

## Changes in Fine Structure and Mechanical Properties Induced by Cyanoethylation of Cotton Yarns. II. Reacted Without Longitudinal Shrinkage\*

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### INTRODUCTION

The extensive reaction of the cellulose of cotton yarns with acrylonitrile (D.S. = 0-2.6) under conditions permitting complete freedom of longitudinal contraction was dealt with in a previous study.<sup>3</sup> Changes in cellulose fine structure were followed by appropriate means and accompanying changes in mechanical properties were reported. The present paper reports the results of a companion study in which the mechanical conditions of reaction prevented any contraction. Changes taking place in the fine structure of the fiber were studied by means of optical microscopy, density measurements, x-ray diffraction, and thermal stress measurements.

The results indicate that in spite of the strong tensions developed in the yarns, the reaction proceeds in both the accessible and the crystalline regions with considerable volume expansion and eventual disappearance of crystalline structure. A slight suggestion of a glassy-rubbery transition temperature appears at substitutions slightly above D.S. = 1. Annealing becomes possible at substitutions above D.S. = 2 with the development of the cyanoethyl cellulose crystal structure and over 40% increase in tensile strength. Changes in other mechanical properties are also reported.

Although electron micrographs of fibrillated fiber specimens and fiber cross sections were prepared during the course of the present studies, an adequate discussion of them would carry us too far afield. They will, therefore, be the subject of a separate report.

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### EXPERIMENTAL METHODS

#### Samples

The cotton yarn used in the present studies was the same as that of the earlier study, namely, 14: Z11/2:S8(42 × 2 tex) of Deltapine cotton with 3.00 TM in both singles and ply.

#### Procedure

In the preparation for reaction, the yarns were first wound lengthwise onto a 9 × 15-in. stainless steel frame. Winding was facilitated by use of a yarn appearance board winder in conjunction with a General Electric\* tensioning device set for 10 g. Approximately 22.5 g. of yarn was laid on the frame in a single layer. The frame with yarn was immersed in 6% sodium hydroxide (ca. 2400 ml.) containing 0.1% Alkamerse,\* and left overnight. No hydrotropic agent was used for this series.

The skeins on the steel rack were centrifuged to 90-100% pick-up and reacted with acrylonitrile in a specially constructed hot water-jacketed bath. Reaction was allowed to proceed at 60°C. for various periods up to 1 hr., selected to give the desired degrees of substitution.

Control samples with toluene in place of acrylonitrile were run for periods of 5, 30, and 60 min.

After completion of the reaction, the yarns still on the frame were immersed in 5% acetic acid to neutralize the residual alkali, washed with water, methanol, and ether, and allowed to dry in a current of warm air. Details of the treatment and characterizations of the products are shown in Table I.

\* Use of a company and/or product name by the Department does not imply approval or recommendation to the exclusion of others which may also be suitable.

TABLE I  
 Conditions and Details of Yarn Preparation

Type of sample	Medium used	Length of treatment, <sup>a</sup> min.	Degree of substitution	Contraction during treatment, <sup>b</sup> %	Weight gain, %	Yarn n <sub>a</sub> , tex
Control	None	0	0	0.76	0	81.2
	Toluene	5	0	1.14	0	79.3
		30	0	0.94	0	80.1
		60	0	1.06	0	79.2
Reacted	Acrylonitrile	5	0.58	0.93	18.4	91.0
		10	0.75	0.48	24.1	96.1
		15	1.17	0.38	37.0	104.8
		20	1.28	0.00	36.9	111.3
		25	1.51	-1.04	44.3	116.9
		30	2.12	0.29	71.8	137.1
		40	2.18	0.45	71.7	146.3
		60	2.38	0.14	69.8	149.0

<sup>a</sup> All treatments were preceded by overnight immersion in 6% NaOH.

<sup>b</sup> Measured on the yarn after removal from the frame.

