STUDIES ON CHEMICAL REACTIONS AND CRYSTALLINE STRUCTURE OF CELLULOSE
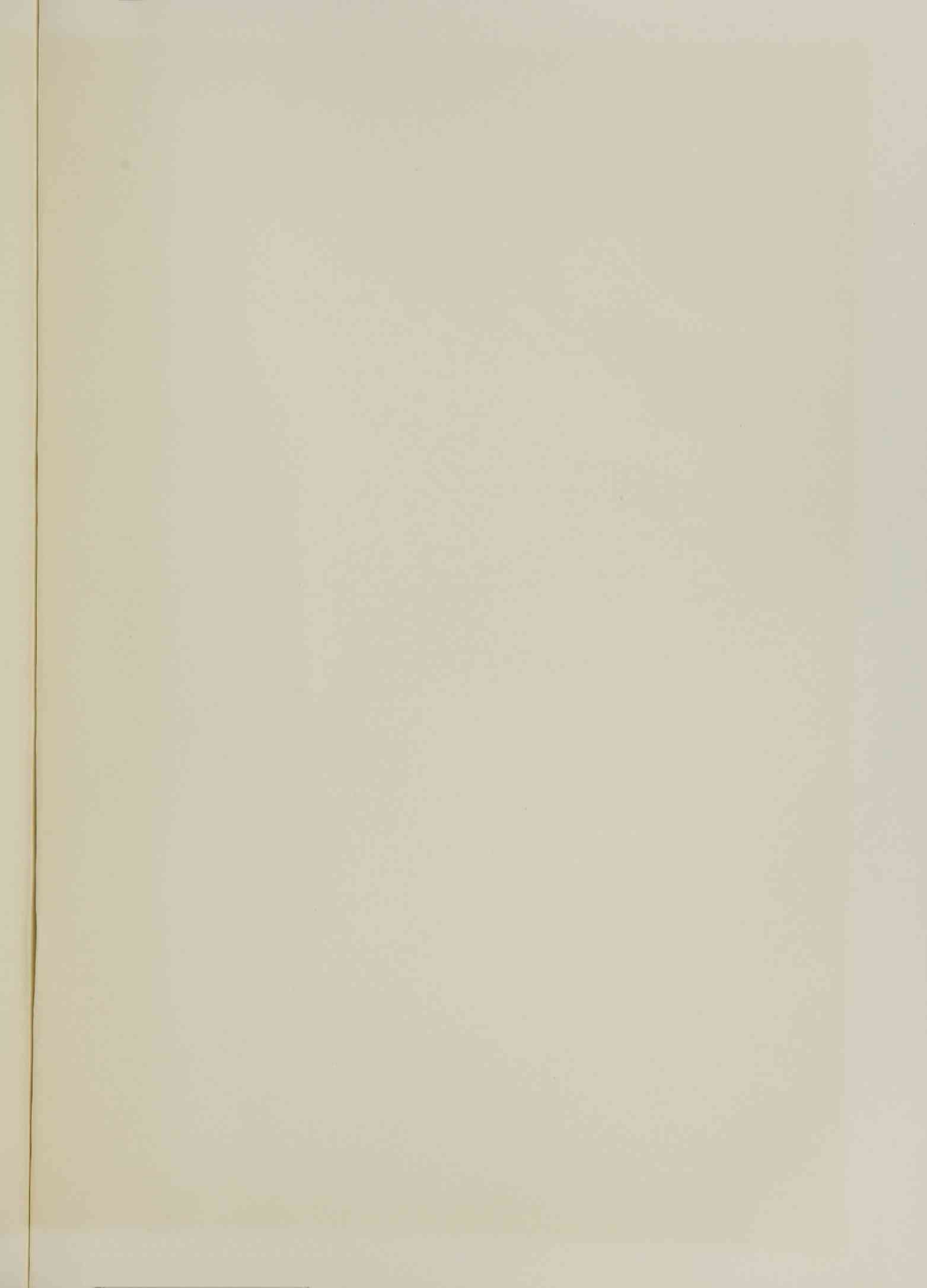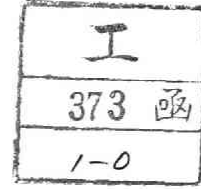
1977

ASAKO HIRAI

STUDIES ON CHEMICAL REACTIONS AND
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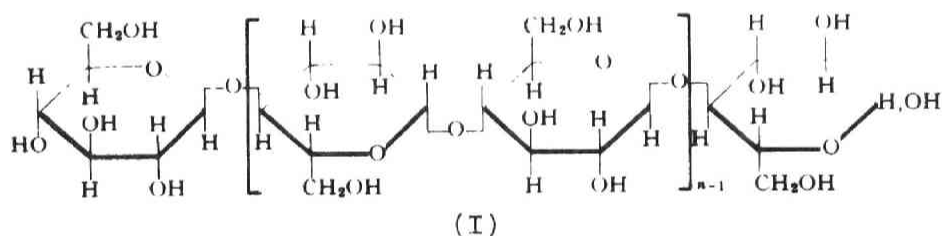# CELLULOSE

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CONTENTS

Chapter 1

Introduction

Cellulose is a linear polymer constructed from the condensation of β-glucose molecules linked together through the 1 and 4 positions (I).

(I)

This formula shows that cellulose contains in each glucose unit three free hydroxyl groups, one primary and two secondary.

The raw materials for the preparation of cellulose derivatives are nearly always fibrous cellulose derived from plant sources. However, a large fraction of the cellulose material in these native fibers is crystalline in nature and the interior of the crystalline region is inaccessible to chemical reagents as long as this native crystalline structure is maintained. Namely, all the three hydroxyl groups are not always uniformly reacted with chemical agents.

The reaction of free hydroxyl groups with chemical agents depends on the fine structure and morphology of the particular cellulose under examination. Therefore, it is necessary to understand the fine structure and morphology of cellulose in order to gain an understanding of the cellulose reactions. In other words, the fine structure of cellulose can be elucidated through the cellulose reaction.

Cellulose shows a distinct tendency for crystallization, probably caused by the relative stiffness of the glucosidic chains and the hydrogen-bonding capacity of its frequent hydroxyl groups. A cellulose fiber however is not a single crystal; it is a polycrystalline aggregate consisting of small crystal regions separated by amorphous or inter-crystalline regions. The crystalline areas in a given cellulose may vary in size, shape and degree of perfection. Native cellulose has a relatively perfect lattice structure by the high cohesive forces in the ordered regions. On the contrary the regenerated cellulose has a number of defects in the lattice.

Mutual interaction between hydroxyl groups plays an important role in aggregation of molecules in an amorphous region as well as in a crystalline region. That is to say, if hydroxyl groups are brought close together, they form hydrogen bonds. Its binding energy is few kilocalories per mole and the strong binding of molecules can be formed.

The strength of cohesive forces per area in an amorphous region depends on the number of hydrogen bonds per area and on the condition of formation.

So the structure of cellulose may be expressed in terms of distribution function (lateral-order distribution curve). A characteristic difference in the distribution is seen between native cellulose and regenerated cellulose fibers, as shown in Figure 1 (1). Native cellulose consists of large crystalline regions separated by amorphous regions of fairly high order. When the cellulose is regenerated a new crystallization must take place. This recrystallization

Fig. 1. Tentative lateral-order distribution curves for various cellulose fibers. Curves: (1) High-tenacity rayon; (2) textile rayon; (3) high-strength, low-elongation rayons; (4) mercerized native fibers; (5) wood pulps; (6) cotton.

consists first of a coagulation followed by a regeneration. Since these procedures usually take place simultaneously in a comparatively short time from a concentrated solution, it is difficult to form ordered arrangements of molecules. Regenerated cellulose consists of relatively large, poorly ordered amorphous regions and small or imperfect crystalline regions.
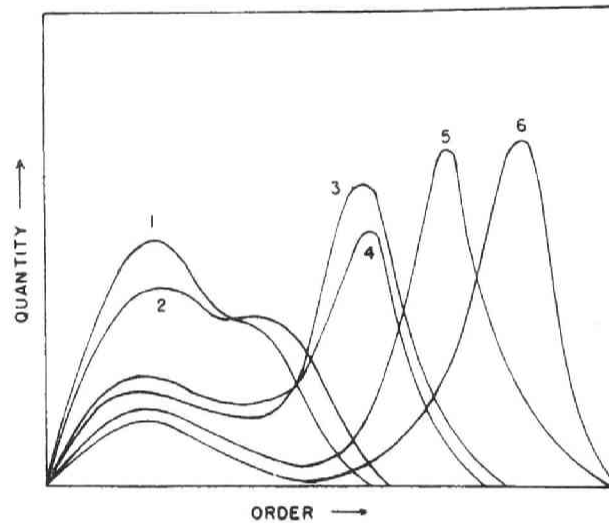
Morphologically, native cellulose fibers consist of a thin outer limiting membrane or primary wall and a thicker secondary wall. The major part of the crystalline cellulose exists in the secondary wall which under the optical microscope appears to be built up of fine fibrils aligned side by side to form layers or lamellas. In most cases they do not lie perfectly parallel to the fibers axis but are inclined at an angle which may vary in different fibers and even in different layers of the same fiber. Fibrils in different layers within the structure may spiral in opposite direction, giving rise to a crossed fibril appearance.

According to Frey-Wyssling (2), the fine structure of cellulose fibers is as follows.

TABLE I
Fundamental Unit of Ramie Fiber

	Cross-section	Number of cellulose chains
molecules	$8.35 \times 3.95 \times \sin 84° A^2 = 32.8 A^2$	1
elementary fibril	$30 \times 100 - 50 \times 60 A^2 = 3000 A^2$	100
microfibril	$250 \times 250 A^2 = 62500 A^2$	2,000
macrofibril	$0.5 \times 0.4 \mu^2 = 0.20 \mu^2$	500,000
ramie fiber	$125 \times 6 \mu^2 = 750 \mu^2$	20,000,000,000

On the other hand, conventional viscose rayon fibers as usually made for textile purposes do not separate into long fibrils, but practically all rayon fibers which have

been strectched during manufacture to produce a high degree
of molecular orientation parallel to the fiber axis will
exhibit fibrillation when beaten or treated with ultrasonic
vibration in the wet state.

As cellulose fiber has the complicated structure des-
cribed above, complicating features are expected to occur
in its reaction with chemical regents. Chemical reagents
penetrate into the outside of fibers and proceed gradually
inward. The existence of several walls mentioned above
influences reaction rate and equilibrium state. In terms
of reaction rate, when V_R designated the velocity of chemi-
cal reaction and V_D designated the penetration rate of
chemical reagents, the relative values of V_R and V_D affect
the mode of reaction. For example, nature of the swelling
agents, their specific interactions with cellulose and the
nature of the order-disorder structure of the cellulose
sample may influence the values of V_R and V_D.

Strong alkali solutions acting on cellulose at low or
roon temperature produce alkali cellulose. This treatment
of cellulose has been known by the textile industry for a
very long time as "Mercerization", so called after John
Mercer who discovered the process in 1844 (3). Further
he (4) realized that 62% sulfuric acid could have a swelling
effect very similar apparently to that of sodium hydroxide.

These treatments of cotton with concentrated aqueous alkali and acid have been important commercial processes. Developments in chemical modifications of cotton have not be seen until recent years. The development in synthetic fibers had a stimulating action on chemical modification of cotton. Studies on the shrink- and crease-proof finishes with intermolecular crosslinking agents are followed by the development of durable press finishing. On the other hand, in both U.S.A. and Japan, chemical modifications in fibrous forms such as esterifications and etherifications have been extensively studied.

Swelling is a characteristic phenomenon closely associated with most cellulose reactions. The nature and extent of swelling vary in the reactivity of different cellulose samples.

, Detailed surveys of most of the early works have been published elsewhere (5) and a brief summary of recent investigations is as follows:

The information with regard to the action of sodium hydroxide on cotton is extensive, but much less is known about the action of other alkaline and of acidic agents. A systematic study of the action of swelling agents on the fine structure of cotton was, therefore, undertaken to compare the action of sodium hydroxide on fine structure of cotton with that of other swelling agents by Warwicker,

Jeffries and co-workers (6). They also investigated by the x-ray and infrared deuteration techique the swelling behavior and structural changes of cotton by washing treatment, by the effects of tension and also by the presence of additives (7). A study on the change in mechanical properties of cotton brought about by swelling agents, such as sodium hydroxide, an iron tartrate complex in sodium hydroxide (EWNN), cuprammonium hydroxide, and sulphuric, phosphoric, nitric and perchloric acids, has been made (8).

Evans and Jeffries (9) investigated the swelling of cotton fiber in solutions of cadoxen [solutions of tris (ethylenediamine) cadmium dihydroxide in ethylenediamine-water mixtures].

Balcerzyk et al. (10) have studied the thermokinetics of the action of water, methanol, ethanol, n-propanol, n-butanol, acetic acid, and concentrated aqueous solutions of NaOH and ethylenediamine on native, mercerized, and regenerated cellulose by a microcalorimetric method. As a result, the penetration rate depended on the structure of accessible regions, dimensions of the penetrant molecule, and the penetrant reaction with hydroxyl groups. The intermolecular distances in the accessible regions of microfibrils seemed to be of the same order of magnitude as that of ethanol molecule with reference to native cellulose and methanol to regenerated cellulose.

High crystallinity of cellulose is the cause of undue stiffness and brittleness as well as low absorption and law chemical reactivity. To overcome these drawbacks and bring about changes in the elastic and other properties of cotton fibers, cottons were treated with anhydrous ethylamine, diethylamine, pyridine, and aqueous solutions of sodium hydroxide (30%) and potassium hydroxide (40%) (11). Crystallinity, moisture regain, degree of polymerization (viscosity method), tensile properties, toughness, and optical properties of treated fibers were measured.

Quaternary ammonium hydroxide has a strong action on cotton. Quaternary ammonium hydroxides, with (12,13) or without (13,14) added alkali metal hydroxides have been used as solvents for cellulose and "mercerizing" agents for cotton yarns (15).

Vigo et al. (16,17,18) compared the effect of alkali metal hydroxides and benzyltrimethylammonium hydroxide (BTMOH), separately and in mixtures, on the cellulose I lattice of cotton by x-ray technique. The breaking strength, elongation-at-break and the energy-to-rupture were also determined.

Next is about swelling and the reactivity of cotton. The reactivity depends more on the type of swelling, whether it is interfibrillar or intrafibrillar, than on the degree of swelling achieved. Furthermore, the reactivity

of the treated cotton depends on whether the reaction is carried out in nonswelling or swelling medium. It is thus important to relate the reactivity of cotton to the morphological and fine structural feactures of the treated cotton than to the degree of swelling attained during the treatment.

The reactivity of cotton treated with alkaline and acid swelling agents has been examined using acetylation as the indicator (19).

In an investigation on the effect of treatment with ethylamine on cotton, Zeronian (20) showed that the solvent used subsequently to remove the ethylamine had a marked influence on the ease of acetylation of the never-dried treated material. Of the solvents tried, pyridine gave the most reactive product. The hygroscopicity of an acetylated product prepared from ethylamine-treated and pyridine-washed cotton was markedly higher than that of a sample of equal acetyl content prepared from ethylamine-treated and water-washed cotton. Special attention has been paid to those materials having a low degree of acetylation (acetyl content about 10%), since there is little possibility of crystalline cellulose acetate being formed (21). Dried ethylamine-treated cotton was easily recrystallized by boiling in water. On the contrary, ethylamine-treated and pyridine-washed cotton that was acetylated and then dried (acetyl content 10.6%) reamined highly disordered after

boiling in water. The importance of adding acetyl groups
in order to prevent a loss in accessibility was confirmed.

In this regard, as early as 1957, Tsuji et al. treated
cotton with acetic anhydride (22) or acrylonitrile (23)
after immersing in 18% sodium hydroxide solution. The
acetyl or cyanoethyl residues thus introduced prevented the
recrystallization during water washing and drying.

Using acetylation as an indicator, comparison have
been made between the reactivity of mercerized, ethanol-
washed, and never-dried cotton and that of mercerized, water----
washed, and never-dried cotton (24). Water (unlike ethanol)
can form more than one hydrogen bond per molecule. Thus, a
water molecule may attach itself to hydroxyl groups in
adjacent cellulose chains and consequently draw the chains
close enough for then to become linked directly by hydrogen
bonds between hydroxyl groups neighboring sites. With the
formation of interchain hydrogen bonds, the cellulose be-
comes less accessible to the acetylating agent and thus less
reactive. Ethanol, in contrast, forms hydrogen bonds with
the free hydroxyl groups in the amorphous regions, thus
preventing the cellulose chains from coming close enough
together to be able to form hydrogen bond crosslinks.

It is to be emphasized that the treatment mentioned
above was performed in fibrous form.

The solvation of cellulose has been the object of

investigation for many decades, and a number of more or less suitable methods have been suggested. Numerous reports on dissolving cellulose in strong mineral acids, such as hydrochloric, sulfuric, and phosphoric acids, have appeared in the literature (5), and solutions in cuprammonium hydroxides were described by Schwizer as early as 1857 (25). While solvation in acids has not been further developed in recent years, solvation in aqueous solutions of metal complex bases has enjoyed considerable development. Traube used ethylenediamine instead of ammonium hydroxide in combination with copper (26), and later, Jayme introduced cadmium as the metal, using it either as ethylenediamine or ammonia complex base (27). Recently, an aqueous solution of the ferric sodium tartrate complex was found suitable for dissolving cellulose (28).

While with nonaqueous media, in 1966 Hata et al. (29) found that natural cellulose is soluble in liquid sulfur dioxide with addition of amines. A new method of dissolving cellulose in nonaqueous media have appeared in the literature (30-36). Cellulose is solvated in strongly polar, aprotic solvents, such as N,N-dimethyl formamide and -acetamide, after introduction of a suffcient amount of dinitrogen tetroxide or nitrosyl chloride (30-33).

Some properties of filaments regenerated from cellulose-triethylamine-liquid sulfur dioxide solution under

various conditions were investigated comparing with those

of viscose model filaments (29). The characteristics of

the fine structure of the model filaments were studies by

x-ray diffraction, and water and iodine sorption methods.

From these examinations, it was recognized that the filament

regenerated in methanol or acetone is highly accessible

(crystallinity: 12-18%, accessibility: 89-93%, calculated

from water sorption data), and the x-ray diffraction pattern

is similar to that amorphous cellulose, while the filament

regenerated in water is less accessible than the filaments

regenerated in methanol or acetone (crystallinity: about

26%, accessibility: about 86%). It was confirmed that the

regenerated cellulose from liquid sulfur dioxide solution

is more amorphous comparing with viscose model filament

(crystallinity: about 34%, accessibility: about 81%).

The crystallinity of cellulose was first confirmed by

Nishikawa and Ono (37,38) who showed that the x-ray diagram

consisted of definite diffraction rings.

Independently (around 1920), Scherrer, Herzog, Jancke

(39,40) recognized that cellulose gives well-defined x-ray

diffraction diagrams. Herzog and Jancke recognized that

cellulose from such widely different sources as cotton,

ramie, wood, jute, and flax gave identical x-ray diagrams

and concluded that all these fibers had identical crystal-

line strucutres. This crystal form has become commonly known as the "native" cellulose form, but the more general term "cellulose I" is now preferred.

On the contrary, if cellulose is dissolved and precipitated from solution or regenerated from some addition compound of cellulose I, such as alkali cellulose which is formed in mercerization, the molecules do not exhibit the characterestic cellulose I lattice but an allotropic modification. This modification is known as "mercerized" or "regenerated" cellulose but it seems better to designate this form simply as cellulose II.

The crystalline structure of cellulose has been recently reviewed by Hayashi (41).

Hayashi et al. have investigated on the chain conformation of cellulose and its derivatives (42-57). From the results on the transformation in crystalline modifications of cellulose, they classified them into two families, namely the Cellulose I family (I, III_I, and IV_I) and the Cellulose II family (II, III_{II}, and IV_{II}). In the Cellulose I family, transformations among I, III_I, and IV_I were possible with each other: the same was true for the Cellulose II family. The Cellulose I family could be transformed into Cellulose II by mercerization or dissolution, but the reverse was not true. The cellulose trinitrate, dinitrate, or triacetate prepared by esterification in fibrous state

from the Cellulose I family was saponified to Cellulose I, and all of the esters from the II family were saponified to Cellulose II. It was considered that the chain conformation of cellulose is different in the two families, and the "memory" of the original structure may be due to the retention of the chain conformation during the reactions.

It is believed that the chain conformations of cellulose are defined essentially by the internal rotation angles between two glucose rings. The angles are fixed by the intramolecular hydrogen bonds $O_3 \rightarrow O_5'$. Accordingly, it must be the relaxation of these bonds that causes change of the chain conformation. If the bonds are relaxed by the hydration, the chain of Cellulose I in the "bent" form must change to the "bent and twisted" form. The distance $H_1 \rightarrow H_4'$ in the "bent" form is very short and must result in large instability to the chain, but when it becomes longer by the twisting of the glucose rings, the stability of the chain must increase. Accordingly, the change of the chain conformation from the "bent" form to the "bent and twisted" form must be irreversible. Also, when the water hydrating the O_3 and O_5' hydroxyls is dehydrated, the water may twist the chain and change its conformation.

In mercerization reactions, there were two opportunities for the change of the chain conformations. First, the crystallites of Cellulose I were fully relaxed by

aqueous alkaline solution, and the molecular chain was
hydrated before forming the crystallites of Na-Cellulose I.
The hydration changes the chain conformation from the Cellu-
lose I type to the Cellulose II type, and this results in
Na-Cellulose I_{II} and Cellulose II.

When mercerization was carried out under the conditions
of less relaxation of the cellulose crystallites (reaction
at high temperature, at fixed length, and with NaOH solution
of lower concentration), the crystallites of Na-Cellulose I
were formed without passing the stage of fully hydrated
cellulose. In this case, the chain conformation of Cellu-
lose I was retained in the Cellulose I type and resulted
in Na-Cellulose I_I.

Second was the stage of regeneration from Na-Cellulose
I_I to cellulose. If the chain was hydrated before forming
,the crystallites of cellulose, the chain conformation of
Cellulose I type was changed into Cellulose II type and
resulted in Water-Cellulose. Water-Cellulose gave Cellu-
lose II by drying. When Na-Cellulose I_I was regenerated at
the lower swelling conditions at high temperature, the
crystallites of cellulose were rapidly formed in a wet
state without passing the stage of hydration. Accordingly,
the chain conformation remained the Cellulose I type and
gave Cellulose I.

Consequently, transformation from Cellulose I to Cellu-

lose II takes place either by hydration of the chain or
dehydration of the hydrate.

Warwicker and Jeffries et al. (58,59) explained the
process of mercerization in terms of the concept of sheets
of cellulose chains.

Literatures regarding chemicl reaction and structure
of cellulose were described above. The object of this
dissertation is to investigate the method of decrystalli-
zation of cotton (in fabric form or fiber form) and to
clarify the structural change and the effect on the proper-
ties of cotton.

Tsuji and Imai (22,23) investigated several properties
of decrystallized cotton by the treatment with alkali-
acetic anhydride and alkali-acrylonitrile; especially high
hygrosopicity and good dyeability were obtained. But the
structures of treated cottons were not studied in detail.
As described previously, the chemical nature of cellulose
and the structure of cellulose fibers are obviously impor-
tant. Studies on the comparison of the change given by
chemical reaction in the structure of cotton and regenerat-
ed cellulose fiber such as polynosic and cuprammonium rayon
will give informations on fine structures of cellulose.

In chapter 2, the effect of the swelling agents were
examined to obtain highly accessible cotton by chemical

method. Various swelling agents including sodium hydroxide were examined to develop previous work (23).

Accessibility is mainly estimated from moisture regain (or sorption ratio) (60-70). In this experiment accessibility was estimated from moisture regain by Valentine's relation (64,69).

In chapter 3, the crystalline structure of alkali-acrylonitrile treated cotton fabric was examined by means of x-ray and infrared. The x-ray diffraction profiles were resolved into Gaussian curves by means of a curve resolver. From the resolved curves, lattice spacing, dimension and cross-sectional area of unit cell, and integral breadth were obtained. Structural change was examined from these parameters.

In chapter 4, the moisture regain and the crystalline structure of partially cyanoethylated cotton fibers were examined in comparison with the results on the cotton fabrics.

In chapter 5, cotton immersed in the sodium hydroxide solutions containing ethanol was cyanoethylated and the crystalline structure and properties of cellulose thus obtained was examined.

In chapter 6, regenerated cellulose fibers, such as cuprammonium rayon and polynosic fibers were treated with alkali-acrylonitrile in the presence of ethanol and the

crystalline structure of the treated cellulose fibers were compared with the results on cotton fibers. The presence of ethanol in the aqueous solution of sodium hydroxide prevents the solvation of regenerated cellulose. How the difference in the fine structure of native and regenerated cellulose influences the structure of alkali-acrylonitrile treated sample will be examined.

In chapter 7, mechanical properties of the cotton fabrics treated with alkali-acrylonitrile before and after crosslinking with dimethylol ethyleneurea and trimethylol melamine were investigated.

As well-known, cotton is an essential textile fiber and finishing of cotton textiles is an important process. Mercerization of cotton with sodium hydroxide has been in practical use for many years. In recent years, chemical treatment has become a matter of an increasing interest to give cotton a new property such as wash and wear performance.

As described previously, cotton fiber has high crystallinity and rigid structure. It is an useful characteristics of cotton, but in some cases relaxing or loosening of the structure of cotton fiber is thought to be an effective way for new finishing process. In connecting with this circumstances, swelling of cotton has become a significant problem not only for scientific but also for practical

meaning. As referred above, many works have been done on swelling of cotton.

