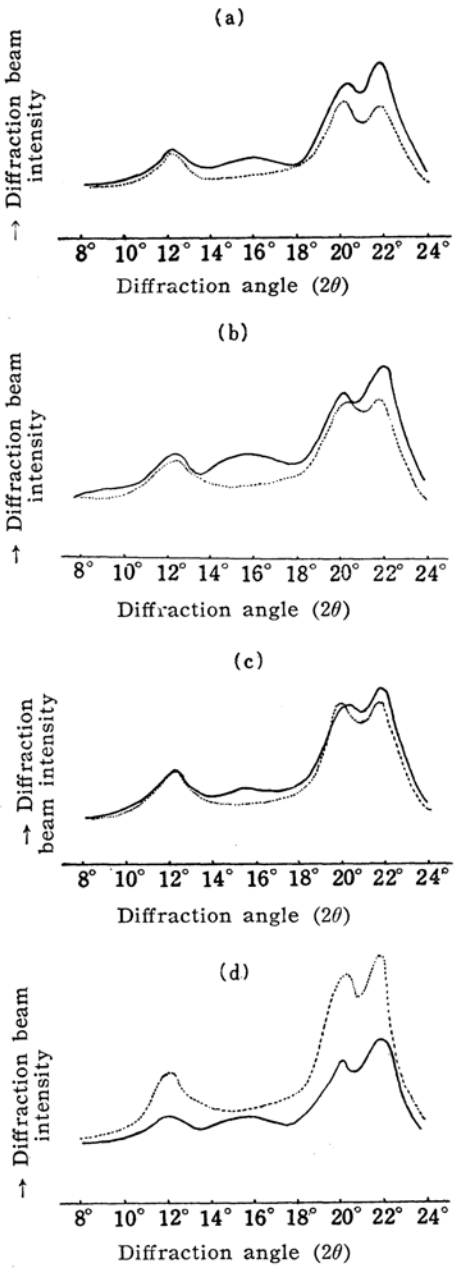

Fig. 4. X-ray diffraction intensity curves of experimental rayon: (a) I, II, (b) III, IV; (c) V, VI; (d) VII, VIII; here I, III, V and VII are drawn in dotted lines and the rests in full lines.

form of cellulose IV, while the samples which passed through the second bath at 60°C contain no crystal form of cellulose IV. In addition, the relative intensity of the peak of cellulose IV as compared of cellulose II increases with that with the increase in the concentration of zinc sulfate in the first bath. These facts will be elucidated as follows. The zinc cellulose xanthate which is formed temporarily in the first bath is brought into the second bath maintained at a higher temperature where it is regenerated. Thus the crystal form of the cellulose IV is included in the sample which passed through the second bath at a sufficiently high temperature. The formation of zinc cellulose xanthate depends on the concentration of zinc sulfate in the first bath. Consequently, the higher the concentration of zinc sulfate, the greater the content of cellulose IV in the regenerated sample.

It may be concluded from the results that the partical formation of cellulose IV in tire cord rayon is due to the higher temperature of the second bath and the higher content of zinc sulfate in the first bath.

Summary

The formation of cellulose IV in the viscose spinning process was investigated by the X-ray diffraction measurements. Zinc cellulose xanthate model filaments were regenerated at various temperatures and their X-ray diffraction diagrams were examined. It was observed that the formation of cellulose IV is remarkable when zinc cellulose xanthate is regenerated at the temperature above a critical temperature which lies between 80°C and 100°C. The mechanism of partial formation of cellulose IV in the viscose spinning process was elucidated as follows: when zinc cellulose xanthate formed in the first bath is regenerated at a sufficiently high temperature in the second bath, the formation of cellulose IV consequently results. The main factors involved for the formation of cellulose IV are higher temperature of the second bath and higher concentration of zinc sulfate in the first bath.

The authors are grateful to Dr. K. Hoshino for premission of this publication. The authors sincer thanks are also due to Professor K. Maeda of Tokyo Institute of Technology and Mr. T. Yurugi of the Textile Research Institute for their kind discussions.

Research Center, Toyo Rayon Company Ltd., Otsu, Shiga Prefecture