### Test Methods

Except as indicated below, the methods used were the same as those of the previous report.<sup>3</sup>

The fiber cross sections were prepared according to ASTM Specification D 1444-56.<sup>1</sup>

Refractive indices were measured as described by Tripp, Giuffria, and deGruy.<sup>11</sup> The equivalent refractive indices of isotropic cellulose,

$$n_{\text{iso}} = 1/3 (n_{\parallel} + 2n_{\perp})$$

were calculated according to the methods described by Hermans.<sup>7a</sup>

Density was determined in an anhydrous ethanol-carbon tetrachloride column as well as in a xylene-carbon tetrachloride column. For the ethanol-carbon tetrachloride medium, in addition to knots, sections of a number of ends of yarn were cut in a Wiley mill to pass a 20-mesh screen. Quantities of the powder (0.1 g.) were boiled out in the alcohol and introduced into the column. After equilibrium had been established, the top and bottom edges of the stratified layer were read off with a cathetometer and the computed densities were averaged. Thus, the range provided a measure of the uniformity of substitution. The averages thus found agreed within experimental error with the averages of values measured on the knots, and the greatest deviation of the powder from its estimated mean was 0.86%.

In computing densities from molar weights and volumes, the density of cellulose was taken as 1.546 g./cc. Since the density of the cyanoethylene group is not known it was computed from its molar

weight and the difference between the molar volumes of  $\beta, \beta'$ -oxydipropionitrile<sup>2</sup> and ethylene cyanohydrin. The resulting density is 1.029 g./cc. and is in fair agreement with the value of 1.04 g./cc. reported by Eaton<sup>4</sup> for "precipitated" polyacrylonitrile.

Density was computed also from the isotropic refractive index,  $n_{\text{iso}}$ , according to the well-known equation of Lorentz and Lorenz, namely,

$$d = [(n_{\text{iso}}^2 - 1)/(n_{\text{iso}}^2 + 2)] (M/R)$$

where  $d$  is the density,  $M$  is the molecular weight of the partially substituted cellulose, and  $R$  is the corresponding molar refraction. The value of  $R$  was computed from the atomic factors tabulated by Gilman (Reference 6, p. 1751).

## RESULTS

### Gross Morphology

Longitudinal views of the yarns at several stages of substitution and of enlarged cross sections prepared from them are shown in Figure 1.

Since the yarns were not free to shrink, they did not show any evidence of kinking or snarling. They increased somewhat in cross section at the highest substitutions. Below D.S. = 2.0 the cross sections show very little change, whereas those at the two highest substitutions show much evidence of swelling and a tendency to agglomerate.

### Refractive Indices

The refractive indices of the control treated with alkali and toluene and of cyanoethylated cotton

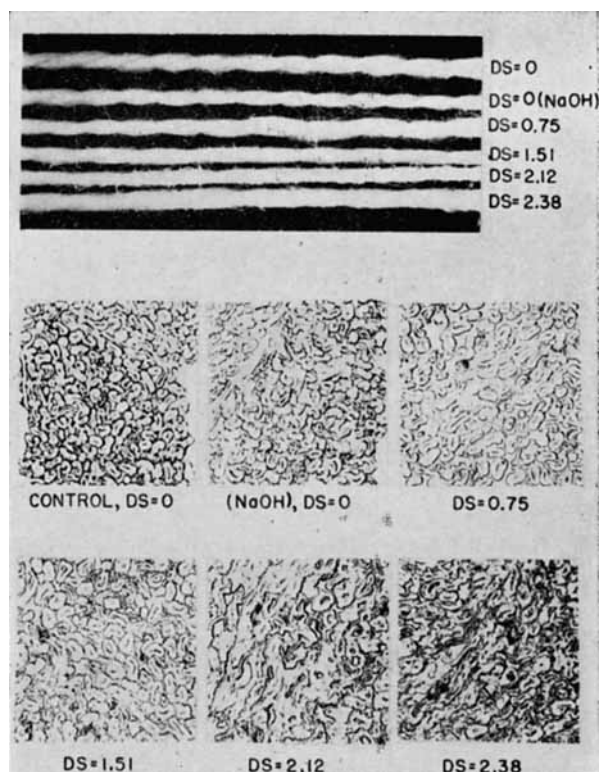


Fig. 1. Longitudinal views of yarns (approximately  $5\times$ ) and cross sections of fibers (approximately  $175\times$ ) at several stages of substitution.

celluloses of selected degrees of substitution are shown in Table II. The data at the bottom of the left-hand column followed by the letter H refer to yarns which after preparation were heated in an oven at  $175^{\circ}\text{C}$ . for 30 min. while supporting 50-gm. weights.