It is a serious problem that cotton fabrics considerably decrease their tensile strength, tearing strength and abrasion resistance by crosslinking in crease proof or wash and wear finishing. The cause of these practically undesirable phenomena is not yet sufficiently clarified, but it is presumed that stress dose not uniformly distribute owing to the molecular structure more tightly fixed by crosslinking. In this sense relaxing or lossening of the structure of cotton fiber may be significant. Mercerization of cotton yarns and fabrics with liquid ammonia is now technologically developing. In this case it is said that more uniform distribution of resin is obtained in wash and wear finishing.

It is expected that present research on swelling or decrystallization of cotton may contribute also to such a technological problem.

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Chapter 2

Preparation of Highly Accessible, Decrystallized Cotton
by Various Chemical Methods

INTRODUCTION

Some interesting research to obtain highly accessible cotton has been carried out in the U.S. by the "decrystallization of cotton" (1). The principle of this method was to decrystallize cotton by swelling cotton fibers at low temperature with lower alkyl amines such as ethylamine and then extract the fibers with nonaqueous solvents such as hexane or chloroform. By this technique, the crystallinity of cotton was markedly decreased. The fiber tenacity was not lowered, and elongation, water absorbency, dyeability, chemical reactivity, and luster of the fabric were improved (2).

It seems, however, that this method has some problems for practical use. Cotton fiber had to be immersed in ethylamine at low temperature (-40°-0°C), and hexane, chloroform, or acetone was needed to extract excess ethylamine. Moreover, cotton cellulose, thus decrystallized, recrystallized readily when immersed in water, especially hot water

(3,4).

It was also reported that amorphous cellulose could be obtained by grinding in a vibratory ball mill (5,6), or by saponification of cellulose acetate in a nonaqueous medium (7), but amorphous cellulose thus obtained was known to recrystallize on immersion in water.

Hereupon, we intended to decrystallize cotton cellulose by a more practical method. The principle of our method was to impregnate cotton fabric with 18% sodium hydroxide solution and then react it with acrylonitrile. In this reaction, a small quantity of cyanoethyl residues was introduced onto cellulose chains in the amorphous region which was promoted by alkaline swelling. It was presumed that the cyanoethyl residues thus introduced prevented the recrystallization during water washing and drying. By this method, permanently decrystallized, highly accessible cotton was obtained (8).

In this chapter, more extensive treating conditions are examined using various swelling agents, and the structure and properties of the modified cotton are investigated.

EXPERIMENTAL

Sample.   Scoured and bleached 40's cotton fabric (plain weave, Toyo Spinning Co.).

Treatment.   10 cm × 10 cm sample fabric (*ca.* 1g) were treated in slack state.

Treatment with Alkali.   Sample fabrics were immersed in an aqueous solution of alkali for 30 min at -40°C-15°C. Then after being squeezed to about 100% pick up, they were rinsed with water for 30 min, immersed in 0.2% acetic acid for 30 min, rinsed again with water for 30 min, and air dried.

Treatment with Alkali and Acrylonitrile.   Sample fabrics were immersed in an aqueous solution of alkali for 30 min at -40°C-15°C. Then, after being squeezed to about 100% pick up, the fabrics were immersed in acrylonitrile for 10-300 min at 0-40°C, squeezed to about 100% pick up, immersed in 0.2% acetic acid for 30 min, rinsed with water for 30 min, and air dried.

Treatment with Acrylonitrile after Pretreatment with Various Swelling Agents.   Sample fabrics were immersed in various swelling agents, squeezed to about 100% pick up, immersed in acrylonitrile, neutralized with 0.2% acetic acid, and rinsed with water.

Moisture Regain.   After vacuum drying for 3 hr at room

temperature, sample fabrics (about 500mg) were conditioned
at 20°C and 65% R.H. (over a saturated aqueous solution of
magnesium acetate) until constant weight was reached and
weighed. The sample was then dried for 24 hr at 40°C under
high vacuum and weighed. The moisture regain was calculated
from the weights before and after drying.

Density.   About 5 mm × 5 mm sample fabrics were dried
for 24 hr at 40°C under high vacuum, and then the densities
were measured by the floating method using a mixture of
carbon tetrachloride and toluene.

Nitrogen Analysis.   Nitrogen contents (%N) of fabrics
treated with acrylonitrile were estimated by the micro-
Kjeldahl method. The degree of cyanoethylation was
calculated using the following formula:

$$\text{Degree of cyanoethylation (mole\%)} = \frac{162 \times N}{42 - 1.59 \times N}$$

where mole% represents the percentage value of cyanoethylat-
ed OH residues against OH residues of cellulose.

Infrared Spectra.   Infrared spectra were obtained with a
Perkin-Elmer Model 521 spectrophotometer by the use of the
KBr pellet technique. Fibrous samples were cut with
scissors into small pieces before mixing with KBr.

RESULTS AND DISCUSSION

Acrylonitrile Treatment of Cotton Pretreated with Various Alkali Metal Hydroxides

Cotton fabrics were swollen in aqueous solutions of various alkali metal hydroxides and then treated with acrylonitrile. Moisture regains of the treated fabrics were measured as an indication of accessibility or degree of decrystallization.

Table I shows the results obtained by the use of various alkali metal hydroxides. In Table I, the moisture regains of cotton before and after acrylonitrile treatment are shown. It is observed that the moisture regain is increased by acrylonitrile treatment, which shows the effect of cyanoethyl residues introduced onto cellulose molecules to prevent recrystallization during water washing and drying (blocking effect). Cotton fabrics having very high moisture regains can be obtained by such a procedure. Cyanoethylation proceeds faster in the order KOH > NaOH > LiOH, and the degree of cyanoethylation shows a maximum at the concentration of alkali in which cotton shows maximum swelling, that is, 4.0, 4.5, and 5.7 N for LiOH, NaOH, and KOH, respectively. The effect of the temperature of NaOH pretreatment on the moisture regain was examined by lowering

TABLE I

Acrylonitrile Treatment of Cotton Pretreated with
Various Alkali Metal Hydroxides[a]

Alkali	conc., N	Moisture regain, %		CN Deg.,[d]
		Alk.[b]	Alk.-AN[c]	mole%
—	—	7.8[e]	—	—
LiOH	4.4	10.5	12.3	3.6
NaOH	2.2	9.3	9.8	6.8
	3.0[f]	10.4	12.0	9.7
	4.5	10.3	12.1	8.6
	5.4	11.7	14.0	7.7
	8.2	12.4	14.3	5.1
KOH	2.2	8.7	9.9	11.9
	3.0	9.3	11.0	16.1
	4.6	10.9	11.8	17.0
	5.4	11.2	11.9	19.1
	6.1	11.0	12.4	15.2
	8.1	11.6	12.2	10.3

a Alkali treatment for 30 min at 15°C; AN treatment
   for 30 min at 20°C.
b Alkali treatment alone.
c AN treatment after alkali treatment.
d Degree of cyanoethylation.
e Original cotton fabric, no alkali treatment.
f Alkali treatment for 30 min at 0°C.

the immersion temperature, but no significant effect was observed, as in shown in Table II. Sodium hydroxide solution, 3N, was used, because it has been reported (9) that cotton shows a maximum degree of swelling at this concentration at 0°C.

Table III shows the results when DMSO was added to acrylonitrile. Since DMSO acts as a solvent for both water and acrylonitrile, acrylonitrile could react more readily with the cotton fibers. However, the degree of cyanoethylation and moisture regain decreased. When the fabric was immersed in acrylonitrile for 60 min, the fabric became yellow and the degree of cyanoethylation did not increase.

Table IV shows the effect of time and temperature on acrylonitrile treatments. As shown in Table IV, the higher the temperature and the longer the time of acrylonitrile treatment, the higher the degree of cyanoethylation.

Treatment of Cotton with Various Swelling Agents

The effect of the treatment of cotton with various swelling agents were examined. Results obtained are shown in Table V. It was shown that various swelling agents, except ethylenediamine and BTMOH, did not give as high moisture regains as alkali metal hydroxides. Washing with acetone seems to give somewhat high values of moisture regain when BTMOH was empolyed.

-31-

TABLE II

Effect of Immersion in NaOH Aqueous Solution
at Low Temperature

NaOH treatment			Moisture regain, %		CN Deg., mole%
Conc., N	Temp., °C	Time, min	Alk.[a]	Alk.-AN[b]	
—	—	—	7.8[c]	—	—
3	-40~-30	30	10.6	12.0[d]	6.9
3	0	30	10.4	12.0[e]	9.7

a Alkali treatment.
b AN treatment after alkali treatment.
c Original cotton fabric.
d Samples were treated with acrylonitrile for 60 min at 0°C and then for 15 min at 20°C.
e Samples were treated with acrylonitrile for 30 min at 20°C.

TABLE III

Effect of DMSO on Acrylonitrile Treatment[a]

AN treatment			Moisture regain, %	CN Deg., mole%
DMSO/AN Vol. ratio	Temp., °C	Time, min		
—	—	—	7.8[b]	—
0/100	20	30	14.0	7.5
90/ 10	20	30	11.2	1.2
90/ 10	20	60	7.9	1.8

a Pretreated with 5.4N NaOH aqueous solution for 30 min at 15°C.
b Original cotton fabric.

TABLE IV

Effect of Time and Temperature
on Acrylonitrile Treatment

AN treatment[a]			
Temp., °C	Time, min	Moisture regain, %	CN Deg., mole%
—	—	7.8[b]	—
—	—	11.0[c]	—
0[d]	30	10.9	0.7
20	10	13.2	2.3
	30	14.0	7.7
	60	13.5	11.7
30	10	12.0	7.9
	30	11.6	15.5
	45	—	20.9
	60	11.0	23.0
40	10	11.9	10.4
	30	10.8	25.8
	60	10.2	28.4

a Pretreated with 5.4N NaOH aqueous solution
   for 30 min at 15°C.
b Original cotton fabric.
c Alkali treatment alone.
d Pretreated with 5.4N NaOH aqueous solution
   for 30 min at 0°C.

TABLE V

Treatment of Cotton with Various Swelling Agents

Swelling agent	Concn., %	Temp., °C	Time, min	Washing[b]	Shrinkage W × F, %	Moisture regain, %
None	—	—	—	water	—	7.8
NaOH	18	15	30	water	20×10	11.0
KOH	32	15	30	water	24×12	11.0
LiOH	9.6	15	30	water	15×6	10.5
EA[a]	95	0	30	cold water	—	9.5
	95	0	30	acetone	—	8.9
	95	0	30	EtOH-water	—	9.2
TEA[a]	100	0	30	cold water	0×0	8.2
EDA[a]	44	20	30	water	17×6	10.5
PP[a]	saturated	20	30	water	0×0	8.6
Urea	50	20	60	squeezed	—	8.2
DMF	100	20	30	water	3×−1	8.5
DMSO	100	20	30	water	5×−3	8.3
BTMOH[a]	35	20	30	water	—	10.6
	35	20	180	water	21×18	10.5
	35	20	30	acetone(10 min),water	—	11.7
	35	40	30	water	24×12	9.6[c]
	35	25	1440	water	—	11.3[c]
	40	25	1440	water	—	11.1[c]
ZnCl$_2$	65	20	30	water	6×2	9.4[c]
	65	25	960	water	—	9.3

a   EA: ethylamine, TEA: triethylamine, EDA: ethylenediamine, PP, piperazine, BTMOH: benzyltrimethylammonium hydroxide.

b   30 min.

c   Measured at 25°C.

Dual Pretreatments of Cotton with Various Swelling Agents
and NaOH

Cotton fabrics were immersed in various swelling agents
and transferred, with or without washing with water, into
5.4N NaOH for 30 min at 15°C. The cotton fabrics, after
being squeezed to about 100% pick up, were then treated
with acrylonitrile for 30 min at 20°C. Results obtained
are shown in Table VI. The effect of acrylonitrile treat-
ment in increasing the moisture regain is notable, suggest-
ing the effect of cyanoethyl residues introduced onto
cellulose molecules to prevent recrystallization during
washing of the swelling agent and during drying. It was
expected that some dual pretreatments including NaOH treat-
ment might give effective results, but any significant
effects were not obtained as compared with the single
pretreatment with NaOH.

Dual Pretreatments of Cotton with BTMOH and NaOH

The effect of the pretreatment with BTMOH, having a
powerful swelling ability for cellulose, was examined in
more detail.

Since it was known that caustic alkali, alkali cyanide,
and quaternary ammonium compounds had catalytic action in
cyanoethylation, cotton fabric was pretreated with a 35%

TABLE VI

Dual Pretreatment of Cotton with Various Swelling Agents and
NaOH before Acrylonitrile Treatment

Swelling agent	Concn., %	Temp., °C[a]	Temp. NaOH, °C[b]	Moisture regain, %		CN deg., mole%
				No AN	AN[f]	
—	—	—	15	11.7	14.0	7.7
EA	95	0	0	—	13.8	8.3
	95	0[c]	0	—	13.7	7.4
	73.5	0[d]	15	—	13.9	6.0
TEA	100	0[d]	0	10.8	13.1	7.6
EDA	100	20	15	12.2	14.2	7.9
PP	saturated	20	15	11.6	13.6	7.8
Urea	50	20	15	11.5	13.6	7.6
DMF	100	20	15	11.1	13.2	7.8
DMSO	100	20	15	11.1	13.0	7.9
BTMOH	35	20	15	—	13.6	5.4
	35	20[e]	15	—	13.1	3.2
$ZnCl_2$	65	20	15	—	13.0	4.9

a   Immersed for 30 min, then washed with water prior to NaOH treatment.
b   Immersed in 5.4N NaOH for 30 min.
c   Washed with acetone (not with water).
d   No washing before NaOH treatment.
e   Washed with acetone for 10 min, then washed with water for 30 min.
f   Immersed in AN at 20°C for 30 min.

BTMOH and immersed into acrylonitrile after being squeezed. But the treated fabric was discolored, excessive shrunk, and hornified.

Betrabet et al. (10) reported the properties and structure of cotton fibers treated with BTMOH. Cotton fiber was treated with a 25-40% (w/w) BTMOH, then washed in water, solvent exchanged in dry methanol and diethyl ether, and air dried. It was found that at BTMOH concentrations above 32%, rapid decrystallization and intracrystalline swelling took place. Vigo et al. (11,12) reported that, although cotton yarn was decrystallized by the treatment with 35% BTMOH, it recrystallized almost to the original degree when BTMOH was washed out with water, benzene, ethanol, or ether and, further, that the conversion of cellulose I to cellulose II lattice was barely observed. But, if BTMOH was exchanged with polar, aprotic water-soluble solvents such as acetone, pyridine, and DMSO, it was found that significant decrystallization and conversion to cellulose II lattice took place even after the solvent was washed out with water.

We examined the effect of pretreatment with 35% BTMOH. Results obtained are shown in Table VII. When cotton fabric was treated with BTMOH alone, it seemed that the moisture regain of samples washed out with acetone before water washing was higher than that of samples washed with water

TABLE VII

Dual Pretreatment of Cotton with BTMOH and NaOH before
Acrylonitrile Treatment

BTMOH				Moisture regain, %			CN deg., mole%
Concn., %	Temp., °C	Time, min	Washing	BTMOH[a]	BTMOH-NaOH[b]	BTMOH-NaOH-AN[c]	
5.4N NaOH alone	—	—	water	—	11.7	14.0	7.7
35	20	30	water	10.6	—	13.6	5.4
35	20	180	water	10.5	12.4	13.6	5.2
35	40	30	water	9.6	12.0	12.7	7.5
35	20	30 ⎫	acetone, water	11.7	12.4	13.3	4.5
35	20	960 ⎭		—	—	13.2	4.3
34.4% BTMOH	20	30 ⎫	acetone, water	—	—	13.1	4.3
-14% EtOH	20	2100 ⎭		—	—	13.9	7.5

a BTMOH → water washing → air drying.
b BTMOH → washing → squeezed| → 5.4N NaOH, 15°C, 30 min → water washing → AcOH
   → water → air drying
c BTMOH → washing → squeezed → 5.4N NaOH, 15°C, 30 min → squeezed → AN, 20°C,
   30 min → AcOH → water → air drying.

alone, though the effect of acetone washing was not distinct after NaOH or acrylonitrile treatment. Anyhow, the dual pretreatment with BTMOH and NaOH resulted in fairly high moisture regains in the cotton fabrics, but did not exceed the value obtained by pretreatment with 5.4N NaOH alone.

Recently, Vigo et al. (13) reported that cotton yarn was drastically decrystallized when the yarn was treated with 33.5% BTMOH in the slack state, and then after centrifugation (without water washing) immersed in 18-23% NaOH. In our experiment described above, BTMOH was washed with water, or acetone and water, prior to immersion in NaOH. The effect of washing out of BTMOH has not yet been examined.

Dual Pretreatments of Cotton with Liquid Ammonia and NaOH

The effect of the pretreatment with liquid ammonia was examined because of its use in mercerization.

Cotton fabrics were treated with liquid ammonia for 1 min, then immersed into 5.4N NaOH for 30 min at 15°C, followed by treatment with acrylonitrile.

Results obtained are showed in Table VIII. With respect to the moisture regain, it seemed that liquid ammonia had no greater effect than 5.4N NaOH. If cotton fabrics treated with liquid ammonia were transferred into

TABLE VIII

Dual Pretreatments of Cotton with Liquid Ammonia and NaOH
before Acrylonitrile Treatment

Liq. NH$_3$ treatment	5.4N NaOH 15°C, min	AN 20°C, min[a]	Moisture regain, %	CN deg., mole%
None	—	—	7.8[b]	—
1 min; air drying	—	—	9.5	—
1 min; 50°C water, 2 min	—	—	9.8	—
1 min; water boil, 2 min	—	—	9.6	—
1 min	30	10	11.8	1.9
1 min	30	20	12.3	4.0
1 min	30	30	12.3	8.6
1 min	—	10	10.3	0
1 min	—	20	10.1	0
1 min	—	30	9.9	0

a   After treatment with acrylonitrile, samples were immersed in
    0.2 % acetic acid, then water rinsed.
b   Original cotton fabric.

acrylonitrile without the pretreatment with NaOH, cyanoethy-
lation of cellulose did not result.

Moisture Regain of Cotton with Various Degrees of
Cyanoethylation

Cotton fabrics were treated with acrylonitrile at 20°C
for various periods of time after pretreatment with NaOH or
KOH of various concentrations, or after dual pretreatment
with BTMOH or ethylenediamine and 5.4N NaOH. In these
treated cotton fabrics of various degrees of cyanoethylation,
the moisture regain was measured (Tables IX and X). The
relations between the moisture regain and the degree of
cyanoethylation are shown in Figures 1, 2 and 3. These
curves are similar in shape and have a maximum at a degree
of cyanoethylation of about 5-8 mole%. It is presumed that
the maximum of moisture regain occurs as a result of balance
of the increase in accessibility and the increasing fraction
of sample weight that is not cellulosic material. It is
noted that the straight lines at higher degrees of cyano-
ethylation are nearly parallel, showing that the blocking
effect is dependent on the degree of cyanoethylation.

The moisture regains obtained by extrapolating these
straight lines to zero degree of cyanoethylation are pre-
sumed to show the values of the treated cottons when the

-41-

TABLE IX

Moisture Regain of Cotton Fabrics Treated with Acrylonitrile
after Pretreatment with NaOH or KOH

AN treatment at 20°C, min	2.2N NaOH[c]		5.4N NaOH[c]		8.2N NaOH[c]	
	CN deg., mole%	M.R.,[b] %	CN deg., mole%	M.R.,[b] %	CN deg., mole%	M.R.,[b] %
NaOH alone[a]	—	9.2	—	11.7	—	12.4
10	2.3	9.5	2.3	13.2	2.1	13.5
20	4.8	9.8	4.0	13.5	3.4	14.0
30	6.8	9.7	7.7	14.0	5.1	14.3
60	13.5	9.1	11.7	13.5	6.6	14.2
120	27.4	8.0	20.2	12.4	9.1	13.8
180	—	—	25.5	11.5	12.5	13.6
300	—	—	—	—	16.3	13.2
	2.2N KOH[c]		5.4N KOH[c]		8.2N KOH[c]	
KOH alone[a]	—	8.7	—	11.2	—	11.6
10	3.5	10.0	8.1	13.2	5.2	12.5
20	8.1	9.8	14.4	12.7	7.9	12.2
30	11.9	9.9	19.1	11.9	10.3	12.2
60	28.0	8.4	30.3	10.4	16.0	11.6

a Moisture regain of untreated cotton, 7.8%.
b M.R.= Moisture regain.
c Alkali pretreatment, 15°C for 30 min.

TABLE X

Moisture Regain of Cotton Fabrics Treated with
Acrylonitrile after Dual Pretreatment with
Either BTMOH or Ethylenediamine, and NaOH

AN treat-ment, min	35% BTMOH[a]		Ethylenediamine[b]	
	CN deg., mole%	M.R., %	CN deg., mole%	M.R., %
10	1.6	12.9	2.6	14.1
20	3.1	13.2	5.0	14.5
30	4.5	13.3	7.2	13.9
60	7.4	13.3	12.6	13.6
120	12.7	12.8	23.0	11.7
180	19.5	11.9	25.1	11.4

a   Samples were treated with 35% BTMOH for 30 min
    at 20°C, washed with acetone for 10 min, washed
    with water for 30 min, squeezed, then immersed
    in 5.4N NaOH for 30 min at 15°C, squeezed, and
    treated with acrylonitrile at 20°C.
b   Samples were treated with ethylenediamine for
    30 min at 20°C, washed with water, squeezed, then
    immersed in 5.4N NaOH for 30 min at 15°C,
    squeezed, and treated with acrylonitrile at 20°C.
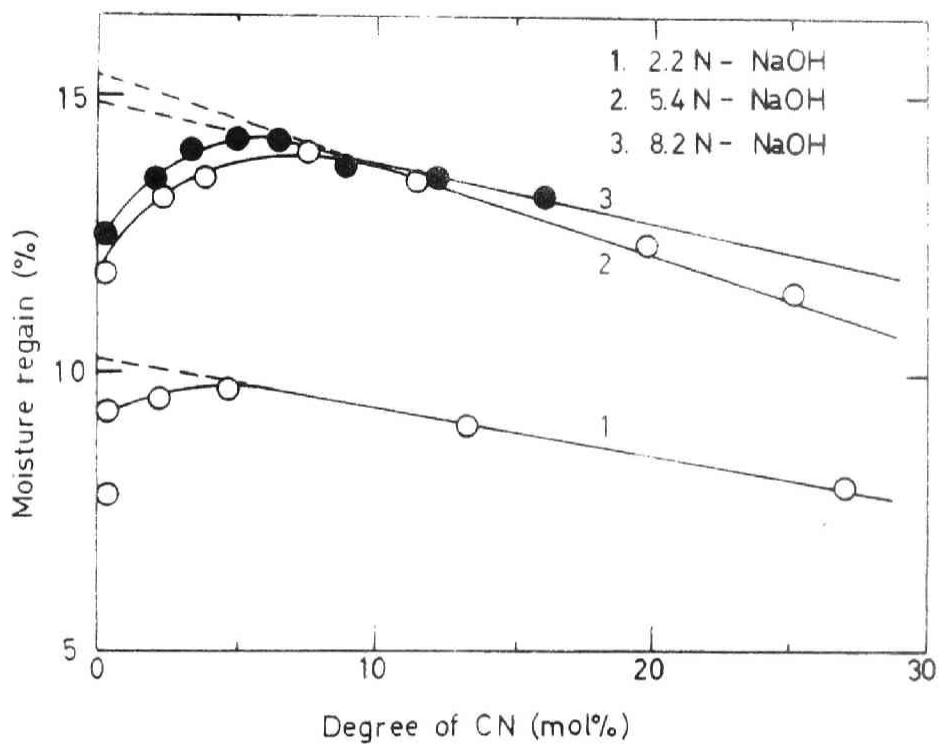
Figure 1.   Relation between the moisture regain and the
degree of cyanoethylation of the cotton fabrics treated
with acrylonitrile at 20°C for different periods of time
after the pretreatment with NaOH of different concentrations.
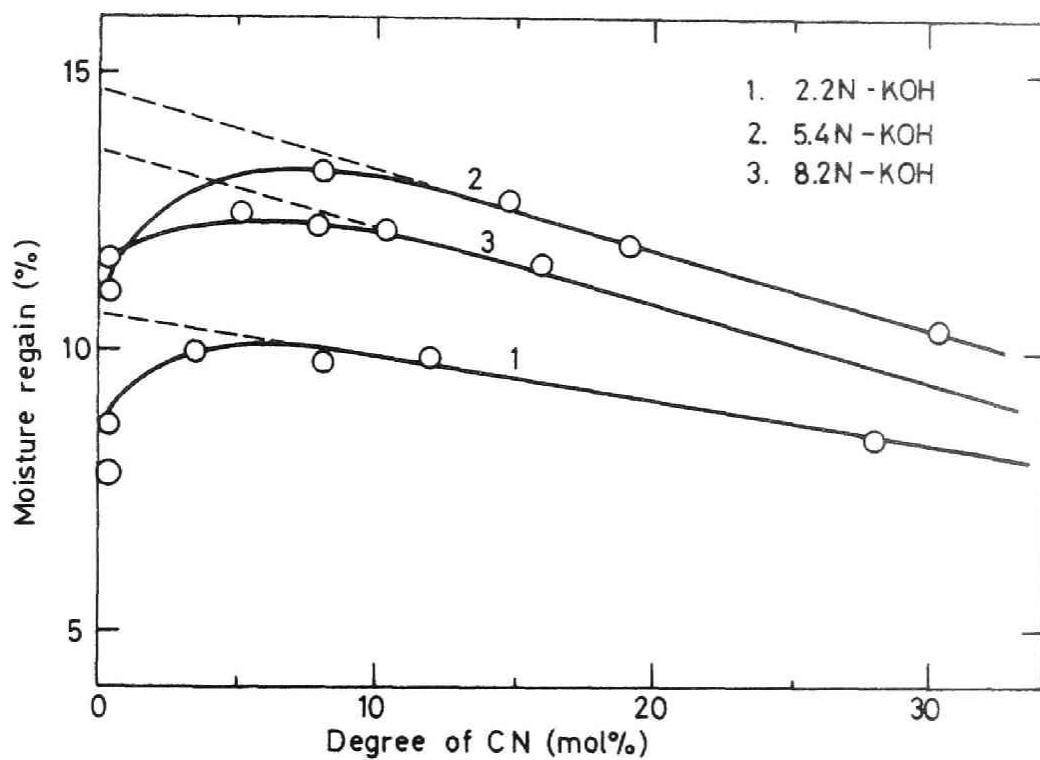
Figure 2. Relation between the moisture regain and the degree of cyanoethylation of the cotton fabrics treated with acrylonitrile after the pretreatment with KOH.
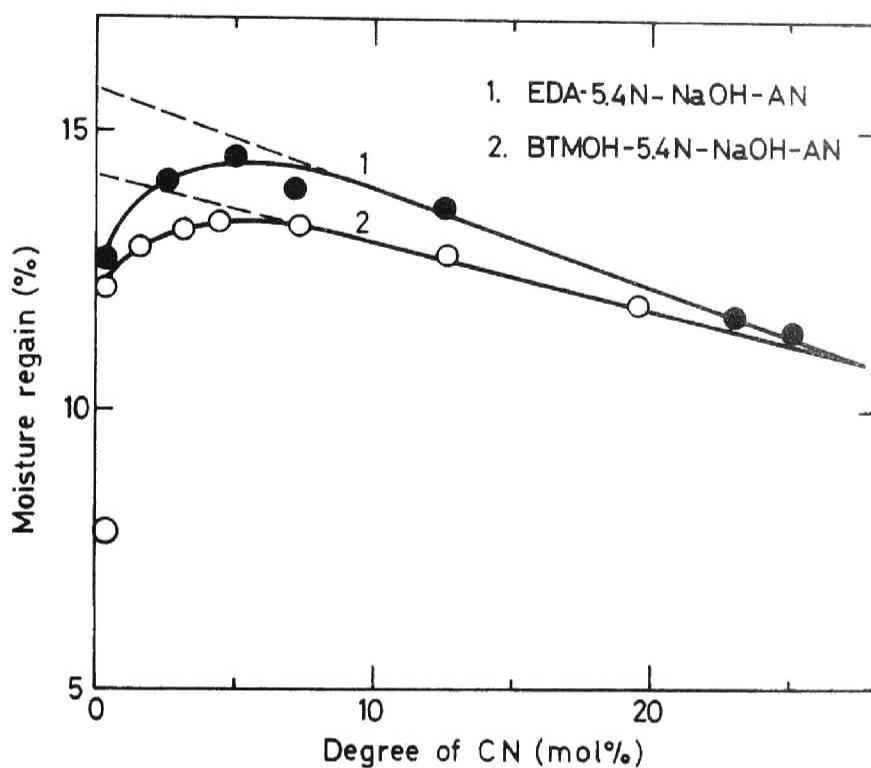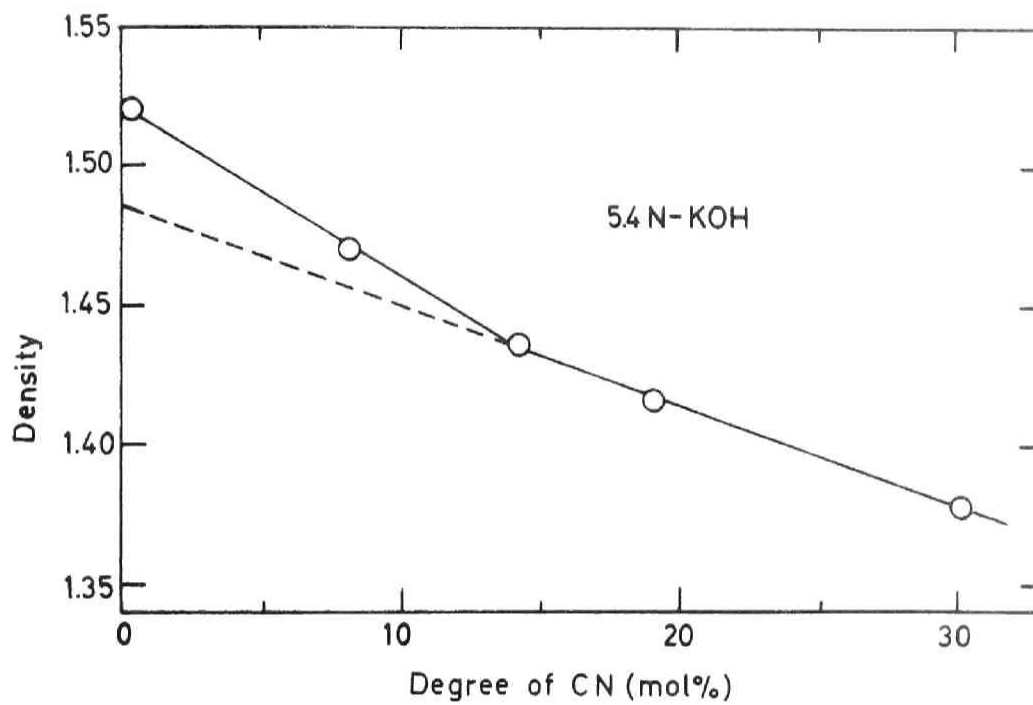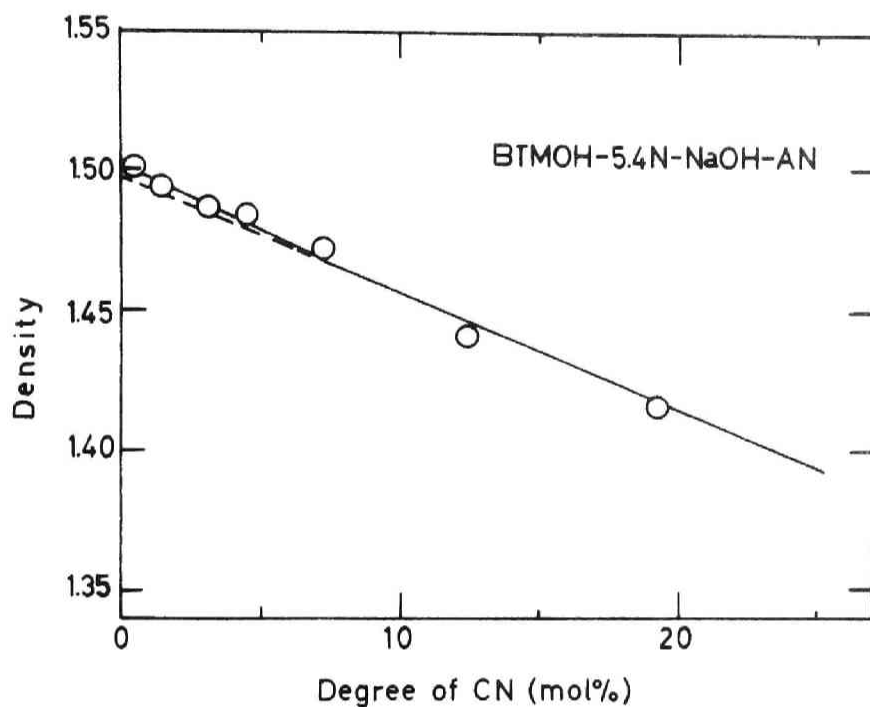
Figure 3.   Relation between the moisture regain and the
degree of cyanoethylation of the cotton fabrics treated with
acrylonitrile after the dual pretreatments with either 35%
BTMOH or ethylenediamine and NaOH.

blocking effect of the cyanoethyl residues is eliminated. That indicates the substantial ability of the treatments to give highly accessible cotton. Thus, it seems that the treatment with 5.4N NaOH or KOH and the dual treatment with the 35% BTMOH or ethylenediamine and 5.4N NaOH have similar effect in making the cotton highly accessible.

It is noted that the assumed moisture regain of about 15% is fairly close to the value of 16.75% obtained by Jeffries (14) for the disordered cellulose prepared by regeneration of cellulose derivatives in a nonaqueous medium.

It is practical and interesting that by our method, cotton fabrics having high moisture regain (*ca.* 14%) can be obtained without decreasing the mechanical strength, and that this value of moisture regain is not lowered even after immersion in boiling water, owing to the effect of cyanoethyl residue to prevent the recrystallization of cellulose.

It is also interesting that cotton fabrics having a high degree of cyanoethylation (20-30 mole%) and moisture regain of 10% or more can be obtained whose practical properties may be interesting. The moisture regain of cotton fabrics cyanoethylated to a similar degree of cyano-ethylation by the ordinary method using 3-5% NaOH will be as low as 4-5%.

Densities of some samples of the treated cotton de-
scribed in Tables IX and X were measured. The results
obtained are shown in Figures 4, 5 and 6. Each density-
cyanoethyl content curve fell into two parts: an initial
linear portion followed by a second linear portion. It
is noted that these straight lines are seemed to show the
knick points that nearly correspond to the maximum points
in the relation curves between moisture regain and the
degree of cyanoethylation (Figs. 1,2,3).

The Fiber Structure by Infrared Spectra

Evidence for the existence of the cyanoethyl residues
introduced onto cellulose molecules by NaOH and acryloni-
trile treatment is shown by the C≡N stretching band at 2240
cm^{-1} (Fig. 7).

As a measure of the crystallinity, an infrared crystal-
linity ratio $a_{1372}cm^{-1}/a_{2900}cm^{-1}$ was adopted according to
Nelson and O'Connor (15). Results obtained are shown in
Table XI together with the amorphous fraction F_{am} (i.e.,
accessibility) calculated from the moisture regain by
Valentine's relation (16) $F_{am} = S.R./2.60$, where S.R. is
the sorption ratio (the ratio of the moisture sorption of
the experimental sample to that of the standard cotton at
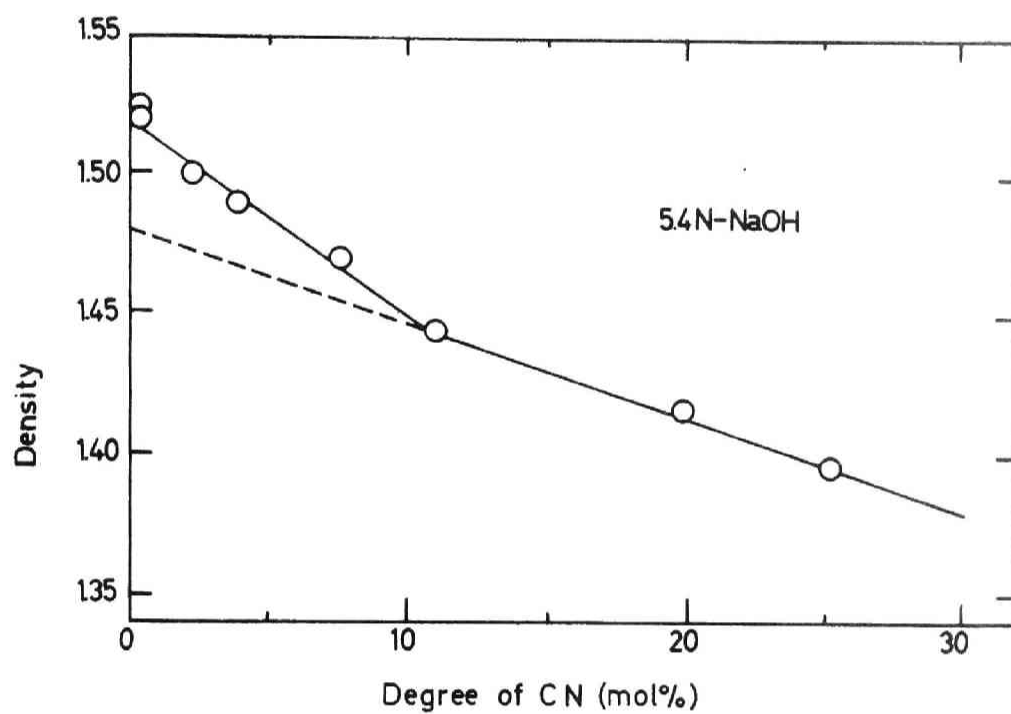
Figure 4.   Relation between the density and the degree
of cyanoethylation of the cotton fabrics treated with
acrylonitrile at 20°C for different periods of time after
the pretreatment with 5.4N NaOH.

Figure 5.   Relation between the density and the degree
of cyanoethylation of the cotton fabrics treated with
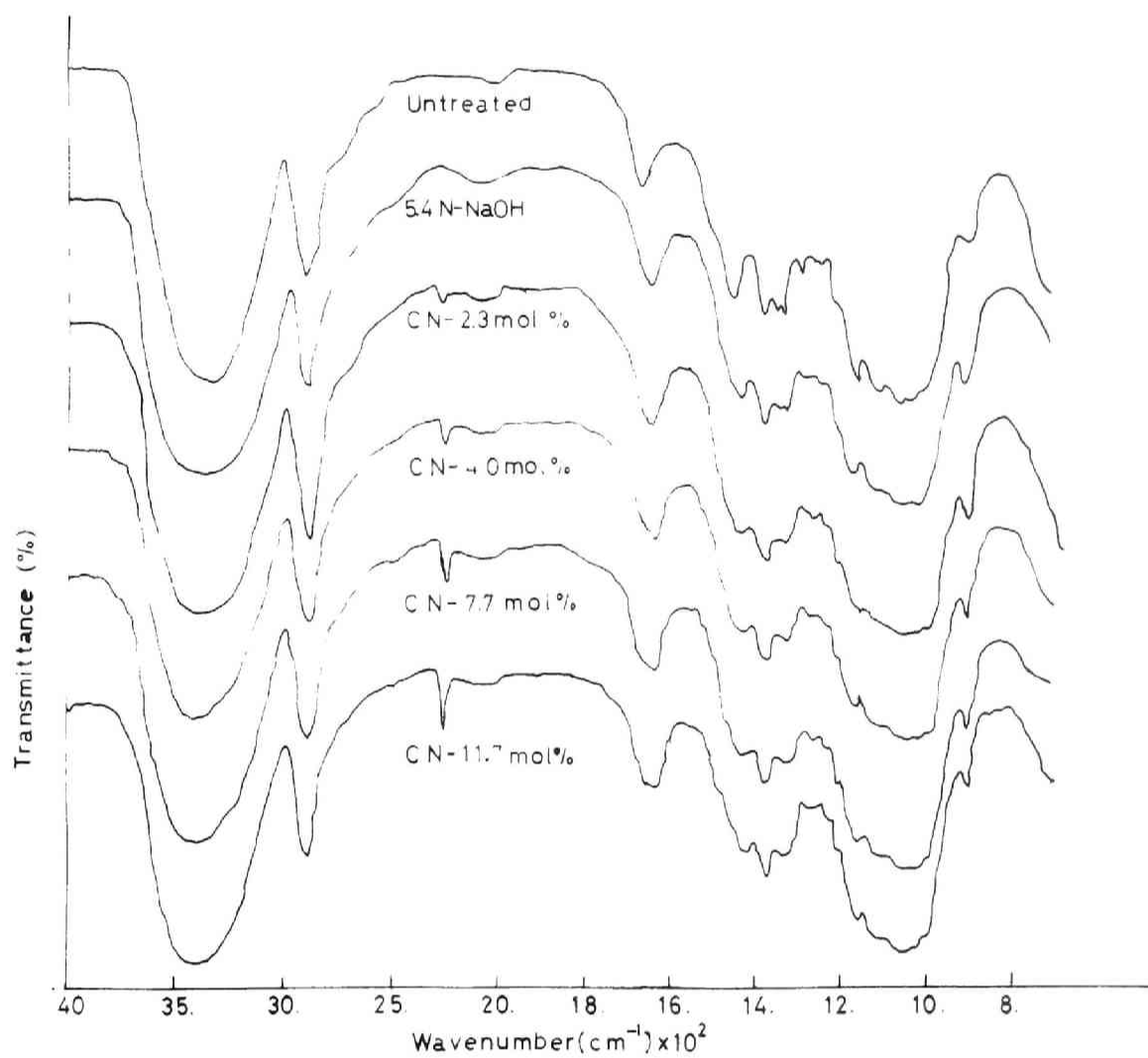acrylonitrile after the pretreatment with 5.4N KOH.

Figure 6. Relation between the density and the degree
of cyanoethylation of the cotton fabrics treated with
acrylonitrile after the dual pretreatments with 35% BTMOH
and 5.4N NaOH.

Figure 7. Infrared spectra of cottons having different degree of cyanoethylation prepared by the treatments with 5.4N NaOH and acrylonitrile.

TABLE XI

Accessibility, Infrared Index, and Crystallinity data of NaOH-AN Treated Cottons

Treatment, min		CN deg., mole%	Moisture regain, %	F_{am},[a]	Infrared ratio $a_{1372}cm^{-1}/a_{2900}cm^{-1}$	X-Ray crystallinity index, %	
5.4N NaOH at 15°C	AN at 20°C					Empirical[b]	Wakelin[c]
Untreated	—	—	7.8	0.38	0.740	82	82
30	—	—	11.7	0.58	0.635	60	58
30	10	2.3	13.2	0.65	0.580	50	43
	20	4.0	13.5	0.67	0.560	43	40
	30	7.7	14.0	0.69	0.503	36	26
	60	11.7	13.5	0.67	0.484	32	21

a Accessibility or amorphous ratio calculated from moisture regain by Valentine's relation (16).

b % Crystallinity = $\dfrac{I_{002} - I_{am}}{I_{002}}$ X 100 (17).

c Correlation method of Wakelin et al. (18). Hydrocelluloses prepared from cotton and Fortisan were chosen as the crystalline standards for cellulose I and cellulose II, respectively, and the materials vibratory ball-milled more than 1 hr were used for the amorphous standards.

the same relative humidity). In Table XI, x-ray crystal-
linity indices are also shown, which were calculated
graphically from the infrared crystallinity ratios using
the linear relation proposed by Nelson and O'Connor (15).
The results of the preliminary examination described above
show that the crystallinity of cotton can be considerably
decreased by these chemical methods.

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Chapter 3

Structure of Decrystallized Cotton Prepared in Fabrics Form
by Alkali and Acrylonitrile Treatments

INTRODUCTION

As described in previous chapter, cotton fibers could
considerably increase their accessibility or decrease their
crystallinity by treatment with acrylonitrile subsequent
to sodium hydroxide treatment. A small quantity of cyano-
ethyl residues introduced onto cellulose molecules prevents
the recrystallization of the decrystallized cotton during
water washing and drying, whereby remarkably high accessi-
bility and a low degree of crystallinity are permanently
attained.

In this chapter, the structure of cellulose of various
degrees of cyanoethylation (1.05-15.5 mole%) prepared by
using 18% sodium hydroxide solution and acrylonitrile is
examined by means of x-ray and infrared studies together
with the relationship between moisture regain and the
amorphous fraction.

Vasil'ev (1) investigated by x-ray method the effect
of mercerization on the distribution of the substituents

in cellulose cyanoethylates. But they only reported the profile 2θ versus x-ray intensity.

In this chapter, the x-ray profile is resolved into six Gaussian curves, (101), (10$\bar{1}$), and (002) of cellulose I and (101), (10$\bar{1}$), and (002) of cellulose II and the structure of treated cotton is examined.

EXPERIMENTAL

Sample. Scoured and bleached 40's cotton fabric (plain weave: Toyo Spinning Co.) was used. Various treatments were carried out with 10 cm × 10 cm sample fabrics in slack state.

Treatment with Alkali. Sample fabrics were immersed in an 18% (wt/wt) aqueous solution of sodium hydroxide for 30 min at 15°C, squeezed, water rinsed for 30 min, immersed in 0.2% acetic acid for 30 min, water rinsed again for 30 min, and air dried.

Treatment with Alkali and Acrylonitrile. Sample fabrics were immersed in an 18% (wt/wt) aqueous solution of sodium hydroxide for 30 min at 15°C, squeezed to about 100% pick up, immersed in acrylonitrile, squeezed, immersed in 0.2% acetic acid for 30 min, water rinsed for 30 min, and air dried.

Nitrogen Analysis.   Nitrogen contents, N%, of samples
treated with acrylonitrile were determined by the micro-
Kjeldahl method.   The degree of cyanoethylation was
calculated from

$$\text{degree of cyanoethylation (mole\%)} = \frac{162 \times N}{42 - 1.59 \times N}$$

Moisture Regain.   After being vacuum dried for 3 hr at
room temperature, sample fabrics were conditioned at 20°C
and 65% R.H. until constant weight was reached, and weighed.
The samples were dried for 24 hr at 40°C in high vacuum and
weighed.   The moisture regain was calculated from the
weights before and after drying.   Dry weight was based on
the residual cellulosic fraction.

X-Ray Analysis.   Fibers from warp yarns were fixed by
using 1% collodion.   The sample cake or pattern was 3 mm
wide, 0.5 mm thick, and 35 mm long.   X-Ray diffractions
were recorded with a Rigaku Denki Geiger Flex wide-angle
x-ray diffractometer, by using an x-ray beam generated with
a copper target at 40 kV and 15 mA.   X-Ray radial tracings
were scanned between the angular limits of $2\theta=5°$ and $2\theta=40°$.
Figure 1 is an illustration of the resolution of a wide-
angle x-ray scattering profile.   Curve a is the experimen-
tal profile.   Curve AA' is air scatter background.   The
region of amorphous scattering is assumed to be the area
below BCD.   The amorphous fraction is the ratio of the area

-58-
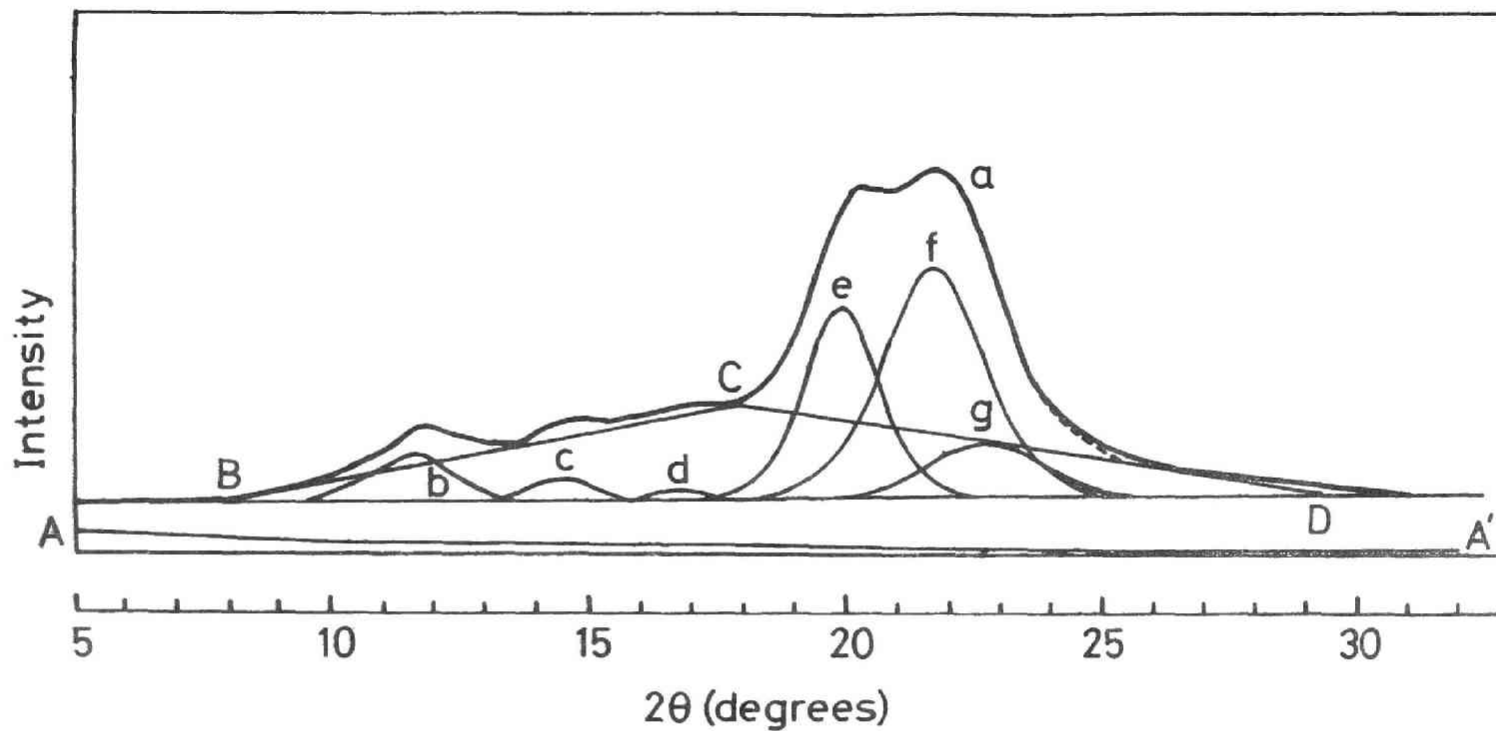
Figure 1.   Wide-angle x-ray scattering pattern for NaOH and acrylonitrile treated cotton sample CN-4.04. Curve a; experimental curve: cruves b, c, d, e, f, and g; resolved components: dotted line; curve calculated by summation of component curves.

of amorphous region to that below the experimental curve. The profile was resolved into six Gaussian curves, (101), (10$\bar{1}$), and (002) of cellulose I, and (101), (10$\bar{1}$), and (002) of cellulose II, by means of a du Pont 310 curve resolver. The dotted line is obtained by summing the component curves. This dotted curve falls exactly on the experimental curve in the range of $2\theta = 5-24°$.