From Table II it is evident that both the parallel and perpendicular indices decreased strongly with

TABLE II  
Refractive Indices, Birefringence, and Computed Densities of Cyanoethylated Cellulose

Degree of substitution	Refractive indices			Birefringence	Computed density, g./cc.
	$n_{\parallel}$	$n_{\perp}$	$n_{\text{iso}}$		
0 <sup>a</sup>	1.575	1.530	1.545	0.045	1.518
0.75	1.534	1.504	1.514	0.030	1.391
1.51	1.535	1.503	1.514	0.032	1.347
2.12	1.513	1.493	1.500	0.020	1.292
2.38	1.509	1.489	1.496	0.020	1.275
1.51H <sup>b</sup>	1.536	1.505	1.515	0.031	1.352
2.12H <sup>b</sup>	1.527	1.501	1.510	0.026	1.314

<sup>a</sup> Control, wetted with 6% NaOH and heated with toluene for 30 min.

<sup>b</sup> The letter H indicates that the sample was heated 30 min. at  $175^{\circ}\text{C}$ . while supporting a 50-g. weight.

the first stage of substitution, then more slowly as substitution increased. Heating the yarns under a mild tension caused a slight increase in both indices.

The birefringence shows a somewhat erratic decrease with substitution, reaching a low value of 0.020 at a substitution of D.S. = 2.12. As will appear below, samples with degrees of substitution above 2.0 no longer display any native crystalline cellulose. Heating under tension causes a distinct increase in birefringence.

### Density

Changes of density with degree of substitution are shown in Figure 2. As in the case of loose-reacted yarns,<sup>3</sup> the density decreased quite extensively with increasing substitution. Densities determined in the xylene-carbon tetrachloride column decreased considerably more than those determined in the ethanol-carbon tetrachloride column except at substitutions below D.S. = 1. However, it has been observed that densities in xylene-carbon tetrachloride, especially those in the more highly cyanoethylated samples, approach equilibrium very slowly, over a period of many weeks, and in doing so gradually increase. For example, the sample of D.S. = 2.12 with an initial density of 1.208 g./c., had a density of 1.264 g./cc. after 18 days and 1.308 g./cc. after 95 days. The densities eventually approach the values reached in a few days in the ethanol-carbon tetrachloride column. Furthermore, the densities computed from a consideration of molar weights and volumes of cellulose, indicated by the unbroken line in Figure 2, agree more nearly with those determined in the ethanol-carbon tetrachloride column. Finally, the densities computed from the molecular weight, from the partial molar refractive contributions, and from the refractive indices, indicated by crosses in Figure 2, lie near the values determined with ethanol-carbon tetrachloride as the buoyant medium.

The greater density of cyanoethylated celluloses in the ethanol-carbon tetrachloride binary mixture, which was observed at substitutions above 1.0, is readily explained with reference to the study of Fortress,<sup>5</sup> of the penetration of a great number of organic liquids into cellulose acetate. However, it is not known why at substitutions below D.S. = 1.0 the densities determined in ethanol-carbon tetrachloride should be less than the corresponding values determined in xylene-carbon tetrachloride. A repetition of the determination of the density of the control in ethanol-carbon tetrachloride, with