Infrared Spectra. Infrared spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer by the use of the KBr pellet technique. Fibrous samples were cut with scissors into small pieces before mixing with KBr.

RESULTS AND DISCUSSION

Relationship Between Moisture Regain and Amorphous Fraction

Figure 2 is the relation between the moisture regain and the degree of cyanoethylation. As is obvious in Figure 2, the moisture regain of the treated samples first increases, passes through a maximum at about 8 mole% of cyanoethylation, and then slightly decreases, with increasing degree of cyanoethylation. The increase in moisture regain at lower degrees of cyanoethylation may be attributed to the fact that the recrystallization during water washing and drying is prevented on account of the introduction of
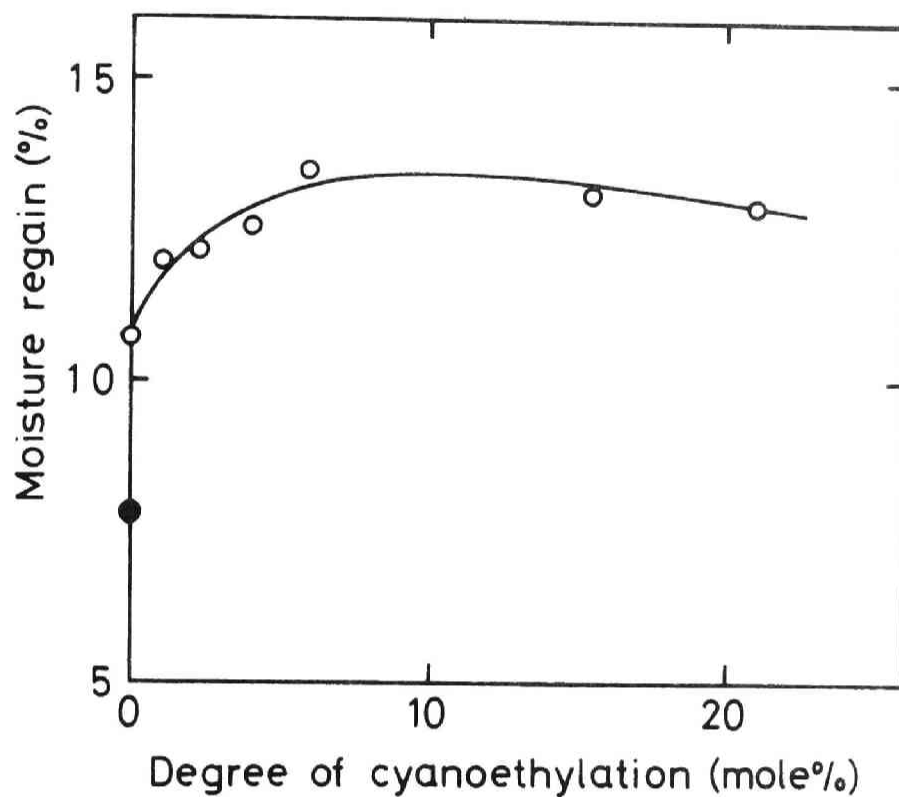
Figure 2.   Moisture regain vs. degree of cyanoethylation.
Filled and open circles at zero degree of cyanoethylation
express data for original and mercerized cotton fabrics,
respectively.

cyanoethyl residues and that, as a result, accessibility to water increases. The occurrence of the maximum moisture regain may result from a balance between the increase in accessibility and the decrease in the number of OH residues with increasing degree of cyanoethylation. The moisture regain, though being calculated based on the residual cellulosic fraction, shows a slight decrease at higher degrees of cyanoethylation. Such a behavior may be under-standable if an increase in the number of nonaccessible sites accompanied by the introduction of cyanoethyl residues is assumed.

The amorphous fraction from x-ray data was plotted against the degree of substitution in Figure 3. It is shown that the amorphous fraction increases gradually and levels off as the cyanoethylation proceeds. The increase of moisture regain in the region of the lower degree of cyanoethylation is well in accord with the lowering of the crystallinity of the samples.

Valentine (2) reported that the sorption ratio of completely accessible (amorphous) cellulose is 2.60. He obtained this value from the relation between the sorption ratio and the fraction of hydroxyl groups which were exchanged with D_2O for various celluloses. Accessibility F_{am} was calculated from the moisture regain by using Valentine's relation (2), $F_{am} = S.R./2.60$. The results are
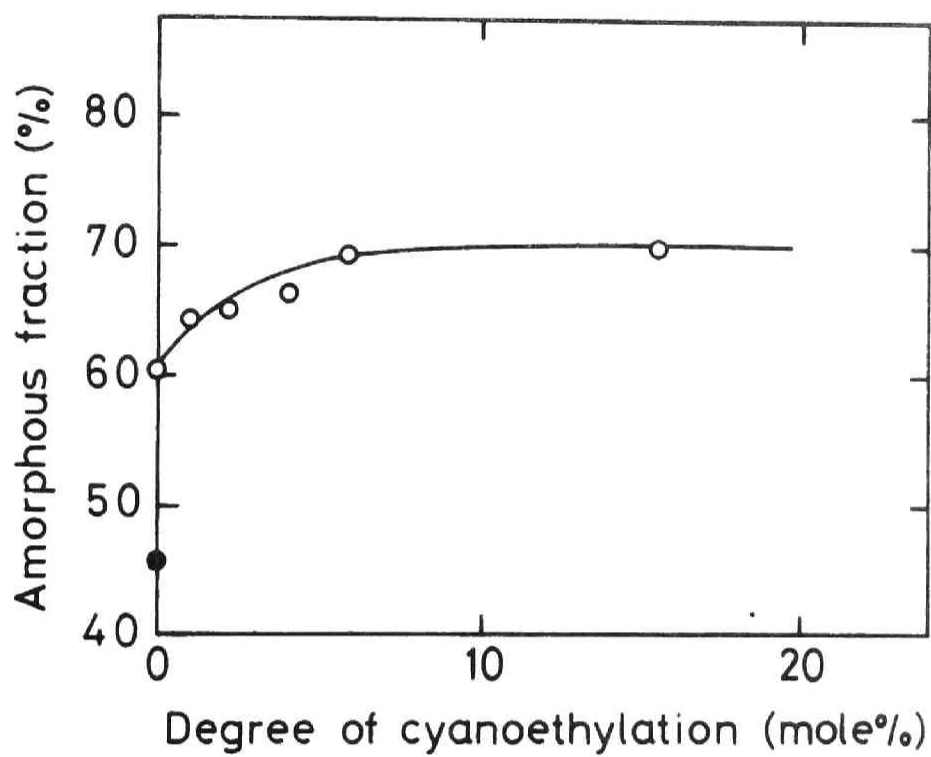
Figure 3.   Amorphous fraction vs. degree of cyanoethyla-
tion.

shown in Table I.

Figure 4 shows the relation between the amorphous fraction obtained from x-ray data and the sorption ratio, where the sorption ratio is the ratio of the moisture regain of the cyanoethylated cotton to that of a standard cotton at the same relative humidity. The sorption ratio, obtained by extrapolating the straight line to an amorphous fraction value of 1, is 2.60, in perfect agreement with Valentine's value; this corresponds to a moisture regain of about 20.28% at 65% R.H.

Crystallinity of NaOH-Acrylonitrile Treated Cotton
by Infrared Spectra

Infrared spectra of the treated samples are shown in Figure 5. The evidence for the cyanoethyl residues introduced into cellulose molecules by NaOH-acrylonitrile treatment is shown by the $C \equiv N$ stretching band at 2240 cm^{-1}. At lower degrees of cyanoethylation, the 2240 cm^{-1} absorption band did not appear. But when the sample weight in the disc was increased, the absorption band at 2240 cm^{-1} did appear.

As a measure of the crystallinity, the infrared absorption ratio a_{1372}cm^{-1}/a_{2900}cm^{-1} was adopted according to Nelson and O'Connor (3), with slight modification. Namely. for the band at 2900 cm^{-1}, a baseline was drawn
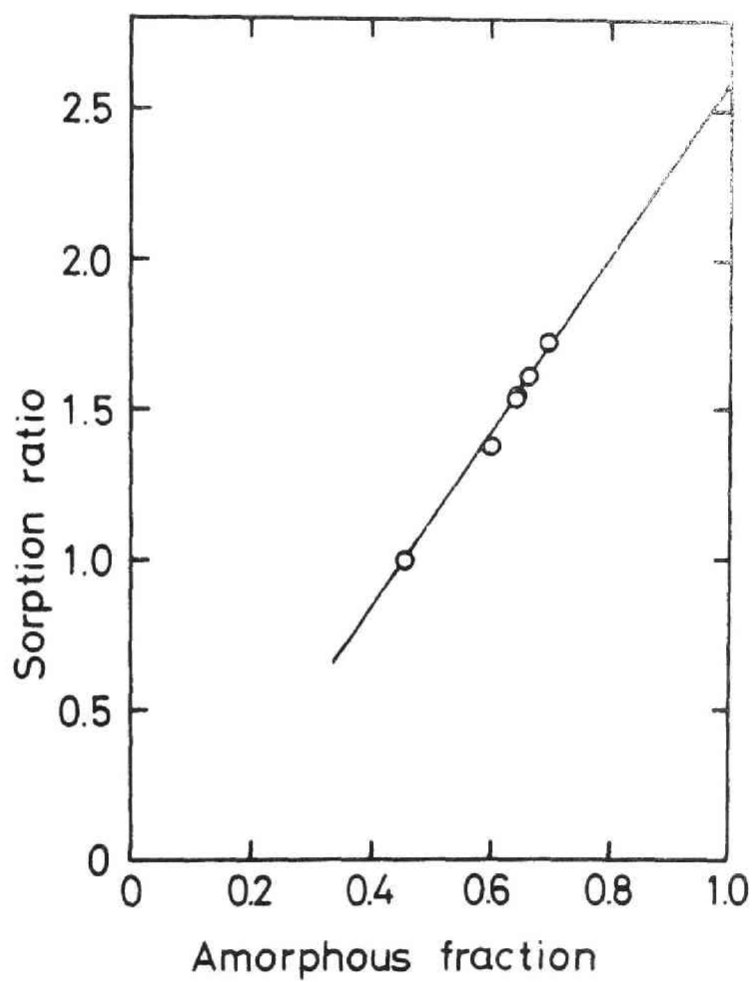
Figure 4.   Sorption ratio vs. amorphous fraction.
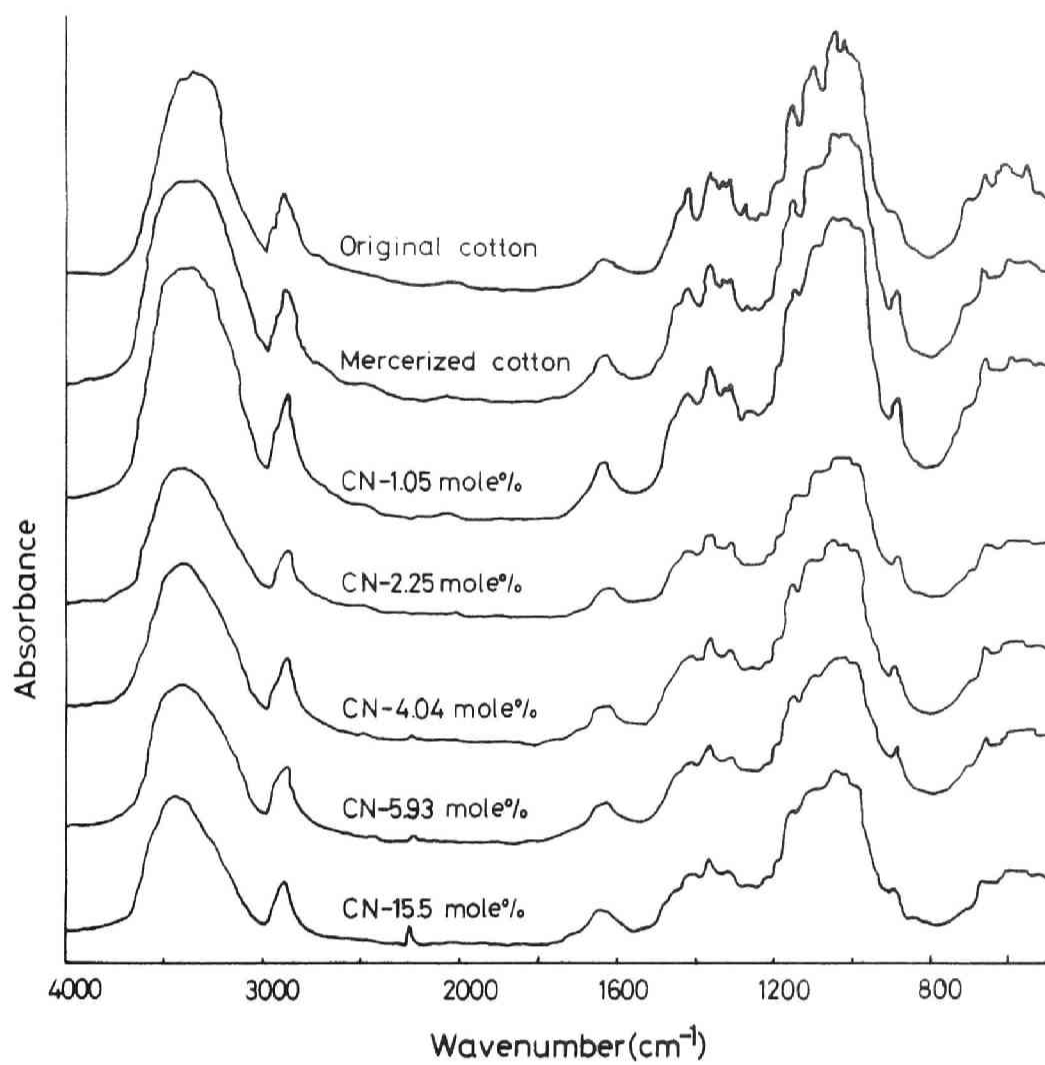
Figure 5.   Infrared spectra of cottons of different
degrees of cyanoethylation prepared with 5.4N NaOH and
acrylonitrile.

between 3900 cm^{-1} and 2400 cm^{-1}. Results obtained are shown in Table I. The infrared spectra of these modified cottons should be examined in more detail hereafter, but the correlation of the crystallinity obtained from infrared spectra with the amorphous fraction obtained by x-ray analysis has a linear relation as shown in Figure 6.

X-Ray and infrared data showed that the crystallinity of cotton could be decreased by these alkali and acrylonitrile treatments. The relative precision of these data is undoubtedly high, despite some uncertainty in absolute accuracy.

Crystalline Structure of Cotton Treated with NaOH and Acrylonitrile by X-Ray Analysis

To clarify the crystalline structure of decrystallized cotton by alkali and acrylonitrile treatments, x-ray diffractograms were analyzed for samples with various degrees of cyanoethylation.

Figure 7 shows x-ray radial tracings of samples with various degrees of cyanoethylation. For cotton fabrics treated with an 18% sodium hydroxide solution, the curve clearly shows an incomplete mercerization of the fabric, arising from a restraining influence of the fabric structure itself on the mercerizing process. The diffractometer tracing of sample CN-4.04 shows the (101) and (10$\bar{1}$)
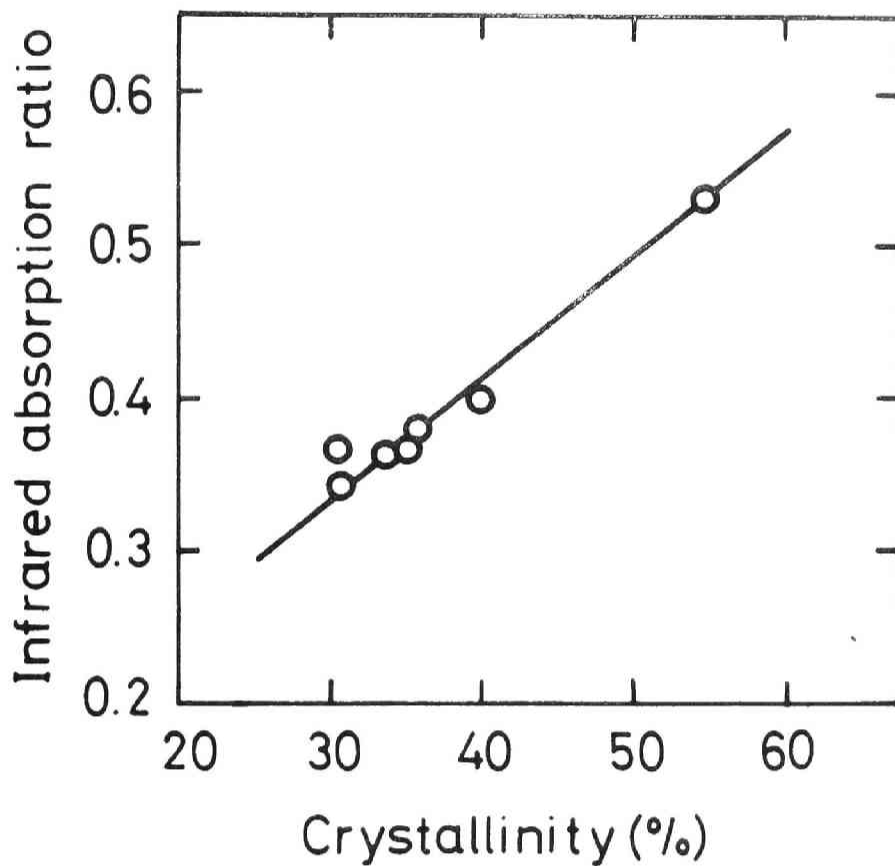
Figure 6.   Infrared absorption ratio $a_{1372cm^{-1}}/a_{2900cm^{-1}}$
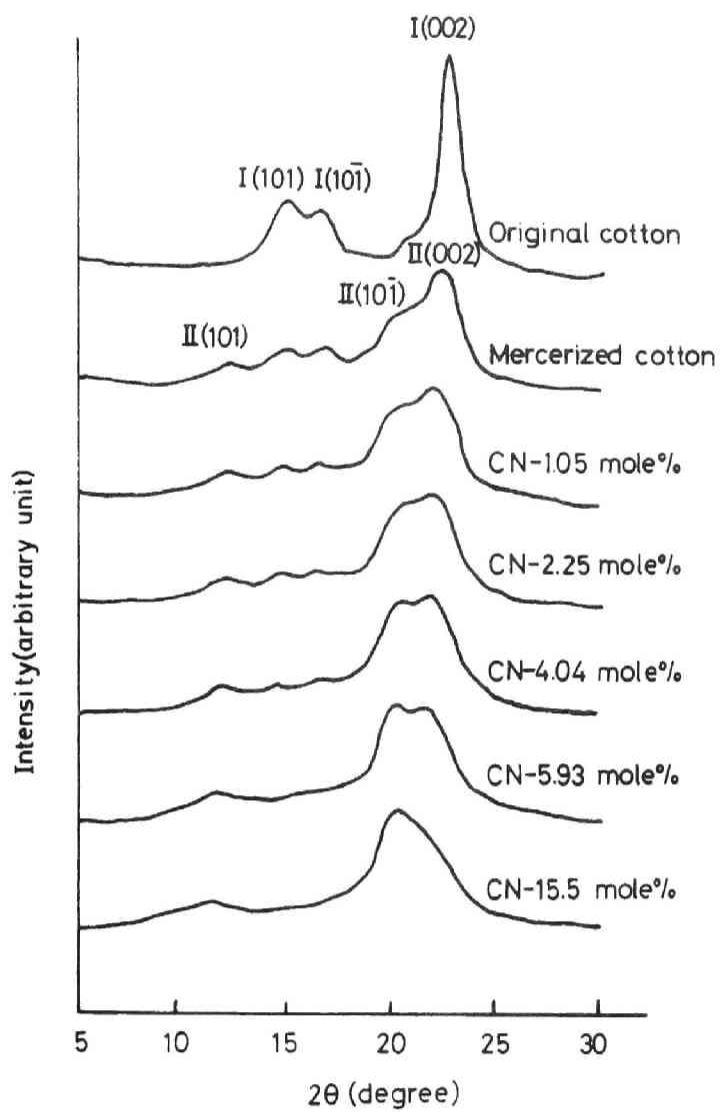vs. crystallinity obtained from x-ray data.

Figure 7.   X-Ray profiles for cyanoethylated cotton
fabrics.

interferences of cellulose I. But in the case of sample
CN-5.93, only cellulose II interferences are observed. In
other words, the intensities of cellulose I interferences
decrease as the cyanoethylation proceeds. This shall be
discussed later.

With respect to the cellulose II structure, the change
of the x-ray diffraction can be more clearly seen by
resolving the experimental profiles into six Gaussian
curves as mentioned earlier. From the peaks of the resolved
curves, lattice spacings and unit cell dimensions were
determined, which are shown in Figure 8 and Table I, res-
pectively. The lattice spacing of the (101) plane of
treated samples increases with increasing cyanoethyl
content, while those of the $(10\bar{1})$ and (002) planes are
nearly constant. With increasing cyanoethyl content, a and
c of the unit cell increase, while b remains constant and
β decreases. The change in cross-sectional area of the
unit cell is shown in Table I. As is obvious in Figure 9,
integral breadths of the (101) and (002) reflections
increase as the cyanoethylation proceeds, and that of the
$(10\bar{1})$ reflection is nearly constant. As is well known,
integral breadths are associated with lattice perfection as
well as crystallite dimensions. But, as shown in Figure 3,
the amorphous fraction increases gradually and levels off
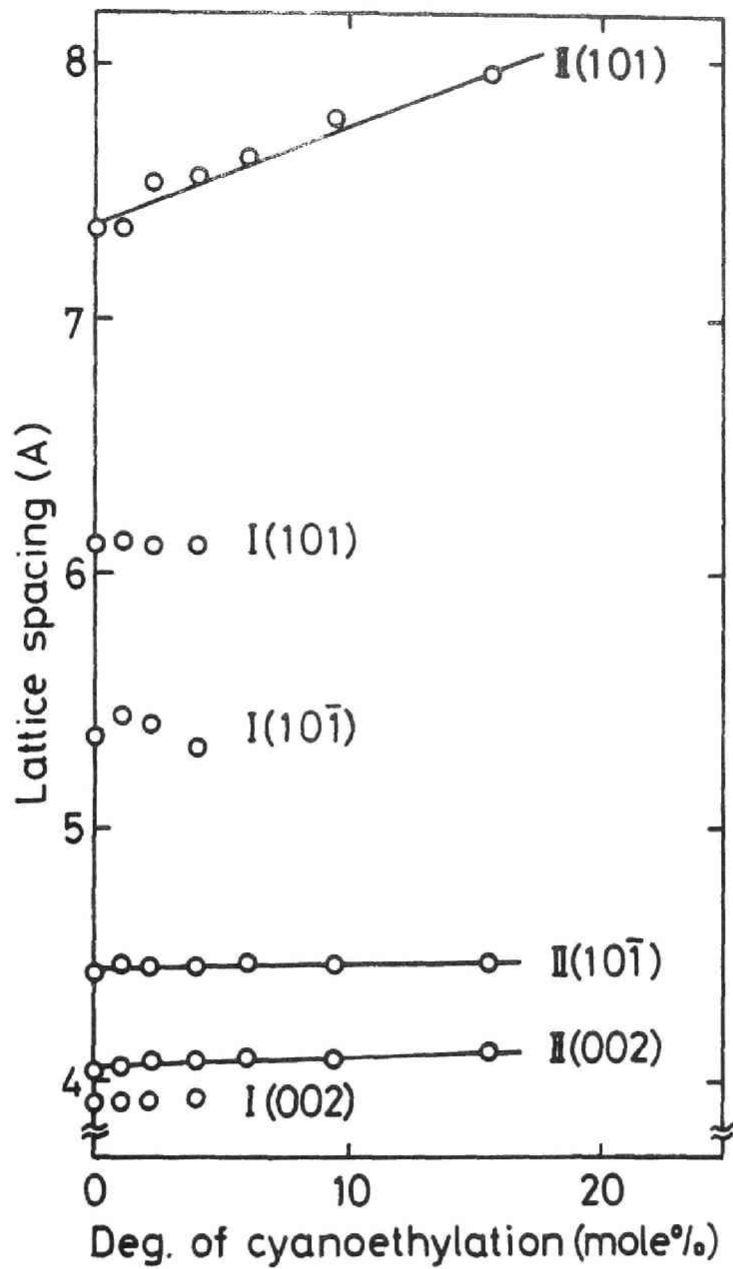as the cyanoethylation proceeds. It seems reasonable to

Figure 8.   Lattice spacing vs. degree of cyanoethylation.

TABLE I

Accessibility, Amorphous Fraction, Infrared Absorption Ratio, and
Dimension and Cross-Sectional Area of Unit Cell of NaOH-AN Treated Cottons

Sample	CN deg., mole%	F_{am}[a]	Amorphous fraction, %	Crystal-linity, %[b]	Infrared ratio[c]	Unit cell dimensions				Cross-Sectional area of unit cell, A^2
						a	b	c	β	
Cellulose I[d]	—	—	—	—	—	8.35	10.3	7.9	84.0	65.6
Untreated	—	0.38	45.7	54.3	0.535	8.20	10.34	7.91	83.5	64.4
Cellulose II[e]	—	—	—	—	—	8.14	10.3	9.14	62.0	65.7
Mercerized	—	0.53	60.3	39.7	0.400	8.15	10.34	9.17	61.8	65.9
C 101	1.05	0.59	64.3	35.7	0.381	8.17	10.34	9.18	62.2	66.3
C 102	2.25	0.60	64.9	35.1	0.368	8.28	10.34	9.34	60.9	67.6
C 103	4.04	0.62	66.3	33.7	0.364	8.32	10.34	9.37	60.9	68.1
CE5-1	5.93	0.67	69.3	30.7	0.343	8.41	10.34	9.40	60.5	68.8
C 104	15.5	0.65	69.6	30.4	0.368	8.71	10.34	9.68	58.4	71.8

a Definition of accessibility is given in the text.
b Crystallinity = 100 — Amorphous fraction.
c Infrared absorption ratio, $a_{1372}cm^{-1}/a_{2900}cm^{-1}$.
d K.H. Meyer and F. Misch, Ber., 70(B), 266 (1937).
e I. Sakurada and K. Fuchino, Scient. Pap. Inst. Phys. Chem. Res., 34, 1164 (1938).
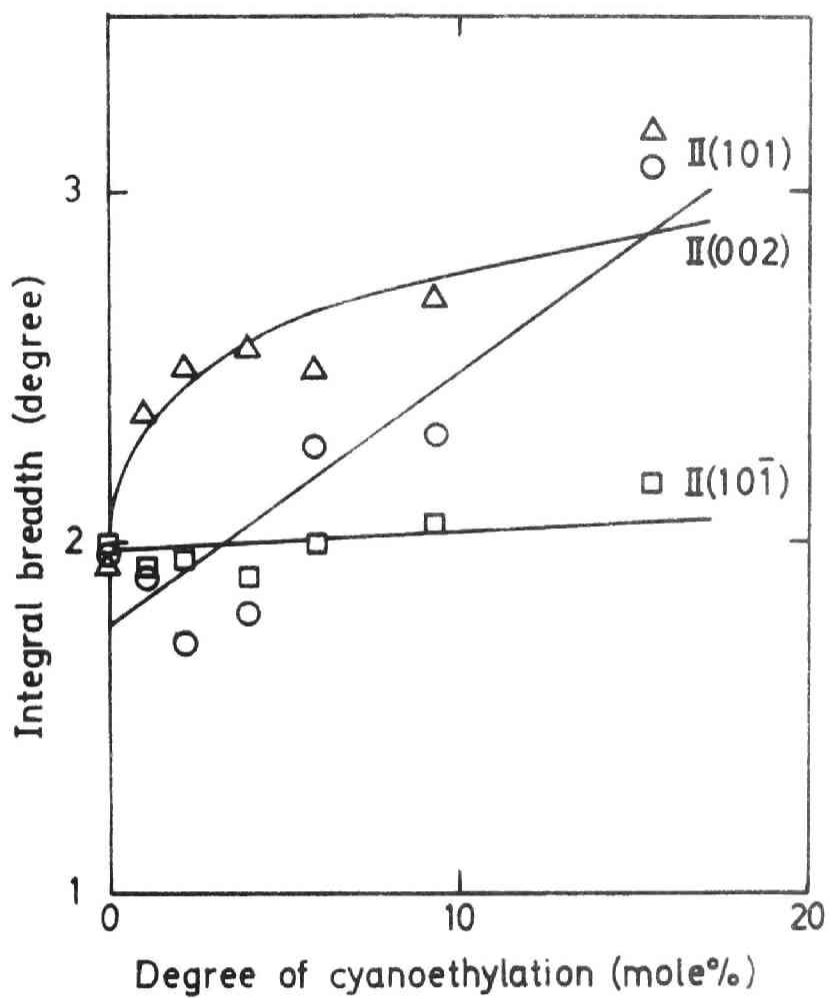
Figure 9.   Integral breadth of resolved curves vs. degree of cyanoethylation.

assume that integral breadth is mainly related to lattice perfection in this case. From these data, it is suggested that the distension and disorder of the unit cell arise primarily in the direction perpendicular to the (101) crystal plane with increasing cyanoethyl content.

The relationship between the degree of substitution and the intensity at the peak of the resolved curves is shown in Figure 10. The intensities of cellulose I peaks decrease rapidly; on the other hand, the intensities of cellulose II peaks decrease less rapidly as the substitution increases.

Jeffries et al. (4) have investigated the mechanism of the interfibrillar and intrafibrillar swelling of cotton by infrared and x-ray methods. The x-ray results showed that complete penetration of sodium hydroxide solution into cotton took place in 5.0N sodium hydroxide under free swelling and also under tension. However, on washing out the sodium hydroxide, the cotton held under tension showed some cellulose I content. Recently, Hayashi et al. (5) reported a similar effect on ramie fibers.

Taking into account these facts, the cellulose I structure found in the final products may be mainly due to a reconversion of soda cellulose I to cellulose I during the washing treatments, because tension is present throughout the mercerization.
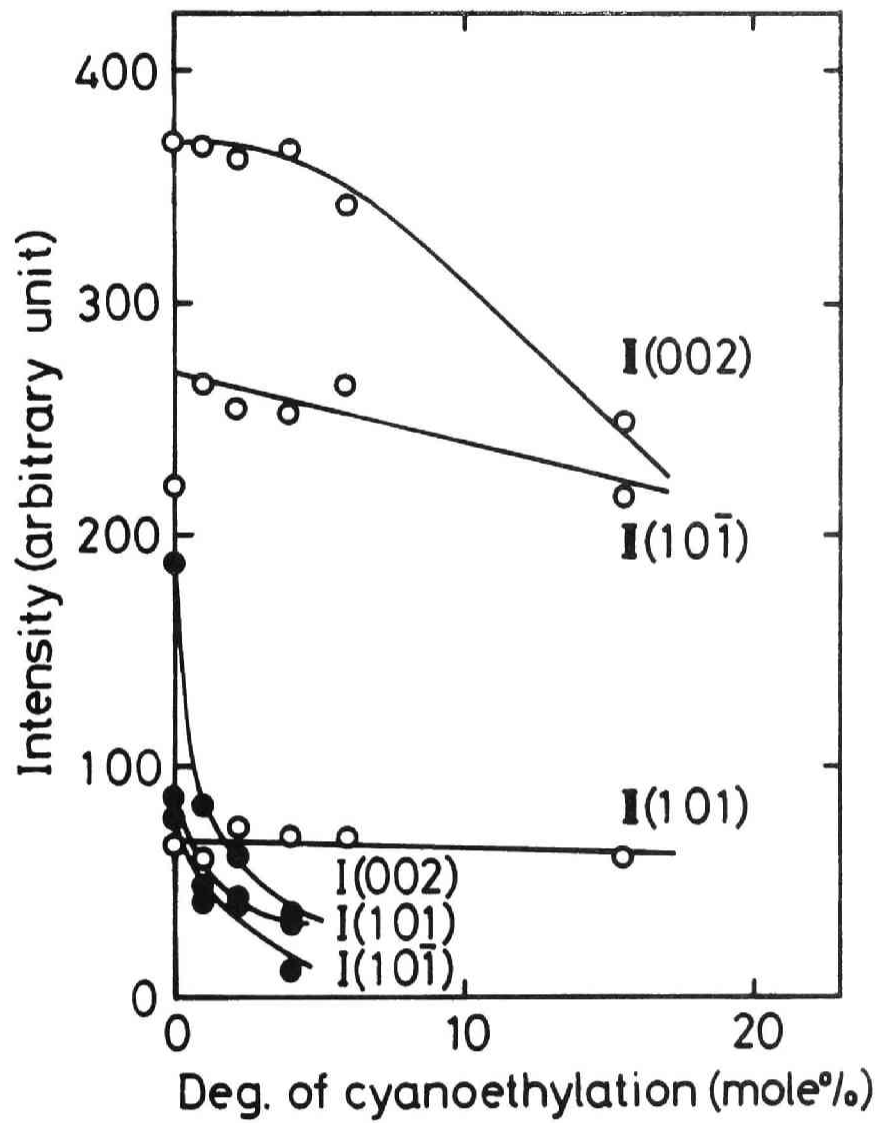
Figure 10.   Intensity at the peak of resolved curves
vs. degree of cyanoethylation.

Warwicker et al. (4,6) pointed out the mechanism of swelling as follows. During intrafibrillar swelling, the hydrogen bonds between the sheets are broken and a complex is formed in which water molecules of the hydrated dipole of the swelling solution are replaced by the hydroxyl groups of cellulose. On washing out the swelling agent, the complex is replaced by water or by another solvent. On subsequent removal of this solvent, the choice whether the cellulose I or cellulose II type of sheet is reformed will, to some extent, depend on the disposition of the group (probably the primary alcohol group) that provided the internal hydrogen bonding of the cellulose I sheet. If this group is in an appropriate position, and the swelling is sufficient to allow the necessary movement, it will swing into a position required for the formation of a cellulose II type of sheet.

The swelling of the cotton fabric treated with NaOH aqueous solution may be insufficient to allow a full hydrogen bond rearrangement neccessary for the conversion to cellulose II. So, a reconversion of soda cellulose I to cellulose I may take place during the washing treatments. When cyanoethyl groups are introduced onto cellulose molecules swollen with NaOH solution, the distended cellu-lose structure is obtained and a hydrogen bond rearrange-ment necessary for the conversion to cellulose II will take

place. So, by introducing the cyanoethyl group, the conversion to cellulose II from soda cellulose I may be promoted, and the decrystallization will then proceed.

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Chapter 4

Structure of Decrystallized Cotton Prepared in Fiber Form by Alkali and Acrylonitrile Treatments

INTRODUCTION

As described in chapters 2 and 3, the crystallinity of cotton fabric was considerably decreased by an alkali-acrylonitrile treatment involving cyanoethylation and accessibility of the fabric could be improved. The crystalline structure of cellulose molecules in the fabric was examined by x-ray and infra-red spectra in connection with the moisture regain. However, the cyanoethylation as well as the alkali swelling involving in this treatment may be influenced by the textile structure of the sample since fabrics are composed of twisted yarns.

In this chapter, the cyanoethylation by the alkali-acrylonitrile treatment is applied to cotton fibers as well as cotton fabrics. The moisture regain and the crystalline structure of cyanoethylated cotton fibers are examined in comparison with the results on the cotton fabrics.

EXPERIMENTAL

Samples.   Egyptian cotton fibers supplied by Unitika Co.
were extracted in a Soxhlet extractor with ethanol and
ether for each 6 hr. Then, they were boiled in 1% aqueous
solution of sodium hydroxide for 10 hr, washed with
distilled water, immersed in 1% acetic acid, washed with
water again and then air dried. As fabric sample, scoured
and bleached 40's cotton fabric (plain weave) supplied by
Toyo Spinning Co. was used.

Alkali-Acrylonitrile Treatment.   Cotton was treated with
following two methods. One method was to immerse cotton
in 18% (wt/wt) sodium hydroxide solution for 30 min at 15°C
and then to treat with acrylonitrile at 20°C (method 1).
The other was to immerse cotton in 18% (wt/wt) sodium
hydroxide solution for 60 min at -5°C and then to treat
with acrylonitrile at 0°C (method 2). Then these treated
cottons were immersed in dilute acetic acid, washed with
water and air dried. These procedures were performed in
the slack state unless otherwise noted.

Moisture Regain.   After vacuum drying for 3 hr at room
temperature, samples were conditioned at 20°C and 65% R.H.
until constant weight was reached and weighed. The samples
were dried for 24 hr *in vacua* at 40°C and weighed. The
moisture regain was calculated by the following equation.

$$\text{Moisture regain (\%)} = \frac{W_b - W_a}{W_0} \times 100$$

Here, W_b and W_a are the weight before and after drying. W_0 is the weight of residual cellulose estimated by subtracting an increase in weight arised by cyanoethyl residue from W_a.

X-Ray Analysis. X-Ray analysis was made with use of bundled fibers fixed with 1% collodion. The equatorial scanning was made on the Rigaku Denki Geiger Flex wide-angle x-ray diffractometer with Cu-Kα beam at 40 kV and 15 mA. The x-ray profiles thus obtained were resolved into Gaussian curves with a du Pont 310 curve resolver.

RESULTS

Figure 1 shows the relation between reaction time with acrylonitrile and degree of cyanoethylation. Curves (a) and (b) denote the results by method 1 for the cotton fibers and fabrics, respectively. Curves (c) and (e) denote the results by method 2 for cotton fibers and fabrics, respectively. The rate of reaction for the fibers is greater than that for the fabrics. This will be because the effective surface area of the cotton fibers is much greater
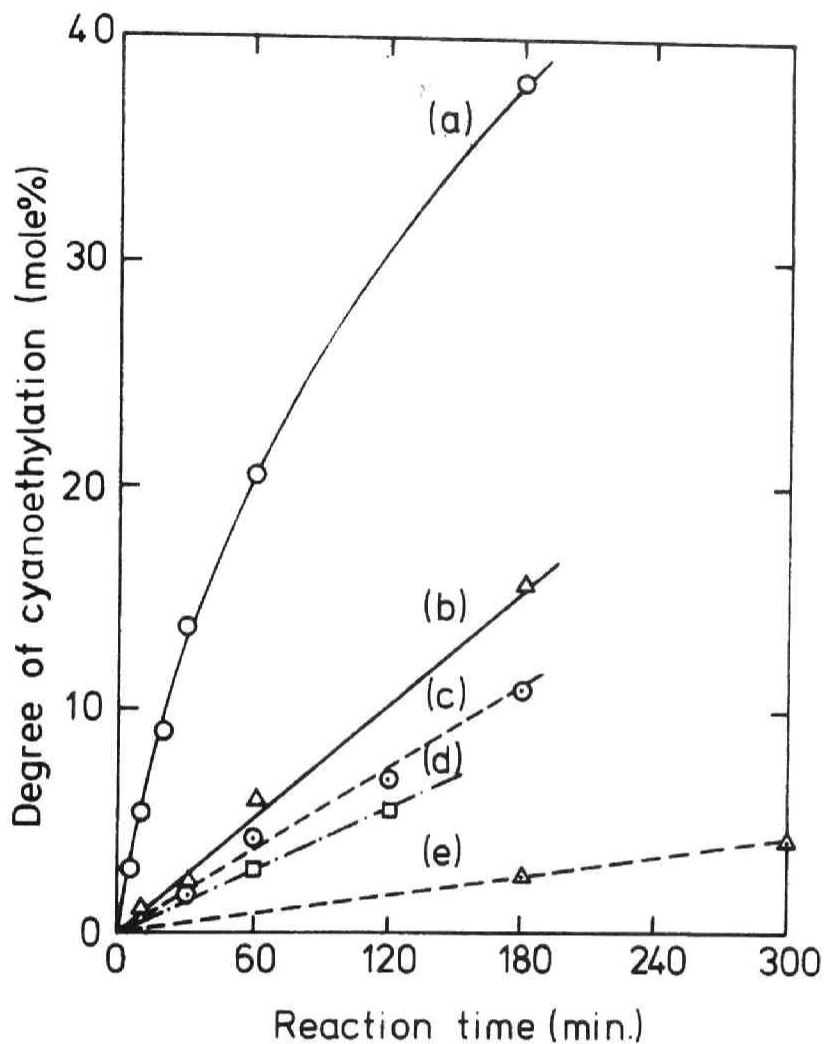
Figure 1.   Reaction time vs. degree of cyanoethylation.
(a) cotton fiber and (b) cotton fabric, in slack state, and
(d) cotton fabric, at constant length; immersed in 18wt%
NaOH for 30 min at 15°C and then treated with acrylonitrile
at 20°C.   (c) cotton fiber and (e) cotton fabric; immersed
in 18wt% NaOH for 60 min at -5°C and then treated with
acrylonitirle at 0°C.

than that of the fabrics consisting of twisted yarns. When
the fabrics were treated at constant length by method 1,
the reaction rates of the samples were much smaller than
those of samples in the slack condition, as shown in
Figure 1, curve (d).

Figure 2 shows the relation between moisture regain
and degree of cyanoethylation. It is seen that notwith-
standing the reaction is performed by method 1 in fiber or
fabric forms, the moisture regain of the cyanoethylated
samples is about the same, though the rate of reaction is
different with each other [(o) and (Δ) in curve (a)].
Contrary, it is found that the moisture regain of fiber
samples prepared by method 2 [curve (b)] is higher than
that of fabric samples [curve (c)]. But the moisture regain
of fabric samples prepared by method 2 is nearly equal to
that of fabric samples by method 1. When the fabrics were
treated at constant length by method 1, moisture regain of
the samples is much smaller than that of samples treated in
the slack conditions, as shown in Figure 2, curve (d).

Figure 3 shows x-ray equatorial scannings for fiber
samples treated by method 1. The figure evidences that
when the cotton fibers are treated only with the alkali
solution (mercerized cotton) presence of the crystalline
form of cellulose I is detected in addition to that of
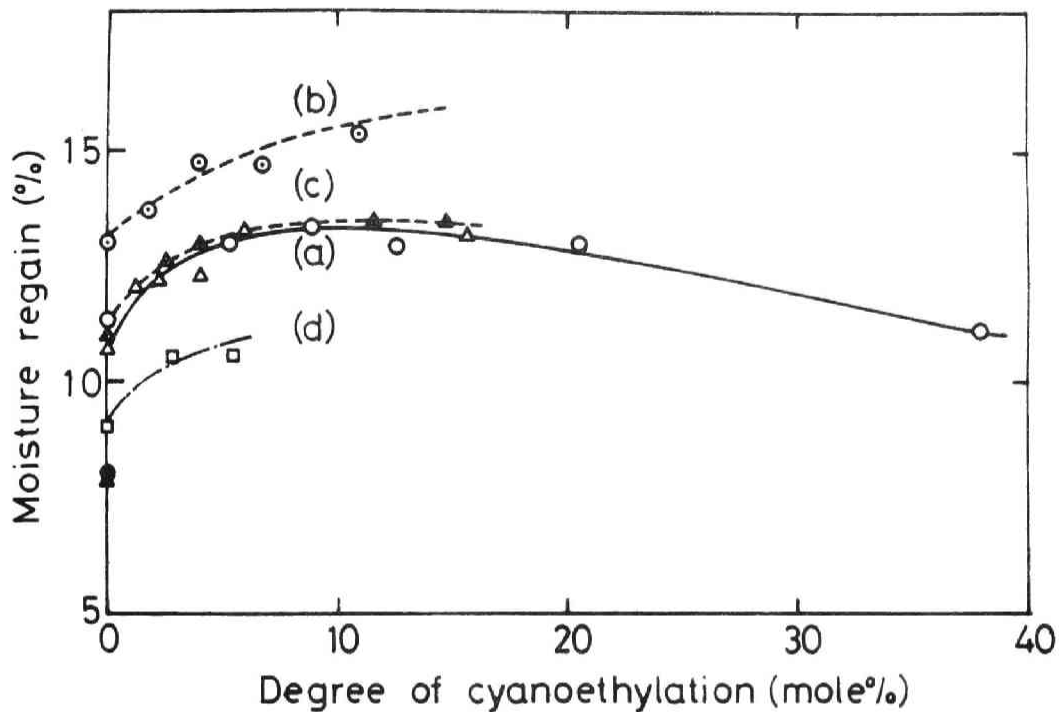cellulose II, but the crystalline form of the alkali-acrylo-

Figure 2.   Moisture regain vs. degree of cyanoethylation.
(o) cotton fiber and (△) cotton fabric, in slack state, and
(□) cotton fabric at constant length; immersed in 18wt% NaOH
for 30 min at 15°C and then treated with acrylonitrile at
20°C. (⊙) cotton fiber and (△) cotton fabric, in slack
state; immersed in 18wt% NaOH for 60 min at -5°C and then
treated with acrylonitrile at 0°C. Filled circles and
filled triangles at zero degree of cyanoethylation represent
the data for original cotton fibers and fabrics, respective-
ly.
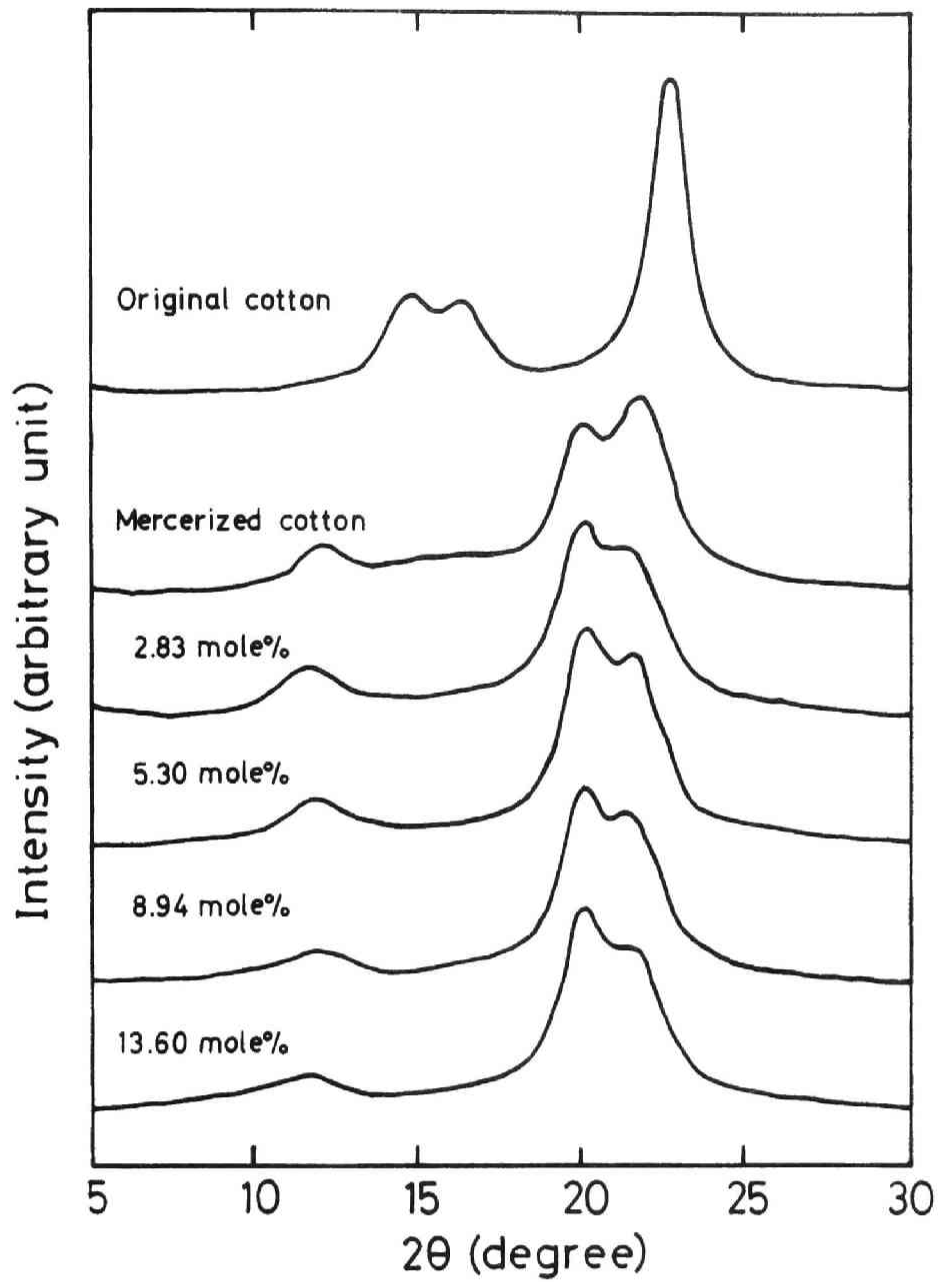
Figure 3.   X-Ray diffractograms of cotton fibers immersed
in 18wt% NaOH for 30 min at 15°C and then treated with
acrylonitrile at 20°C.

nitrile treated fibers is fully in the form of cellulose II.
However, as already described in chapter 3, when the same
alkali-acrylonitrile treatment was applied for cotton
fabrics, e.g. for a treated fabric with a degree of cyano-
ethylation of 4.04 mole%, the presence of the crystalline
form of cellulose I was evidenced by the x-ray diffraction
from the crystal planes (101) and (10$\bar{1}$), though for a
sample with a degree of cyanoethylation of 5.93 mole%, such
evidence was not obtained. To inquire the crystalline
structure of samples treated in the fiber form in more
detail, x-ray diffraction profiles were resolved into
Gaussian curves by means of a curve resolver. Figure 4
illustrates a result for a sample with a CN content of 5.30
mole%. Here, curve a is the experimental profile and the
straight line $\overline{BD}$ indicates its baseline. The amorphous
scattering is assumed to correspond to the area BCD.
Curves b, c and d are of the resolved components, and the
dotted line shows the composite curve of all these component
curves.