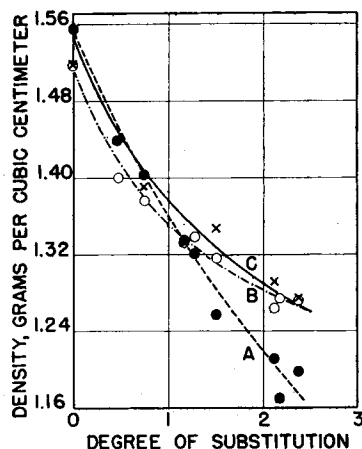


Fig. 2. Changes in density with degree of substitution. Dark circles represent observed densities in xylene-carbon tetrachloride; open circles represent observed densities in ethanol-carbon tetrachloride; curves A and B represent least square fits of observations in xylene- and ethanol-carbon tetrachloride media, respectively. Curve C represents densities based on considerations of partial molar weights and volumes of cellulose and cyanoethyl groups; the crosses indicate densities computed from the refractive indices.

six knots of yarn in place of the powdered fiber, gave 1.527 g./cc. This figure is slightly higher than that for the powdered sample, but again much lower than the value determined in the xylene-carbon tetrachloride column. If, as was discussed by Hermans,<sup>7b</sup> the amorphous component swells in the ethanol, then the density should increase. If we assume that the cellulosic structure ought to be more accessible to ethanol than to xylene, then again the density should be higher in the former than in the latter.<sup>10</sup>

If we accept the density determined in ethanol-carbon tetrachloride, we may then conclude that as substitution takes place, approximately additive volumes of cellulose and cyanoethyl groups are utilized in the new cyanoethyl cellulose molecule. The equations expressing the relations of the density  $d$  to degree of substitution  $S$  may be expressed as follows:

$$d_x = 0.258 + \frac{7.401}{S + 5.711}$$

$$d_e = 1.113 + \frac{0.5872}{S + 1.4578}$$

$$d_m = 1.029 + \frac{1.0542}{S + 2.0386}$$

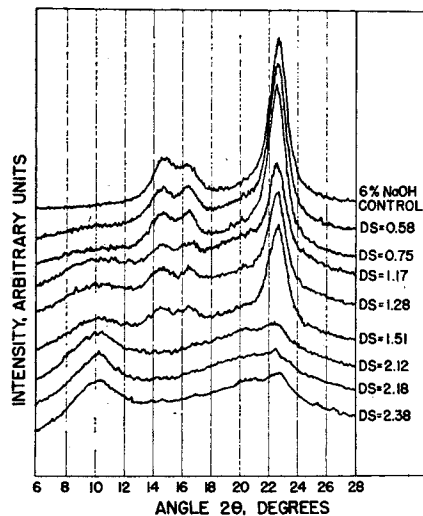


Fig. 3. Radial x-ray diffractograms of cellulose reacted without shrinkage.

In these equations the subscripts  $x$ ,  $e$ , and  $m$  indicate xylene and ethanol media and the molar values, respectively.

### Crystal Structure

The changes in crystal structure with increasing degree of substitution are shown by a family of curves in Figure 3. Although it is not entirely evident from the curves, the intensity of the 002 interplanar spacings remains fairly constant through D.S. = 0.75. A substitution of D.S. = 1.17 results in a very distinct reduction of the intensity of this diffraction, which seems to reach a minimum between D.S. = 1.51 and 2.12. After this no further change occurs.

The sample with the highest substitution shows slight evidence of residual diffraction at the 002 spacing. However, the shape of this curve seems to agree well with that of cyanoethyl cellulose of about the same degree of substitution, as reported by Segal and Conrad (Reference 9, Fig. 12.).

The amorphous nature of the cyanoethyl cellulose in samples substituted to D.S. = 2.0 or higher is best shown by annealing experiments. Figure 4 shows a series of curves for samples of two different degrees of substitution before and after heating at 175°C. for 30 min. It will be observed that the curves for the D.S. = 1.51 sample before and after heating are identical, indicating that no crystallization occurs in this sample as a result of heating. The upper curve for the D.S. = 2.18 sample heated for 30 min. shows a significant sharpening of the peak at  $2\theta = 10.3^\circ$  in contrast to the lower curve for