Lattice spacings determined from the peak positions of
the resolved curves are plotted against the degree of cyano-
ethylation in Figure 5. The open circles and triangles
denote the results for fibers and fabrics, respectively.
Here the result for fabrics was quoted from the data in
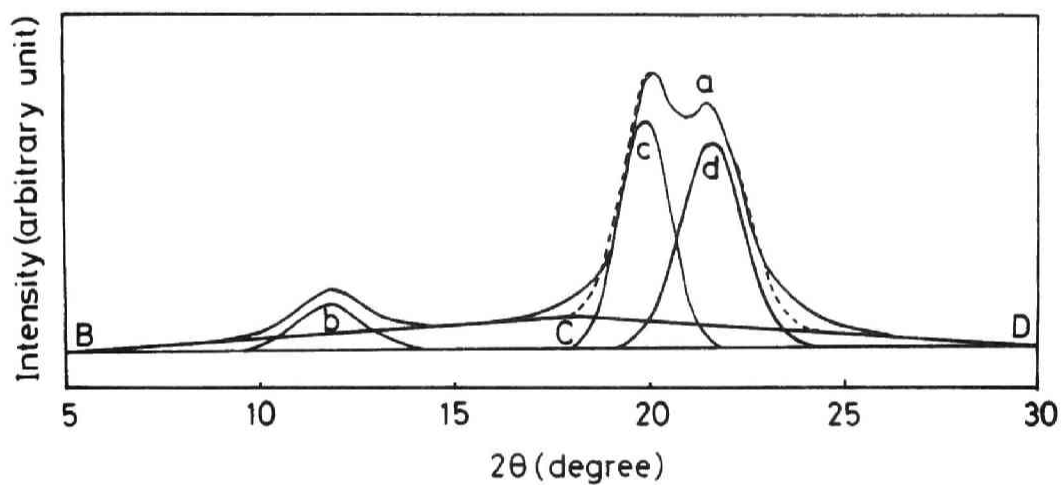chapter 3. The lattice spacing of (101) plane of cellulose

Figure 4.   Wide angle x-ray scattering pattern of cotton fiber treated under the same conditions as that for Fig. 3 (CN content, 5.30 mole%). Curve a; experimental curve. Curves b, c, and d; resolved curves. Dotted curves; composite curve.
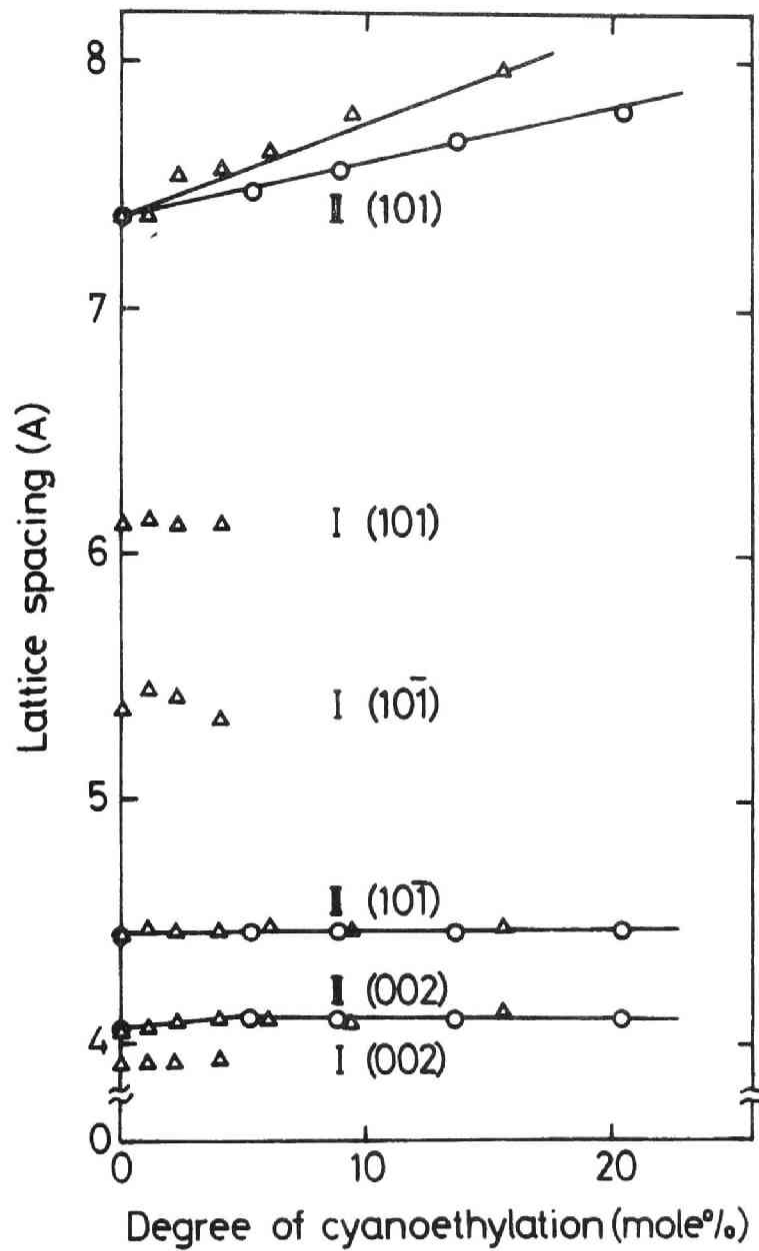
Figure 5.   Lattice spacing vs. degree of cyanoethylation.
(o) cotton fiber and (△) cotton fabric; immersed in 18wt%
NaOH for 30 min at 15°C and then treated with acrylonitrile
at 20°C.

II increases with increasing cyanoethyl content, while those of (10$\bar{1}$) and (002) planes stay nearly unchanged.

Figure 6 shows x-ray equatorial scannings for cotton fibers prepared by method 2. The crystalline form of the alkali-treated fibers (mercerized cotton) is completely cellulose II. From the resolved curves we determined the lattice spacings shown in Figure 7. In Figure 7, symbols (o) and (⊙) denote the results for fibers prepared by method 1 and for fibers prepared by method 2, respectively. Increase of lattice spacing of (101) plane denoted with (⊙) is somewhat greater than that of samples denoted with (o). Integral breadth of samples prepared by methods 1 and 2 are shown in Figure 8. The increase of integral breadth of the (101) and (002) reflections for samples prepared by method 2 is greater than that of the results by method 1.

From the results mentioned above, it was confirmed that greater decrystallization effect associated with greater gain of moisture regain was obtained in the case of fiber samples treated by method 2. On the other hand, x-ray diffractograms of fabric samples by method 2 were similar to that of fabric samples by method 1 [see Figure 9]. In this case, the crystalline form of cellulose I was also detected in addition to that of cellulose II at a few degrees of cyanoethylation. As shown in Figures 10 and 11, there is no marked difference in crystalline structure of
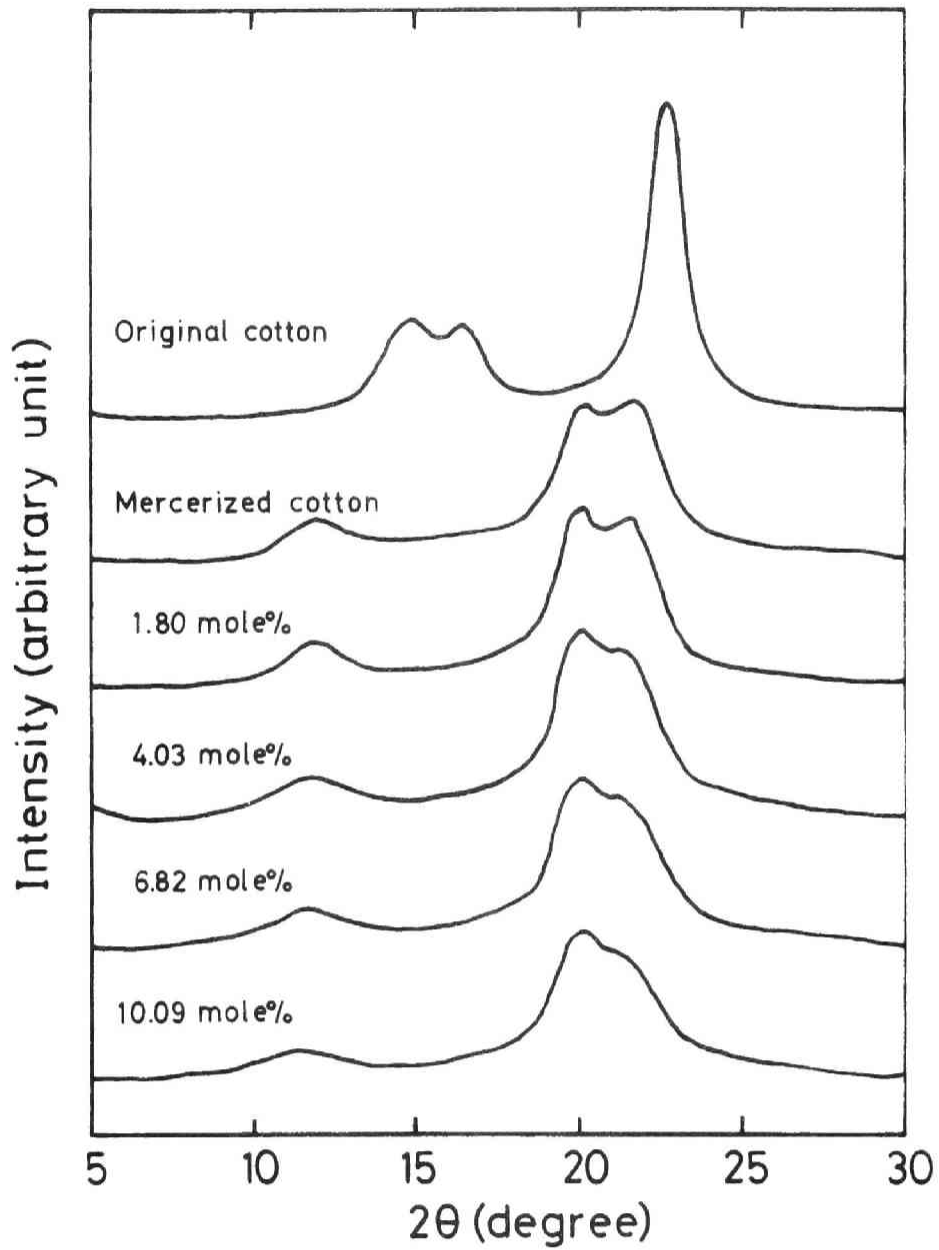
Figure 6.   X-Ray diffractograms of cotton fibers immersed in 18wt% NaOH for 60 min at -5°C and then treated with acrylonitrile at 0°C.
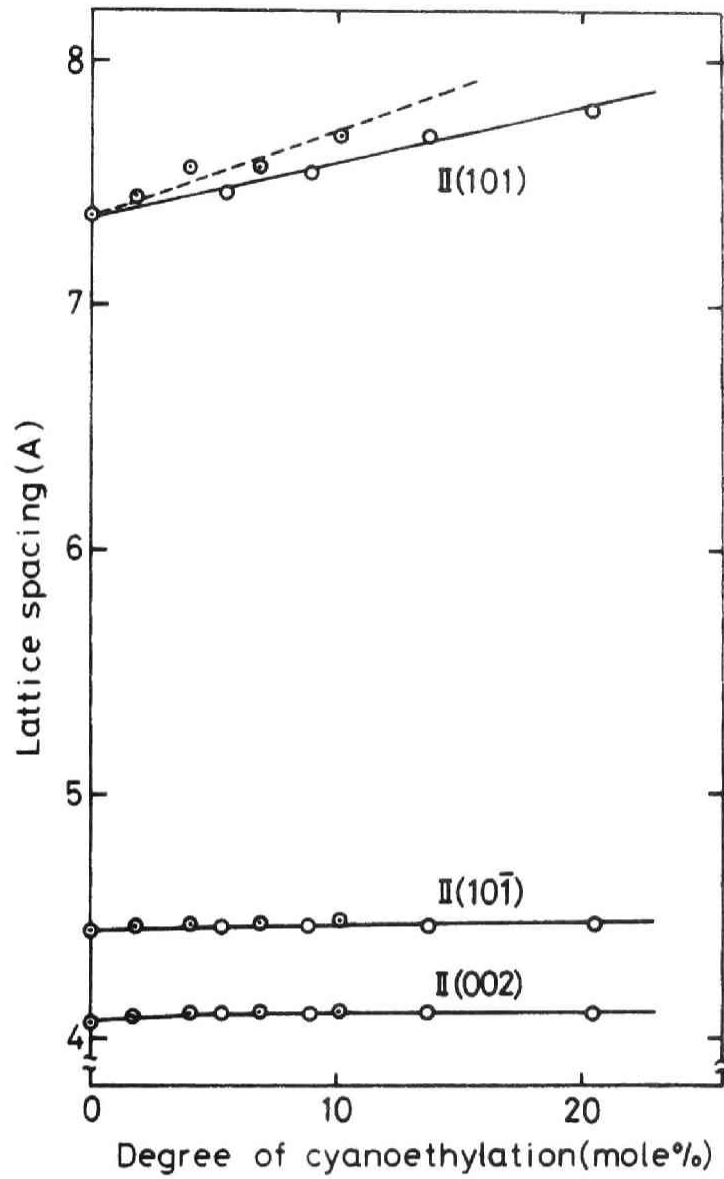
Figure 7.   Lattice spacing vs. degree of cyanoethylation.
(⊙) cotton fibers; immersed in 18wt% NaOH for 60 min at -5°C
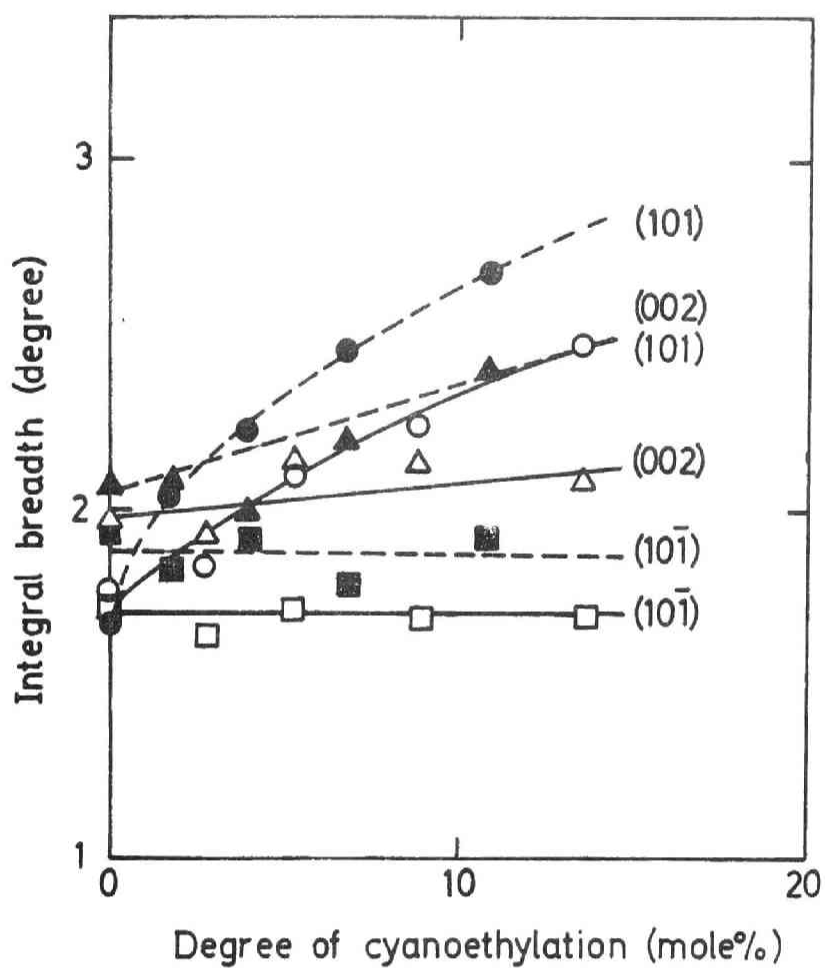and then treated with acrylonitrile at 0°C.   (o) cotton
fibers; quoted from Fig. 5.

Figure 8.   Integral breadth of resolved curves of treat-
ed cotton fibers. (o) (101) plane, (□) (10$\bar{1}$) plane and
(Δ) (002) plane of samples prepared by method 1. (●) (101)
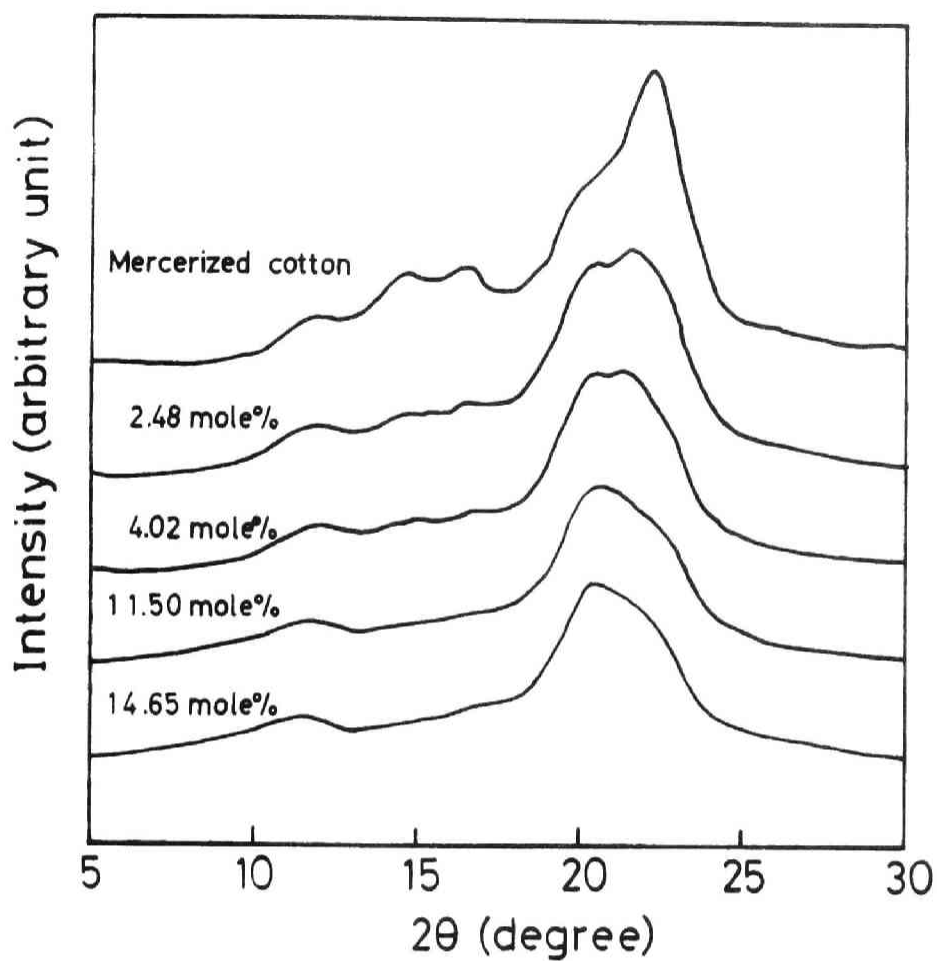plane, (■) (10$\bar{1}$) plane and (▲) (002) plane of samples
prepared by method 2.

Figure 9. X-Ray diffractograms of cotton fabrics immers-
ed in 18wt% NaOH for 60 min at -5°C and then treated with
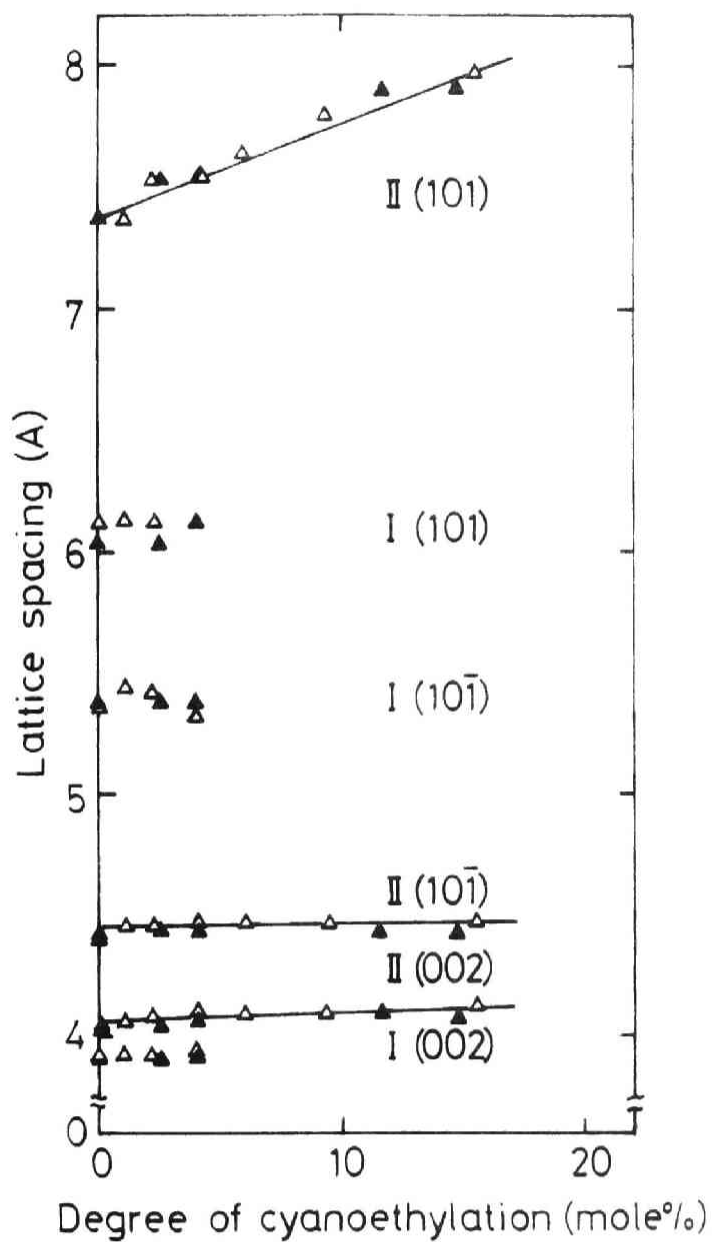acrylonitrile at 0°C.

Figure 10. Lattice spacing vs. degree of cyanoethylation. (△) cotton fabrics prepared by method 1. (▲) cotton fabrics prepared by method 2.
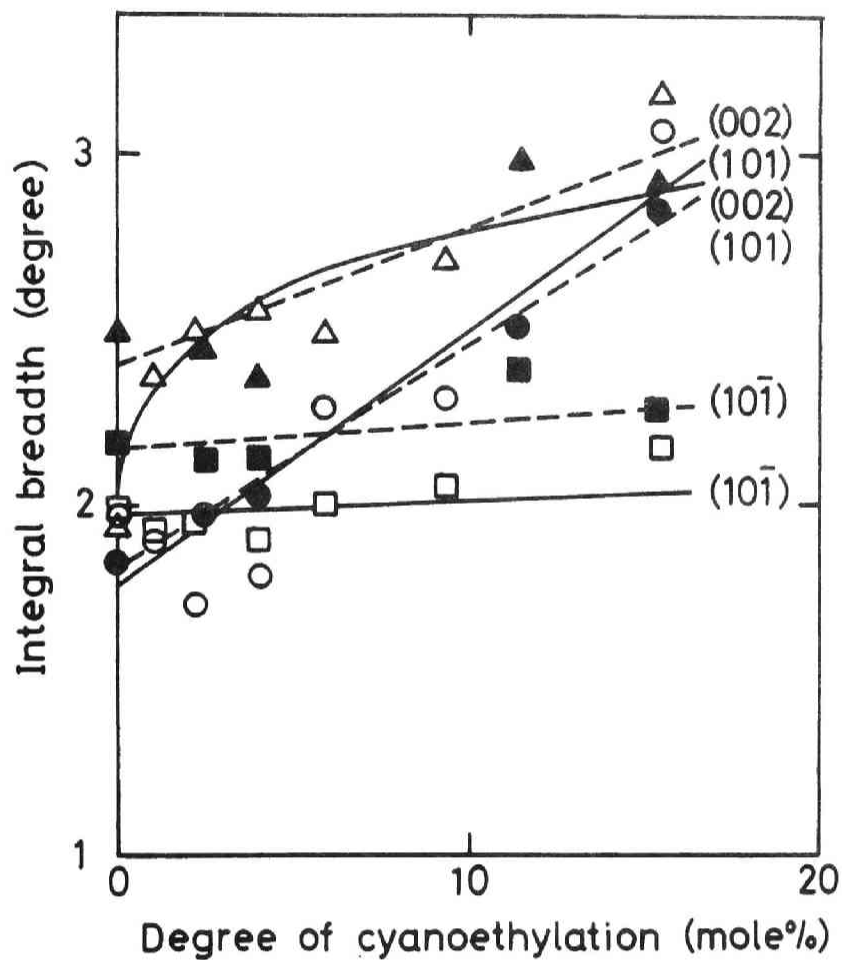
Figure 11. Integral breadth of resolved curves of treated cotton fabrics. (o) (101) plane, (□) (10$\bar{1}$) plane and (△) (002) plane of samples prepared by method 1. (●) (101) plane, (■) (10$\bar{1}$) plane and (▲) (002) plane of samples prepared by method 2.

fabric samples between methods 1 and 2.