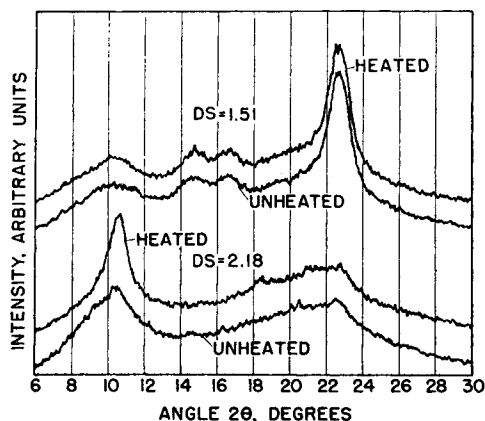


Fig. 4. Effect of annealing treatments on crystalline structure.

the unheated sample with the same substitution. The peak at  $2\theta = 10.3^\circ$  is characteristic for cyanoethyl cellulose and indicates increased crystallinity. The sample substituted to D.S. = 1.17 was also heated and also showed no change of curve as a result of heating. The logical conclusion seems to be that annealing is possible in samples substituted beyond about D.S. = 2.0, in which the cellulose has become essentially amorphous, but that it cannot be achieved at substitutions at which a substantial amount of crystalline cellulose is still present.

### Thermal Stress Behavior

In the previous study<sup>3</sup> the thermal stress behavior was shown for yarn samples cyanoethylated under conditions permitting maximum contraction. The yarns were subjected to a strain sufficient to produce an initial stress of 120 g. and then repeatedly extended to this same strain as the temperature was raised stepwise to a maximum of about  $220^\circ$ . It was observed that the modulus underwent characteristic changes as substitution increased. Figure 5 shows a corresponding family of curves for yarns cyanoethylated under conditions which prevented contraction. Each curve begins at a stress of 120 g. and, for ease of comparison, is displaced vertically from its neighbors. The two upper curves, representing the alkali-toluene control and the D.S. = 0.58 samples, respectively, display similar loss of stress with increasing temperature except that the loss in the slightly reacted sample is twice as great as that in the unsubstituted one. The third and fourth curves from the top, representing substitutions of D.S. = 1.17 and 1.51, respectively, show a distinct change of shape. A definite increase in the rate of loss occurs in the neighborhoods of 150 and

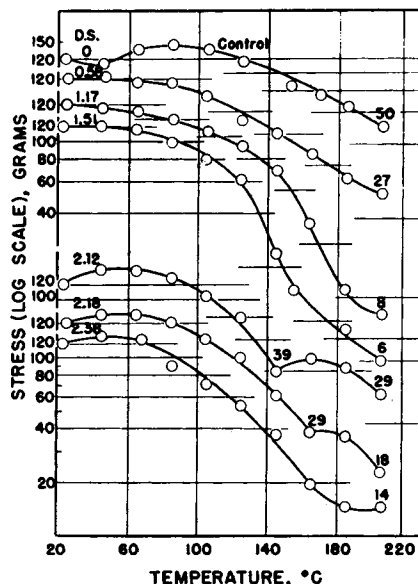


Fig. 5. Thermal stress relaxation of yarns substituted to different degrees under conditions preventing contraction.

$130^\circ\text{C.}$ , respectively. At the highest temperature the loss of stress is over 90% of the initial stress. The increase in rate of loss was associated in the earlier study with what was interpreted as a somewhat imperfect glass transition temperature. Recently, several differential thermal analyses kindly run by R. F. Schwenker<sup>8</sup> have indicated that the changes may be considerably more complex than was thought at first. It was also shown that samples in this range of substitution have lost their original crystalline structure to a considerable extent.

The thermal stress curves for D.S. = 2.12 and greater seem to behave as a group and somewhat differently from those for substitutions less than D.S. = 2.0. The stress never descends to as low a value and there is usually a break in the continuity after which the stress may flatten out or even increase before continuing its downward trend. We have associated this discontinuity with initiation of crystallization of cyanoethyl cellulose. However, at times the initiation of crystallization may be less abrupt or the discontinuity may fail to appear, as demonstrated by the lowest curve for the D.S. = 2.38 sample. The effect here is reminiscent of a supersaturated solution in which seeding might be necessary to induce crystallization.

The recoverable nature of the thermal stress loss may be seen by following the stress as the temperature is raised to the maximum and then lowered again. Figure 6 shows the change of stress with

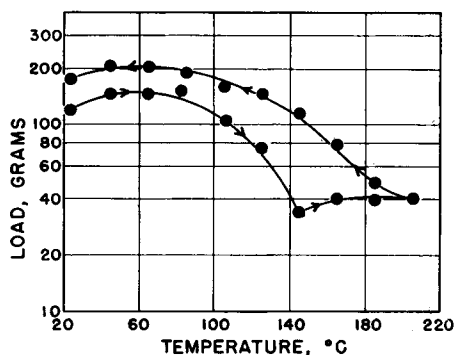


Fig. 6. Thermal stress behavior of yarn (D.S. = 2.12) cyanoethylated under conditions preventing contraction, as the temperature is raised and lowered.

temperature increase and decrease. The stress first increases slightly with temperature then decreases to a minimum of about 35 g. at 145°C. At this point crystallization suddenly begins, resulting in a slight increase of stress as the temperature continues to increase above 200°C. As the temperature now decreases the stress increases directly, passes through a slight maximum, and maintains a substantial elevation above the values associated with increasing temperature. The final stress of 172 g. at room temperature is 43% above the starting stress. The very favorable effect of annealing on the tensile properties of yarns reacted under conditions which prevent contraction is evident.

### Mechanical Properties

The mechanical properties of yarns before and after substitution to various degrees is summarized

TABLE III  
Mechanical Properties of Yarns

D.S.	Elongation at break, %	Tensile strength, g./tex <sup>a</sup>	Tenacity, g./tex	Energy of rupture, g./tex	Tensile stiffness, g./tex	Elastic recovery, %			Energy recovered, %
						Immediate	Delayed	Permanent set	
0	8.54	14.4	14.4	0.64	168	8.7	41.8	49.5	44.5
0 <sup>b</sup>	7.80	16.1	16.1	0.59	206	8.7	38.8	52.5	48.0
0 <sup>c</sup>	7.39	16.2	16.2	0.56	219	7.8	39.7	52.5	47.5
0 <sup>d</sup>	7.63	16.6	16.6	0.58	218	8.0	37.8	54.2	47.4
0.58	7.09	19.7	16.9	0.56	278	10.3	39.2	50.5	48.4
0.75	7.70	24.6	17.8	0.64	319	9.7	40.5	49.8	46.2
1.17	7.49	24.6	17.8	0.66	328	11.0	35.5	53.5	51.0
1.28	8.13	26.3	18.6	0.72	324	10.3	36.3	53.4	50.2
1.51	14.44	23.2	15.5	0.88	161	8.8	30.5	60.7	46.3
2.12	13.56	19.1	11.2	0.70	141	14.0	32.3	53.7	48.3
2.18	15.17	17.4	10.1	0.75	114	13.7	31.0	55.3	52.5
2.38	18.21	16.7	9.4	0.72	92	12.8	32.8	54.4	47.9

<sup>a</sup> Breaking load expressed per tex of unsubstituted control.

<sup>b</sup> Immersed overnight in 6% NaOH, then heated in toluene for 5 min.

<sup>c</sup> Immersed overnight in 6% NaOH, then heated in toluene for 30 min.

<sup>d</sup> Immersed overnight in 6% NaOH, then heated in toluene for 60 min.

in Table III. The second column shows that the ultimate elongation begins to increase somewhat at about D.S. = 1.28. We have already noted that this is roughly the degree of substitution at which all noncrystalline cellulose originally present in the fiber has been exhausted and the crystalline regions are giving way.

The tensile strength increases somewhat with increasing substitution, and then drops off again at the highest degrees.

The tenacity also increases somewhat with increasing substitution, but the increasing tex due to the added weight of cyanoethyl groups eventually predominates, so that the tenacity at the highest substitution is only about 60% of the initial value.