DISCUSSION

When the fabric is immersed in sodium hydroxide solution, textile structure composed of twisted yarns acts as a restriction on swelling. As a result each swollen fiber in the fabric is supposed to be under pressure or tension. Tension or pressure within fabric may be responsible for the restricted extent of mercerization compared with yarn and fiber as shown by Jeffries (1). In fact, when the fabrics were treated at constant length by method 1, the reaction rate and moisture regain of the samples were much smaller than those of samples treated in the slack condition, as shown in Figures 1 and 2. It is clear that the velocity of diffusion of acrylonitrile into fabrics and effective surface area of fabrics are small compared with those of fibers in the slack state owing to the restraing influence of fabric construction. Consequently the distribution of cyanoethyl residues will be nonuniform and hence the effect of cyanoethyl residues to retain the highly decrystallized state of treated cotton will decrease. On the other hand, the fibers swell freely under the alkalitreatment. So it is expected, in the case of cotton fibers,

that the velocity of penetration of acrylonitrile into
fibers and effective surface area will be larger than those
in fabrics.

(a) Cyanoethylation at 20°C (method 1).

The reaction rate at 20°C may be more rapid than the
rate of diffusion of acrylonitrile, so that the cyanoethy-
lation may be taken place mainly on fiber surface and the
distribution of cyanoethyl groups may be nonuniform. There-
for the cyanoethylation by method 1 yields products having
nonuniform distribution of cyanoethyl groups for both fibers
and fabrics. The difference in the effect of nonuniformity
of cyanoethyl groups on accessibility between fiber and
fabric samples treated by this method is hardly discernible
from the moisture regain at the same degree of cyanoethyla-
tion (see Figure 2). However, it is presumed from the
results in Figure 5 that there is a difference in nonuni-
formity of cyanoethylation between fibers and fabrics from
the standpoint of crystalline structure.

(b) Cyanoethylation at 0°C (method 2).

The permanent decrystallization effect of the alkali-
acrylonitrile treatment is probably caused by the cyano-
ethyl groups introduced into cotton cellulose in the
swollen state of samples which prevent the recrystallization
of cellulose molecules. Hence, more uniform distribution
of cyanoethyl groups resulted from a slower rate of cyano-

ethylation and more sufficient penetration of acrylonitrile
into fiber may be preferred to obtain more pronounced
decrystallization effect. Thus in order to delay the
reaction of cyanoethylation while keeping the swollen state
the alkali-acrylonitrile treatment was carried out at a
lower temperature. In order to decide the proper condition
for the alkali pretreatment, it is to be noted that when
cotton is immersed in alkali solution different crystal
forms are produced depending on the immersing temperature.
When cotton is treated with 18% NaOH below 5°C, soda cellu-
lose V is obtained (2). Whereas, soda cellulose I is
obtained when treated with 18% NaOH at 15°C. The composi-
tion of soda cellulose V is $C_6H_{10}O_5 \cdot NaOH \cdot 4.5-5H_2O$ and that
of soda cellulose I is $C_6H_{10}O_5 \cdot NaOH \cdot 3H_2O$. So the unit cell
of soda cellulose V is larger than that of soda cellulose
I. To promote even distribution of cyanoethyl residues the
soda cellulose V seems to be preferable to the soda cellulose
I. Furthermore time of immersing in alkali solution also
could affect the decrystallization (3). Namely it was
reported that the crystallinity decreased and degree of
substitution increased with an increase of swelling time
but leveled off at 45 min.

Taking into account these facts, cotton immersed in
18% NaOH for 60 min at -5°C was treated with acrylonitrile
at 0°C (method 2). In the case of fabrics, influence of

temperature on alkali-pretreatment is small and penetration
of acrylonitrile into fabric is poor on account of fabric
construction. Therefore, there is not a marked difference
in accessibility and crystalline structure of fabric samples
between methods 1 and 2.

On the contrary, in the case of fibers, the influence
of temperature on alkali-pretreatment was observed unequiv-
ocally; alkali-treatment for 60 min at -5°C affects the
decrystallization of cellulose more than alkali-treatment
for 30 min at 15°C does. Moreover, the reaction is slow
because of low temperature and penetration of acrylonitrile
into fiber is well done because any restriction does not
exist. Consequently the distribution of cyanoethyl
residues in fiber sample may be more uniform compared to
that in fabric sample and also to that in fiber sample
prepared by method 1. Therefore the greater gain of mois-
ture regain was obtained in fiber samples prepared by method
2. The effect of cyanoethyl group on the crystalline
structure of treated fibers by method 2 was greater than
that of treated fibers by method 1.

These results suggest that in addition to the uniform-
ity of the distribution of cyanoethyl groups, the mass
fraction of the regions which are and are not influenced by
the reaction may contribute to the change in the x-ray
patterns of alkali-acrylonitrile treated cotton.

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Chapter 5

Effect of Ethanol on Alkali and Acrylonitrile Treatments
for Cotton

INTRODUCTION

The treatment of cellulose fibers with alkalines is
one of the oldest and most important commercial reactions
for cellulose in viscose industries. Study of aqueous
solutions is of primary importance (1). The addition of
alcohol, alone or in combination with water, has been used
by several investigators as a means of determining the
nature of alkali cellulose (2). But the structure of cellu-
lose thus treated was not examined well.

Recently, Jeffries (3), by x-ray and infrared
deuteration technique, investigated the swelling behavior
and structural changes of cotton in sodium hydroxide by the
presence of alcohol. When dissolved in water alone, 2.0
or 3.0 N sodium hydroxide did not penetrate the fibrils or
causes further lateral disorder in original cotton. But,
if 2N sodium hydroxide was made up in 75/25 ethanol/water
solution, the x-ray results showed that a soda cellulose
was produced. Washing in the 75/25 ethanol-water mixture

removed the sodium hydroxide and resulted in a reconversion
to cellulose I. With 3N sodium hydroxide in 50/50 ethanol/
water, general picture was similar, but the conversion to
cellulose II was increased.

The presence of alcohol, therefore, had caused the
sodium hydroxide to penetrate the crystalline fibrils. It
would appear that this action is a result of the interac-
tion of the alcohol with the dipolar hydrated of sodium
hydroxide in solution, reducing the size sufficiently to
permit penetration in the crystal lattice.

The addition of alcohol to 6.0N sodium hydroxide,
which itself can cause intrafibrillar swelling, had no
marked effect on the hydrogen bond disorder, in accordance
with the infrared deuteration technique.

In chapters 2, 3, and 4, cotton was treated with alkali
and acrylonitrile, using mainly sodium hydroxide solution
under various conditions and the crystalline structure
and properties of these treated cottons were investigated.
Since the alkali-acrylonitrile treatment is heterogeneous
reaction, the condition of alkali-pretreatment and the
distribution of cyanoethyl residues affected the structural
change of cotton as already described in chapter 4.

In order to prevent the dissolution of regenerated
cellulose in 5.4N sodium hydroxide solution, alcohol was
added to 5.4N sodium hydroxide solution, which shall be

discussed in chapter 6. Furthermore, as ethanol is a good solvent for acrylonitrile, acrylonitrile was expected to penetrate into the fibrils. Researches on the treatment of cotton with alcoholic sodium hydroxide have been very few in number. And it was found that cotton treated with 5.4N sodium hydroxide in a mixture of ethanol-water showed high accessibility and remarkable broadening of x-ray profile compared with cotton treated with 5.4N sodium hydroxide solution. Thus, it seems interesting to investigate the reaction of cellulose with alcoholic sodium hydroxide in combination with water, and the structural change of these treated cellulose. In this chapter, the crystalline structure of cotton cyanoethylated with NaOH-ethanol-water system is compared with that of cotton cyanoethylated with NaOH-water system. Physical properties of cotton fabrics treated with alkali-acrylonitrile by the presence of alcohol is examined in terms of wash-and-wear finishing.

EXPERIMENTAL

Samples.   Purified egyptian cotton fibers were used.
The purification procedure was described in chapter 4.
Scoured and bleached 40's cotton fabric (plain weave) was
used. Average molecular weight by viscosity method (tri-
nitrates in acetone) was 4070 and 3080 for egyptian cotton
fibers and cotton fabric, respectively.

Treatment.   Cotton immersed in 5.4N NaOH in a mixture of
ethanol and water (volume ratio 30:70) for 1 hr at -5°C was
treated with acrylonitrile at 10°C, or, after immersed in
acrylonitrile for 30 min at -5°C, treated with acrylonitrile
at 10°C. Then these treated cottons were immersed in 1%
acetic acid in a mixture of ethanol and water (volume ratio
30:70) and washed with a mixture of ethanol and water
(volume ratio 30:70), and air dried.

Treatment in Boiling Water.   Samples prepared by the
alkali-acrylonitrile treatment were boiled in water for
3 hr and air dried.

Moisture Regain.   The procedure was described in chapter   .
4.

X-Ray Analysis.   The procedure was described in chapters
3 and 4.

RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction patterns of
cotton fibers prepared by the alkali-acrylonitrile treat-
ment with or without alcohol. As is obvious in x-ray
diffraction pattern of alkali-treatment, perfect mercerized
cotton can be obtained by treatment with 5.4N NaOH aqueous
solution [see Fig. 1 (A)]. On the contrary, partially
mercerized cotton is obtained by treatment with 5.4N NaOH
in a mixture of ethanol and water, but x-ray profile is
much broader than that of fibers treated with NaOH aqueous
solution. Cellulose I content found in the final products
must be due to a reconversion of soda cellulose to cellulose
I during the washing treatment, presumably because of a
decrease in the degree of swelling by adding ethanol.

Figure 2 (A) and (B) show the relation between the
integral breadth of x-ray diffractograms and the degree of
cyanoethylation for NaOH-water system and NaOH-ethanol-
water system, respectively. Integral breadths of the $(10\bar{1})$
and (002) planes of cotton treated with alcoholic sodium
hydroxide are greater than those of cotton treated with
sodium hydroxide solution. With respect to NaOH-water
system, integral breadth of (101) plane of cellulose II
increases with increasing cyanoethyl content, while those
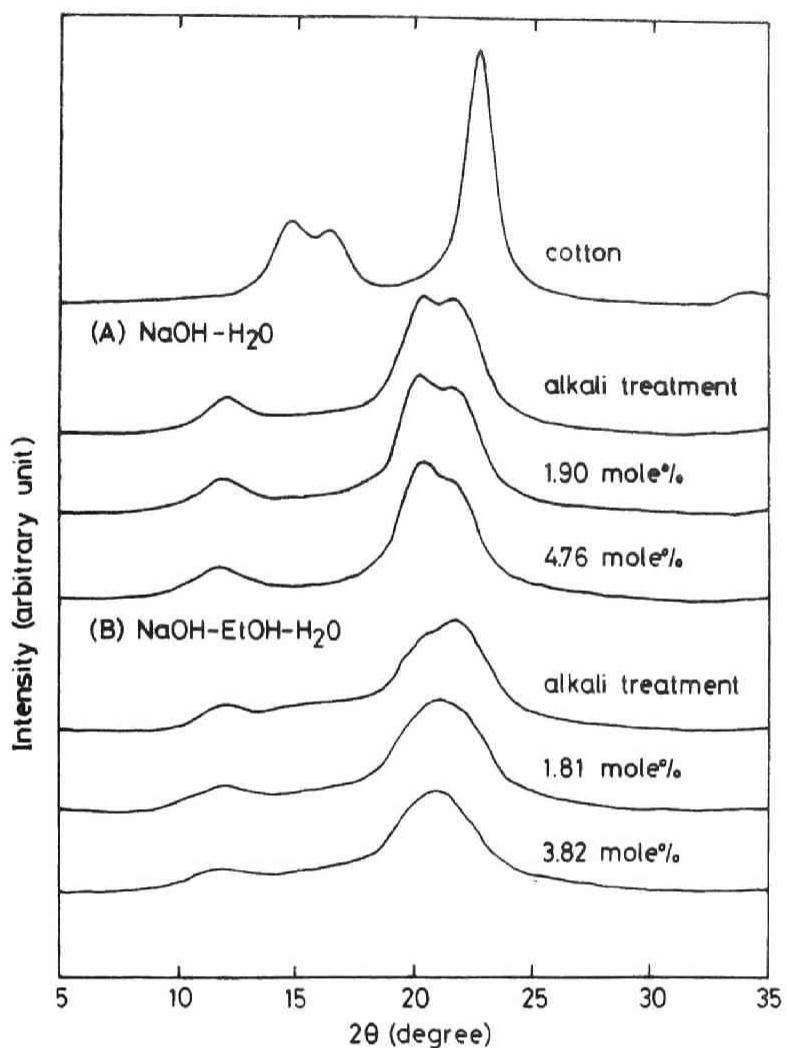of $(10\bar{1})$ and (002) planes stay nearly unchanged [see Fig. 2

Figure 1.   X-Ray equatorial scannings of treated cotton
fibers.   (A) immersed in 5.4N NaOH aqueous solution for
60 min at -5°C, and treated with acrylonitrile at 10°C.
(B) immersed in 5.4N NaOH in a mixture of ethanol and water
(volume ratio 30:70) for 60 min at -5°C, and treated with
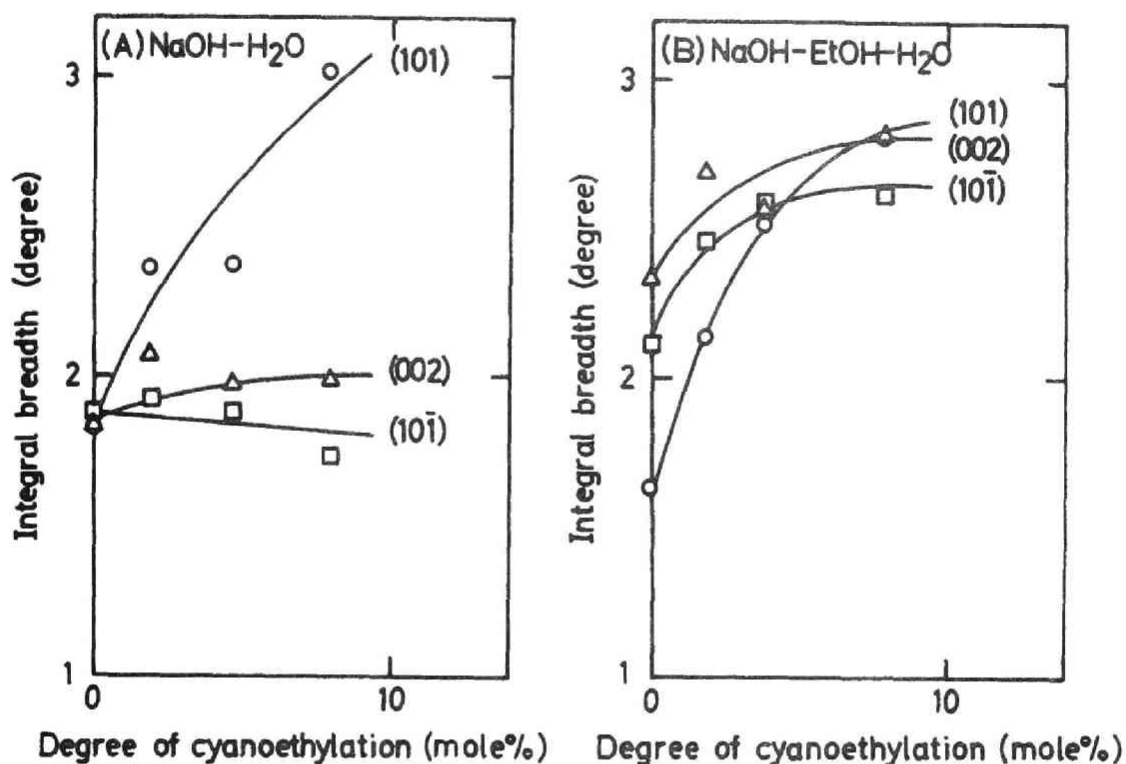acrylonitrile at 10°C.

Figure 2.   Integral breadth of x-ray diffractograms vs.
degree of cyanoethylation for alkali-acrylonitrile treated
cotton fibers.   (A) immersed in 5.4N NaOH aqueous solution
for 60 min at -5°C, and treated with acrylonitrile at 10°C.
(B) immersed in 5.4N NaOH in a mixture of ethanol and water
for 60 min at -5°C, and treated with acrylonitrile at 10°C.
The values at zero degree of cyanoethylation represent the
data for alkali-treated samples.

(A)]. On the other hand, with respect to NaOH-alcohol-water system, the integral breadths of (10$\bar{1}$) and (002) planes as well as that of (101) plane increase as the cyanoethylation proceeds.

Figure 3 shows the relation between the cumulative intensity and the degree of cyanoethylation for alkali-acrylonitrile treated cotton. X-Ray analysis reveals that the cumulative intensity of the (10$\bar{1}$) plane is much weaker than that of the (002) planes when cotton treated with 5.4 N NaOH in a mixture of ethanol and water, while those of the (10$\bar{1}$) and (002) planes are about the same when treated with 5.4N NaOH aqueous solution. The intensity of (002) plane decreases with increasing cyanoethyl content, while those of (10$\bar{1}$) and (101) planes stay nearly unchanged in both cases.

Lattice spacing was plotted against degree of cyano-ethylation as shown in Figure 4. Symbols (●) and (□) denote the results for fibers prepared by alkali-acrylo-nitrile treatment with and without alcohol, respectively. Lattice spacing of (101) plane increases as the cyanoethy-lation proceeds, while those of (10$\bar{1}$) and (002) planes stay nearly unchanged in both cases. Symbol (o) denote the result for fibers in alcoholic system pretreated with acrylonitrile for 30 min at -5°C before cyanoethylation at 10°C. In order to make acrylonitrile penetrate sufficiently
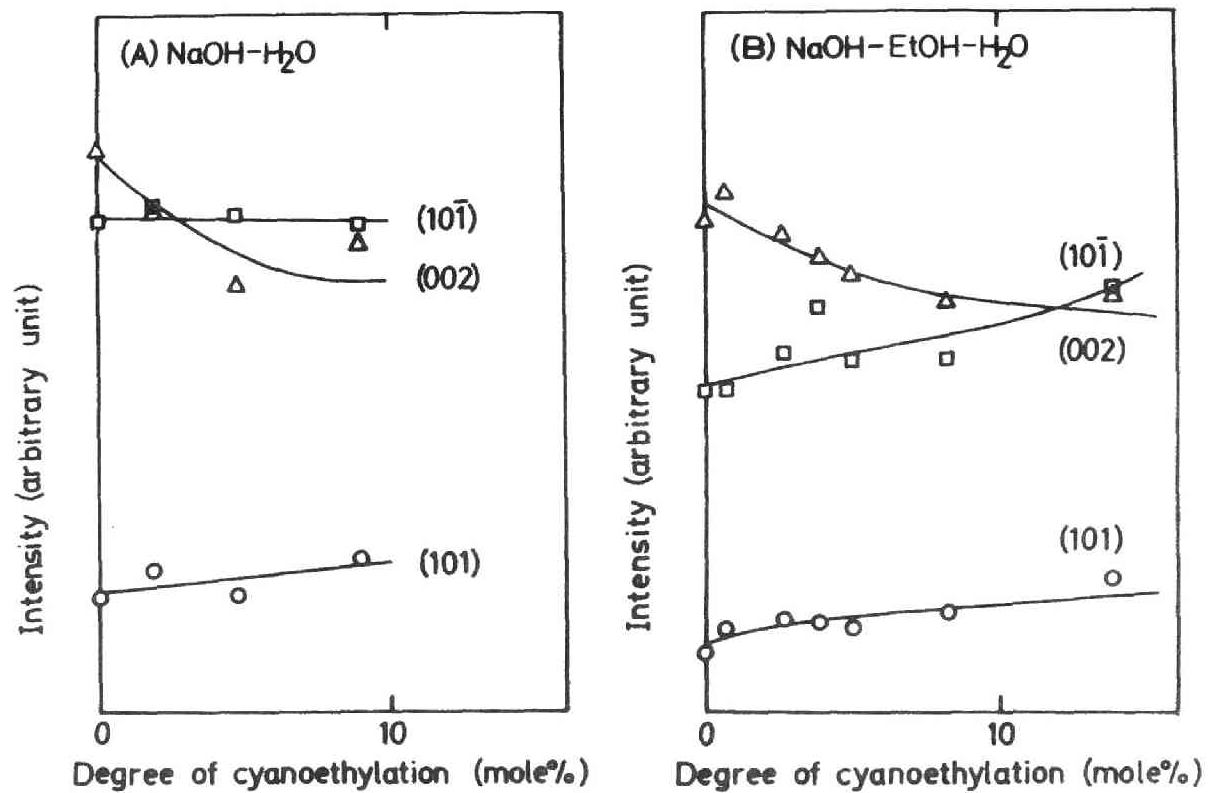
Figure 3.   Cumulative intensity vs. degree of cyanoethylation for alkali-acrylonitrile treated cotton fibers. Conditions of treatments are described in Figure 2.
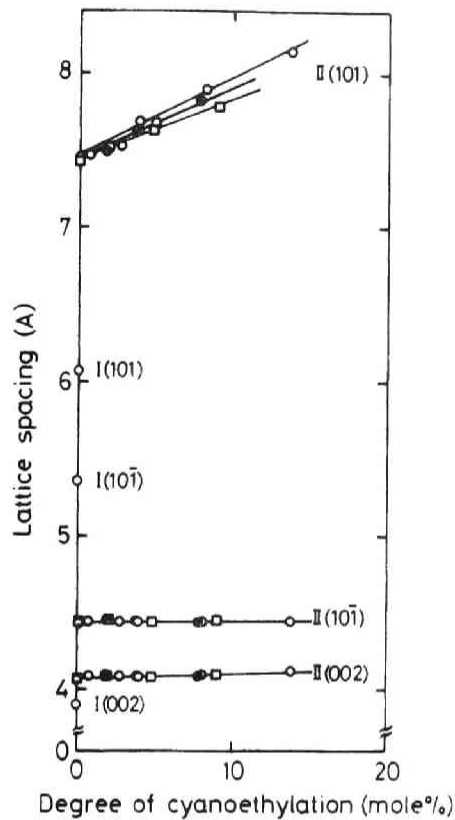
Figure 4.   Lattice spacing vs. degree of cyanoethylation
for treated cotton fibers.   (□) immersed in 5.4N NaOH aque-
ous solution for 60 min at -5°C, and treated with acrylo-
nitrile at 10°C.   (●) immersed in 5.4N NaOH in a mixture of
ethanol and water (volume ratio 30:70) for 60 min at -5°C,
and treated with acrylonitrile at 10°C.   (○) immersed in
5.4N NaOH in a mixture of ethanol and water, and treated
with acrylonitrile at 10°C after immersion in acrylonitrile
for 30 min at -5°C.   The values at zero degree of cyano-
ethylation represent the data for alkali-treated samples.

into the fibrils before reaction, cotton was pretreated
with acrylonitrile for 30 min at -5°C. But no difference
could be detected compared with the results on cotton treat-
ed without pretreatment of acrylonitrile for 30 min at -5°C.

Figure 5 shows the relation between the moisture regain
and the degree of cyanoethylation. No difference in their
tendencies to increase the moisture regain is observed for
cotton fibers by the alkali and acrylonitrile treatment
with or without ethanol. Symbol (△) denote the result for
fabric treated with alkali and acrylonitrile in the presence
of alcohol after pretreatment in acrylonitrile for 30 min
at -5°C. The moisture regain of cotton in fabric form is
lower than that of cotton in fiber form, as described in
chapter 4. But the moisture regain of fabric treated in
the presence of alcohol is higher than that of fabric
without alcohol (denoted by ▲).

Consequently, it was confirmed that highly accessible
and highly disordered cotton was obtained by treatment with
NaOH-ethanol-water system. The main factor for such result
may be the structural change of mercerized cotton by the
addition of ethanol.

To clarify the difference in the crystalline structure
between mercerized cotton and alkali-acrylonitrile treated
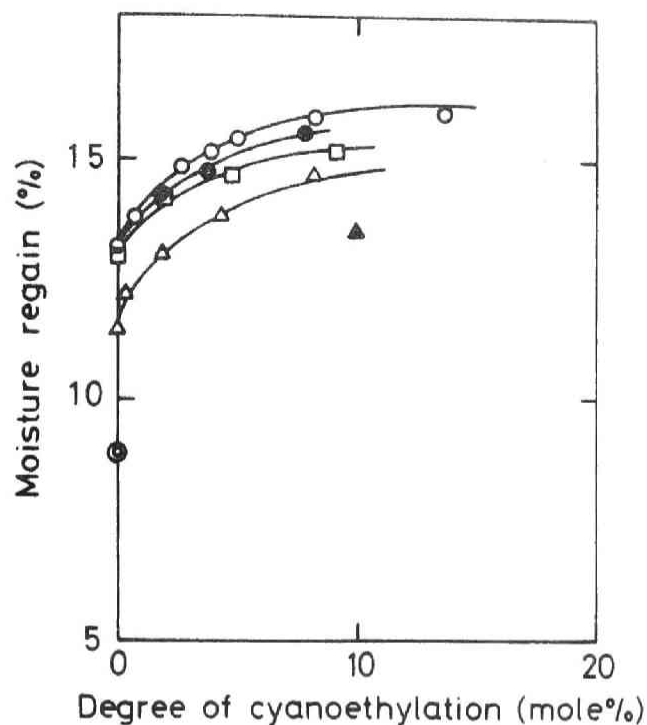cotton, the air-dried samples were boiled in water for
3 hr.

Figure 5.   Moisture regain vs. degree of cyanoethylation.
Cotton fibers; (□) immersed in 5.4N NaOH aqueous solution
at -5°C and treated with acrylonitrile at 10°C. (●) immersed
in alcoholic 5.4N NaOH at -5°C and treated with acrylonitrile
at 10°C. (o) immersed in alcoholic 5.4N NaOH at -5°C and
treated with acrylonitrile at 10°C after immersion in acrylo-
nitrile for 30 min at -5°C. Cotton fabric; (△) immersed in
alcoholic 5.4N NaOH at -5°C and treated with acrylonitrile
at 10°C after immersion in acrylonitrile for 30 min at -5°C.
(▲) immersed in 5.4N NaOH aqueous solution at -5°C and treat-
ed with acrylonitrile at 10°C after immersion in acrylo-
nitrile for 30 min at -5°C. (◎) original cotton.