The energy of rupture begins to show improvement with increasing substitution at about the stage where the crystalline regions originally present are being attacked.

Tensile stiffness goes through a maximum with increasing substitution, but the trend eventually reverses and at the highest substitution the value has fallen to less than half its initial value.

Immediate elastic recovery increases somewhat as substitution increases, but largely at the expense of the delayed elastic recovery component. Permanent set shows relatively minor increase.

The total energy recovered from 6% extension varies slightly and rather indecisively about a mean value, as substitution increases. It seems reasonable to conclude that no significant change in this property occurs.

## DISCUSSION

The results presented for yarns cyanoethylated under conditions which prohibit longitudinal shrinkage reproduce to a large extent those observed for yarns reacted loose. The density decreases similarly as reaction proceeds. The use of ethanol-carbon tetrachloride in place of xylene-carbon tetrachloride as the medium in the density gradient tubes appears to favor rapid attainment of equilibrium and to give densities more in line with those computed from molar weights and volumes and the assumed densities of the reaction components. This observation applies more to the more highly substituted samples than to the unsubstituted ones. The figures obtained in ethanol-carbon tetrachloride are paralleled by the density values computed from the refractive indices.

The changes in crystalline structure, as deduced from the diffractograms, seem to parallel fairly closely the changes of structure in the loose-reacted yarns. Reaction appears to proceed with little, if any, change in the crystalline structure until a substitution exceeding D.S. = 1.0 (6.5% N) has taken place. Between this substitution and D.S. = 2.0 a rapid loss of crystalline structure appears to occur. The intensity of the diffraction, corresponding to the 002 interplanar spacing, disappears rapidly and is essentially missing at D.S. = 2.0. Between these substitutions annealing of cyanoethyl cellulose does not occur, but at D.S. = 2.12 and higher it can be brought about readily. Also, above D.S. = 2.0 spontaneous crystallization evidently occurs during stress relaxation measurements, as is indicated by discontinuities in the curves and interruption of decay or even increase of stress with further heating.

The thermal stress curves of the present series of samples show some evidences of a glass transition temperature at substitutions of 1.17 and higher, similar to those shown in the previous series. However, at substitutions above D.S. = 2.0 the evidence for glass transition is less characteristic, since in two out of the three curves observed in this range discontinuities developed as a result of crystallization of cyanoethyl cellulose.

The physical properties of the present series were considerably more promising from a practical standpoint than those measured on loose-reacted yarns. Tensile strength, ultimate elongation, toughness, and immediate elastic recovery showed interesting possibilities, the further exploration of which might lead to useful results.

These results have exposed a new area of research in cellulosic textile fibers. They have demonstrated that by certain means the native, somewhat brittle, crystalline structure of these fibers can be changed to less crystalline or even noncrystalline modifications. This can be done without loss of the fibrous structure. The results give rise to the prospects that with use of appropriate chemical groups, either already at hand or still to be discovered, and a suitable degree of substitution, fibers can be prepared offering a much wider range of choice than has been available, and that eventually fibers may be deliberately modified or tailored to meet the performance requirements of the service contemplated.

## Summary

A study has been carried out on the effect of cyanoethylation of cotton yarns on cellulose fine structure and related phenomena over a range of substitutions from D.S. = 0 to 2.38 under conditions preventing shrinkage. The results may be summarized as follows:

(1) The gross structure of the fibers appears to be little affected except at substitution above D.S. = 2.0, where some swelling occurs. At D.S. = 2.12 and above, the fibers become somewhat plastic and tend to agglomerate as the result of treatment.

(2) Refractive indices decrease as substitution increases and the birefringence decreases. At the higher substitutions, heat, in conjunction with tension, causes increases in the refractive index.

(3) The density of the fiber decreases progressively as substitution proceeds, eventually reaching a value some 20% below that of the native fiber. The density seems to follow approximately the values predicted on the basis of molar weights and molar volumes of the components.

(4) X-ray diffraction observations indicate that up to about D.S. = 1 cyanoethylation is confined to the noncrystalline cellulose, that the crystalline structure is largely destroyed between D.S. = 1.0 and 2.0, and that above this range essentially noncrystalline, incompletely cyanoethylated cellulose is present. They also show that above about D.S. = 2.0 the reaction product can be partially crystallized into a pattern typical of cyanoethyl cellulose.

(5) Thermal stress observations over temperatures up to about 220°C. indicate that a relatively small proportion of cyanoethyl groups in the cellulose is needed to impart signs of a glass transition temperature; and above D.S. = 2 the curves often display discontinuities corresponding to the onset

of crystallization. In samples substituted to this stage, if stress measurements are continued as the temperature is lowered from its maximum value, the stress may greatly exceed that developed during the heating portion of the test.

(6) Certain physical properties of the yarns are reported. It is observed that under the conditions employed and at certain substitutions some improvements are experienced in such properties as tensile strength, tenacity, ultimate elongation, energy of rupture, and immediate elastic recovery.

(7) The results suggest a new area of exploration whereby the fine structure of the cellulose in plant fibers may be selectively tailored to more adequately meet specific service requirements.

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### Synopsis

The cellulose of cotton yarns was reacted with acrylonitrile under conditions preventing their longitudinal contraction.

Changes taking place in the fine structure of the fiber were studied by means of optical microscopy, density measurements, x-ray diffraction, and thermal stress behavior measurements. The results indicate that in spite of the strong tensions developed in the yarns, the reaction proceeds in both the accessible and the crystalline regions with considerable volume expansion and eventual disappearance of crystalline structure. Suggestions of a glass transition temperature appear at substitutions slightly above D.S. = 1. Annealing becomes possible at substitutions above D.S. = 2 with the development of the cyanoethyl cellulose crystal structure and over 40% increase in tensile strength. Changes in tenacity, ultimate elongation, energy of rupture, and immediate elastic recovery were also observed.

### Résumé

La cellulose des fils de coton a été traitée par l'acrylonitrile dans des conditions où une contraction longitudinale est empêchée. Les changements de structure fine d'une fibre ont été étudiés par la microscopie optique, des mesures de densité, la diffraction des rayons-X et des mesures de tension thermique. En dépit des tensions fortes, développées dans les fils, les résultats indiquent que la réaction se passe dans les régions accessibles et cristallines avec une expansion considérable de volume et avec perte éventuelle de la structure cristalline. L'hypothèse d'une température de transition vitreuse apparaît à un degré de substitution un peu au-dessus de D.S. = 1. Un post-traitement devient possible au-dessus d'un D.S. = 2 concomitamment avec un agrandissement de la structure du cristal de la cellulose cyanoéthylée et avec une augmentation de 40% de la force à la tension. Des changements dans la tenacité, l'élongation extrême, l'énergie de rupture et le recouvrement élastique immédiat sont aussi observés.

### Zusammenfassung

Baumwollgarnecellulose wurde unter Verhinderung einer Längskontraktion mit Acrylnitril zur Reaktion gebracht. Die Feinstrukturänderungen der Faser wurden mittels Lichtmikroskopie, Dichtemessungen, Röntgenbeugung und Messung des thermischen Spannungsverhaltens untersucht. Die Ergebnisse zeigen, dass trotz der starken, in den Garnen auftretenden Spannungen, die Reaktion in den durchringbaren und in den kristallinen Bereichen unter beträchtlicher Volumszunahme und schliesslichem Verlust der kristallinen Struktur verläuft. Anzeichen einer Glasumwandlungstemperatur treten bei einer Substitution schwach oberhalb D.S. = 1 auf. Eine Temperung wird bei einer Substitution oberhalb D.S. = 2 möglich, wobei sich die Kristallstruktur der Cyanäthylcellulose entwickelt und eine über 40% Steigerung der Zugfestigkeit eintritt. Auch Änderungen der Zähigkeit, Reissdehnung, Reissenergie und der unmittelbaren elastischen Rückstellung wurden beobachtet.

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