Figure 6 shows the x-ray profiles of alkali-acrylo-
nitrile treatment in the presence of alcohol before and
after boiling in water. As already described, cotton
treated with 5.4N NaOH in a mixture of ethanol and water
contained a slight cellulose I. With such sample, each
diffraction peak of cellulose I and II increases. But no
peak is observed with cellulose I diffraction in the cyano-
ethylated samples and these cyanoethylated samples remain
highly disordered after boiling in water.

Figure 7 shows the x-ray profile of cotton treated
with NaOH-water and NaOH-ethanol-water system before and
after boiling in water. Effect of alcohol is obvious.
X-Ray diffractogram of original cotton fibers shows cellu-
lose I structure. The memory of cellulose I structure was
pronounced by adding alcohol to 5.4N sodium hydroxide.
For example, the intensity of (002) plane was stronger than
that of (10$\bar{1}$) plane in the region of the lower degree of
cyanoethylation.

As shown in Figure 8, when the cyanoethylation with
5.4N NaOH in a mixture of ethanol and water (volume ratio
30:70) was applied to cotton fabric as well as fibers, the
same tendency in the structural change was observed except
that strong peaks of (101) and (10$\bar{1}$) diffractions of cellu-
lose I remained at a few degree of cyanoethylation on
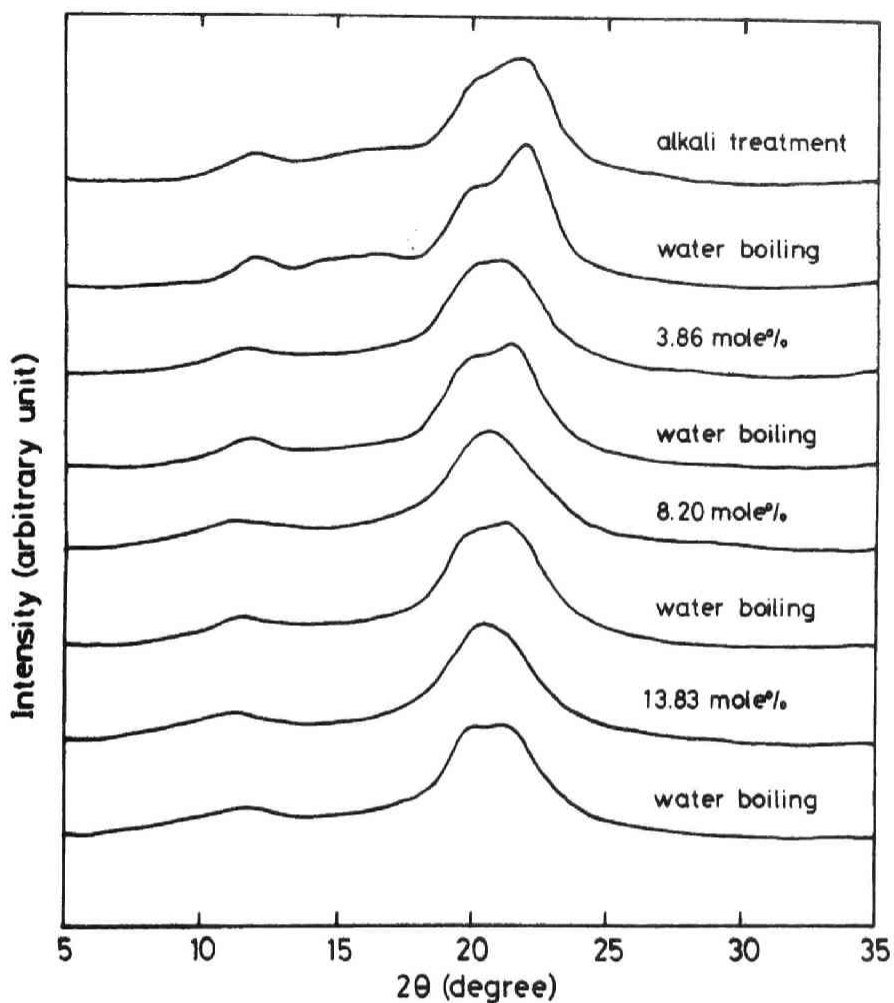account of fabric construction.

Figure 6.   X-Ray diffractograms of treated cotton fibers before and after boiling in water for 3 hr. Cotton was immersed in alcoholic 5.4N NaOH for 60 min at -5°C, and treated with acrylonitrile at 10°C after immersion in acrylonitrile for 30 min at -5°C.
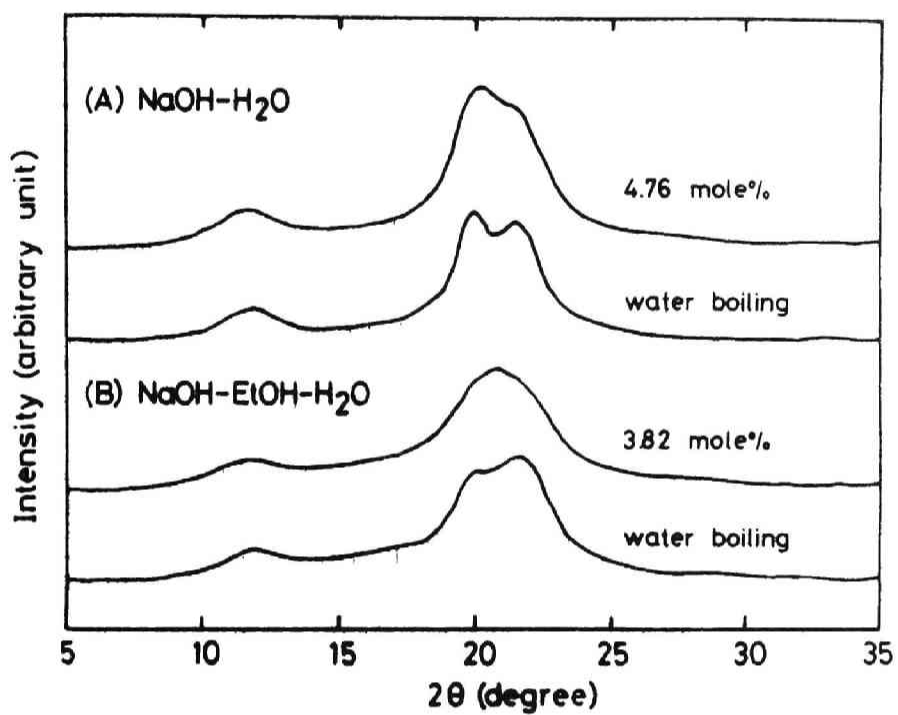
Figure 7.   X-Ray diffractograms of treated cotton fibers

before and after boiling in water.   (A) immersed in 5.4N

NaOH aqueous solution for 60 min at -5°C and treated with

acrylonitrile at 10°C.   (B) immersed in alcoholic 5.4N NaOH

for 60 min at -5°C and treated with acrylonitrile at 10°C.

Figure 8.   X-Ray diffractograms of treated cotton fabric.
Cotton fabric was immersed in 5.4N NaOH in a mixture of
ethanol and water, and treated in acrylonitrile at 10°C
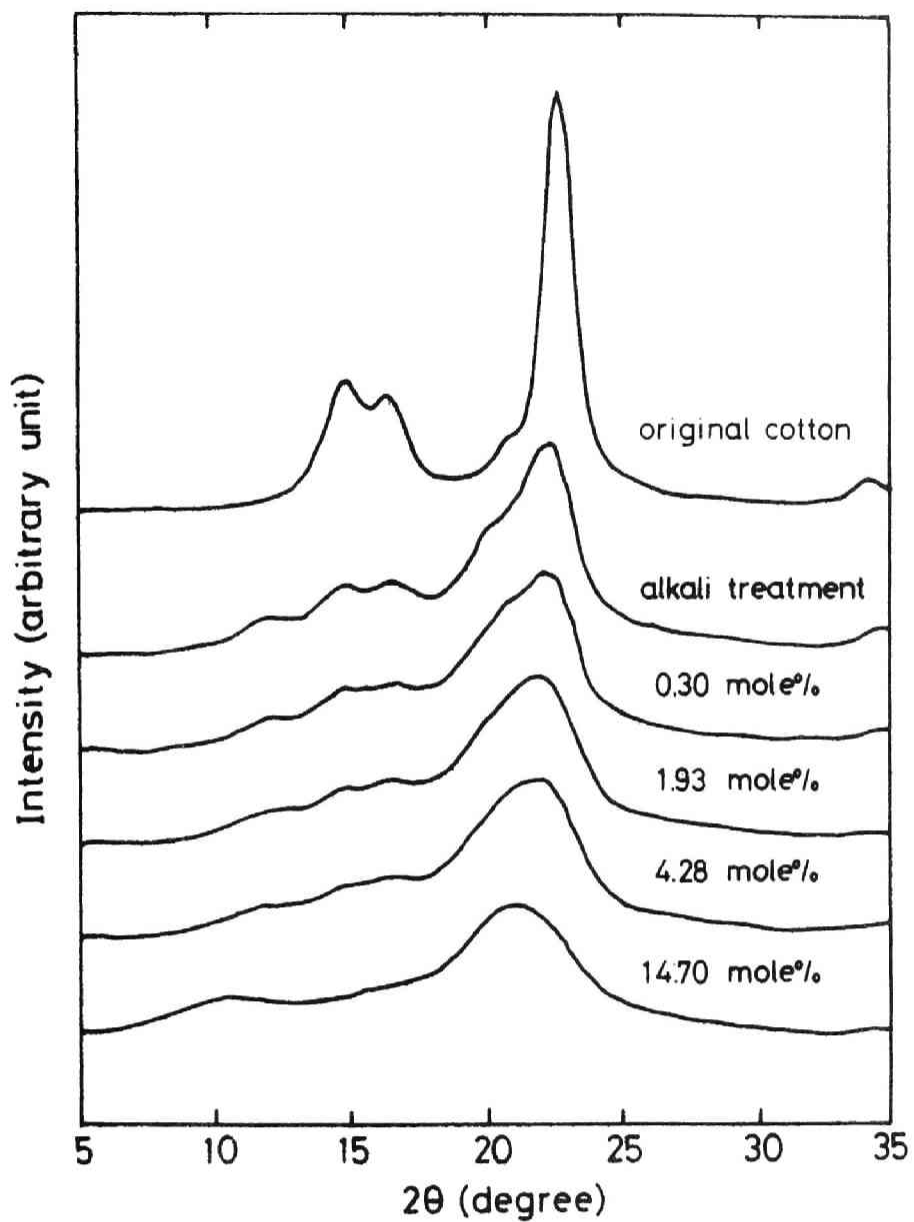after immersion in acrylonitrile for 30 min at -5°C.

After cyanoethylation with NaOH-ethanol-water system, it was necessary to immerse the treated cotton in 1% acetic acid in a mixture of ethanol and water and then wash with a mixture of ethanol and water. Because after cyanoethylation, the cotton immersed in 1% acatic acid aqueous solution swelled to a great extent and partially disappeared fibrous form. Cotton fabric treated with alcoholic system retained the softness together with the same degree of dry crease recovery as original cotton fabric, while cotton fabric treated with NaOH aqueous solution system had high stiffness and low crease recovery. Once dried, thus obtained fabric with alcoholic system remained the softness even after boiling in water.

Table I shows the physical properties of NaOH-acrylonitrile treated cotton. Cyanoethylated cotton with NaOH-ethanol-water system gives no change in tensile strength of warp yarn, but exhibits an increase in elongation and has high moisture regain.

TABLE I

Properties of NaOH-Acrylonitrile Treated Cotton Fabric

(Effect of Alcohol)

Sample	Treatment	Crease recovery,%		Strength[a] g	Elongation[a] %	Moisture regain,%
		Dry	Wet			
cotton	——	42	32	285	6.7	7.8
FM3	NaOH-EtOH-H_2O[b]	44	41	277	10.7	11.5
FC4	NaOH-EtOH-H_2O, AN (4.28mole%)[c]	42	46	266	10.0	13.3
A-2	liq. NH_3[d]	48	42	254	7.4	9.5
3M2	NaOH-H_2O[e]	36	44	265	8.7	11.1
C-1	NaOH-H_2O, AN (3.90mole%)[f]	18	38	260	9.3	12.1

a) values of warp yarns taken from fabric.
b) Cotton was treated with alcoholic 5.4N NaOH for 60 min at -5°C.
c) Cotton was treated with alcoholic 5.4N NaOH for 60 min at -5°C, and treated with acrylonitrile at 10°C after immersed in acrylonitrile for 30 min at -5°C.
d) Cotton was immersed in liquid ammonia for 1 min and air dried.
e) Cotton was immersed in 5.4N NaOH aqueous solution for 30 min at 15°C.
f) Cotton was immersed in 5.4N NaOH aqueous solution for 30 min at 15°C and treated with acrylonitrile at 20°C.

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Chapter 6

Crystalline Structure of Polynosic and Cuprammonium Rayon
Treated with Alkali and Acrylonitrile
in the Presence of Ethanol

INTRODUCTION

The fibers grow as single cells which emerge from the epidermic or outer layer of the cotton seed and form a dense cover over the surface. Cotton is a hair attached to the seed of several species of the botanical genus *Gossypium*. The cotton fibers grow in a tubular form: through the center runs a canal known as the lumen. Naturally when the boll opens and the fibers are exposed to air, moisture evaporates. This in turn causes the seed hair to shrink making the lumen smaller and flatter until finally the walls collapse. A drastic change of shape of this kind naturally causes stresses to be set up and the collapse fibers show convolutions arizing from this. The collapse of the walls is accompanied by changes in the shape of the cross section of the fiber, the original circular cross section being transformed to one which may be of a variety of shapes ranging from linear, elliptical to dumb-bell.

Regenerated cellulose is made by dissolution of a

natural cellulosic material such as cotton or wood pulp,
followed by coagulation and regeneration. Since these
procedures usually take place simultaneously in a compara-
tively short time, it is difficult to form ordered arrange-
ments of molecules. Regenerated cellulose consists of
relatively large, pooly ordered amorphous regions and small
or imperfect crystalline regions.

Table I shows the structure of polynosic fiber,
ordinary viscose rayon and cotton (1).

TABLE I

The Structure of Polynosic Fiber, Ordinary Viscose Rayon
and Cotton

	polynosic fiber	ordinary viscose rayon	cotton
cross section	circular all skin	irregularly oval skin and core	ribbon-like
helical structure	—	11°	30°
degree of polymerization	500-600	300	2000
degree of orientation (x-ray method) %	87	84	71
degree of crystallinity (x-ray method) %	45	30-40	70
length of crystallite A	130-150	90-110	500
width of crystallite A	31-16	11-14	27

cross-sections of cuprammonium rayon are round or occassionaly slight oval. Cuprammonium filaments show no distinct differentiation into skin and core as is found in viscose rayon. Degree of polymerization is 450-550 for cuprammonium rayon.

Hayashi et al. (2) have investigated the crystalline structure of cellulose. In native cellulose, a leveling-off degree of polymerization (LODP) is 200 and crystallite length from wide-angle x-ray diffraction is 200A. In mercerized cellulose, LODP is 80 and crystallite length is 200A. In regenerated cellulose, LODP is 40 and crystallite length is 120-160A. Table II shows the long period and crystallite size measured by x-ray method with some cellulose modifications hydrolyzed with 2.4N HCl at 50°C for 16 hr (2).

TABLE II

Long Period and Crystallite Size Measured by X-Ray Method with Some Cellulose Modifications Hydrolyzed with 2.4N-HCl at 50°C for 16 hours

Material	Original DP	Long period A	Crystallite Size length A	width A	LODP
Mercerized ramie	4100	410	180	53	80
Mercerized cotton	3400	380	200	55	80
Polynosic fiber	560	210	180	55	40
Ordinary viscose rayon	280	180	170	52	40

As described above, fine structure of regenerated celluloses is quite different from that of native cellulose. So different behaviors are expected on alkali-acrylonitrile treatment.

In this chapter, regenerated celluloses such as poly-nosic fiber and cuprammonium rayon are cyanoethylated after pretreatment with 5.4N NaOH in a mixture of ethanol and water (volume ratio 30:70), and crystalline structure thus obtained is investigated.

Regenerated cellulose is dissolved in 5.4N NaOH aqueous solution, but the addition of alcohol to sodium hydroxide solution prevents the dissolution of cellulose and the treatment in fibrous form can be performed.

EXPERIMENTAL

Samples. Polynosic fibers (Toramomen Advanced 61) supplied by Tachikawa Institute were extracted in a Soxhlet extractor with a mixture of ethanol and benzene (volume ratio 1:1) for 6 hr and then with ethanol for 6 hr, and washed with water and air dried. Cuprammonium rayon 120 (90) supplied by Asahikasei Co. was sampled before oil treatment. It was washed with water, then with hot water, and air dried. Egyptian cotton fibers were purified as

described in chapter 4. Average molecular weights by viscosity method (trinitrates in acetone at 20°C) were 588, 456, and 4020 for polynosic fiber, cuprammonium rayon, and cotton fibers, respectively.

Treatment. Cellulose immersed in 5.4N NaOH in a mixture of ethanol and water (volume ratio 30:70) for 60 min at -5°C was treated with acrylonitrile at 10°C after immersed in acrylonitrile for 30 min at -5°C. Then the treated cellulose was immersed in 1% acetic acid in a mixture of ethanol and water (volume ratio 30:70), washed with a mixture of ethanol and water (volume ratio 30:70), and air dried.

RESULTS AND DISCUSSION

Figure 1 shows the relation between the immersing time in acrylonitrile at 10°C and the degree of cyanoethylation. The value at zero degree of cyanoethylation represents the value for cotton fiber immersed in acrylonitrile for 30 min at -5°C after immersed in alcoholic 5.4N NaOH. The rate of reaction of regenerated cellulose is nearly equal to that of cotton.

Figure 2 shows the relation between the moisture regain and the degree of cyanoethylation. The moisture regain of each cellulose sample increases with an increase of cyano-
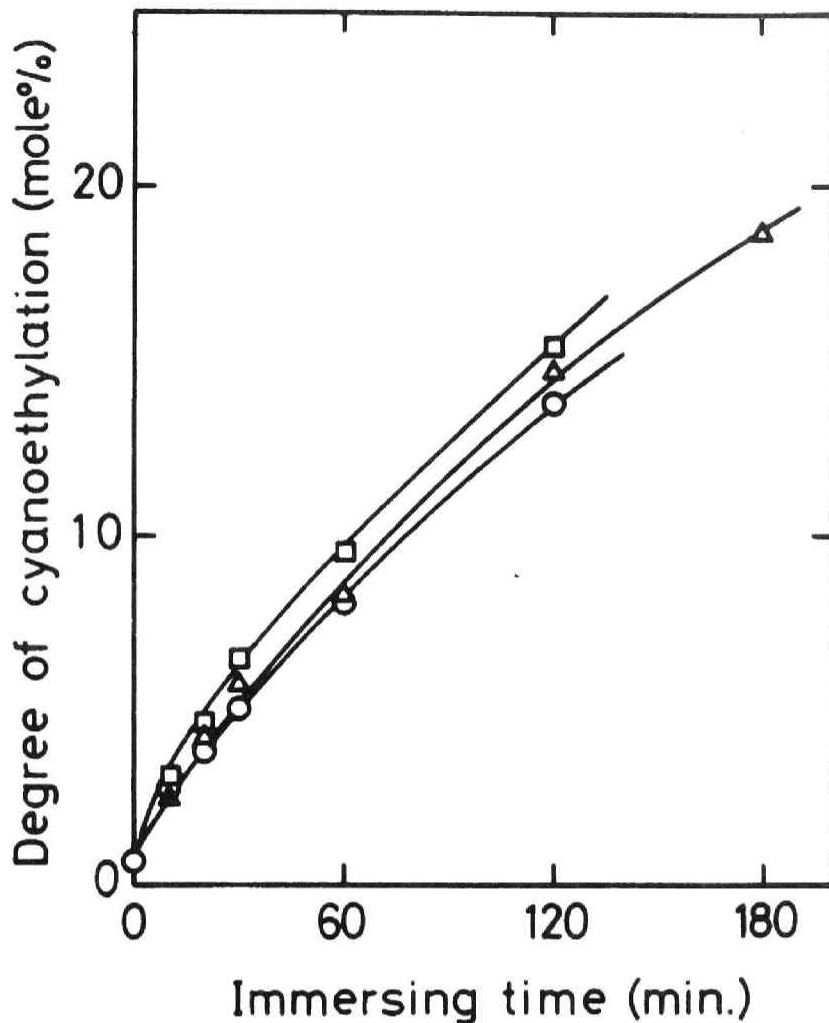
Figure 1.   Immersing time in acrylonitrile at 10°C vs.
degree of cyanoethylation. The value at zero degree of
cyanoethylation represents the value for cotton fiber
immersed in acrylonitrile for 30 min at -5°C after immersing
in alcoholic 5.4N NaOH. (□) polynosic fiber, (△) cuprammo-
nium rayon, (o) cotton fiber.

ethyl content and levels off at about 10 mole%. The values

of moisture regain of original cotton fibers and regenerated

cellulose are about 8.0 and 15%, respectively. High value

of regenerated cellulose is attributed to small crystals

and low degree of crystallinity. The moisture regain of

cuprammonium rayon is 15.7% and that of alkali-treated

rayon is 15.8%. At a degree of 8.09 mole%, moisture regain

of 17.2% is obtained for cuprammonium rayon. Whereas,

moisture regain of treated cotton with a degree of cyano-

ethylation of 8.20 mole% is 15.9%. Accessibility

calculated by Valentine's relation (3) was designated in

parentheses in Figure 2.

To clarify the structural change of alkali-acryloni-

trile treated cellulose in the presence of alcohol, x-ray

diffractograms were analyzed for samples with various

degrees of cyanoethylation. Figures 3, 4, and 5 show x-ray

diffractograms for polynosic fibers, cuprammonium rayon

and cotton fibers, respectively. Lattice spacings of

samples determined from the peaks of the resolved curves,

were plotted against the degree of cyanoethylation in

Figure 6. For each cellulose sample lattice spacing of

(101) plane increases as the cyanoethylation proceeds,

while those of (10$\bar{1}$) and (002) planes stay nearly unchanged.

Figures 7, 8, and 9 show the relation between the

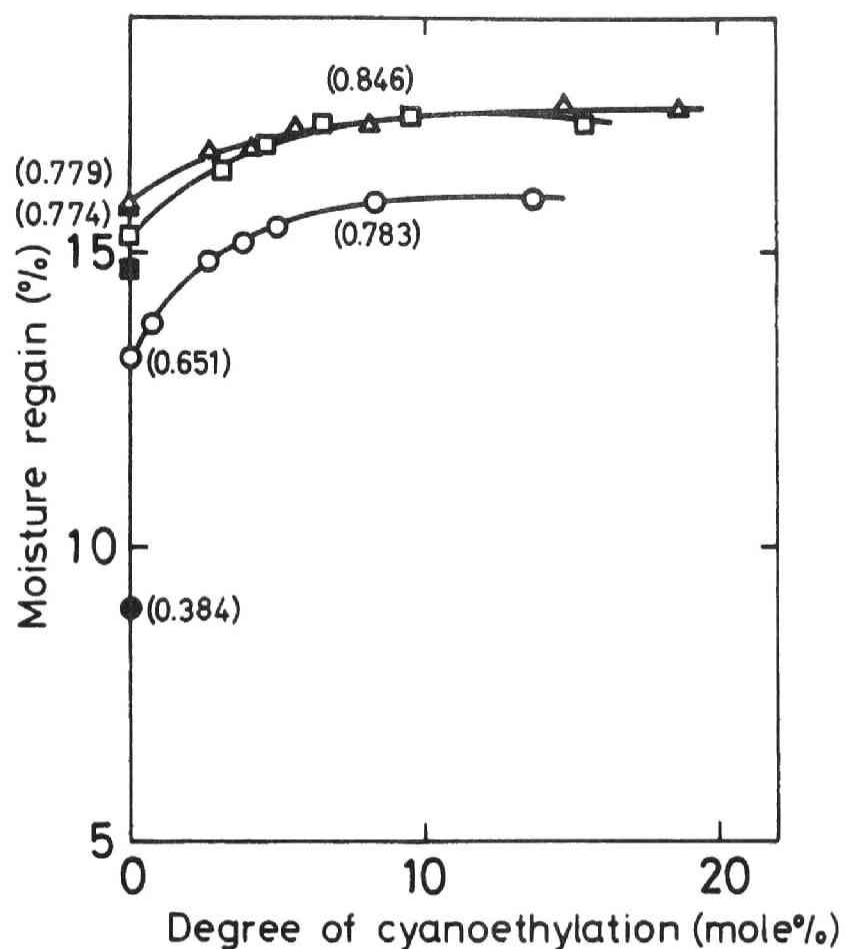integral breadth and the degree of cyanoethylation for

Figure 2.   Moisture regain vs. degree of cyanoethylation.
The values at zero degree of cyanoethylation represent the
values for samples immersed in alcoholic 5.4N NaOH.
(■) original polynosic fiber, (▲) original cuprammonium
rayon, (●) original cotton, (□) treated polynosic fiber,
(△) treated cuprammonium rayon, (o) treated cotton fiber.
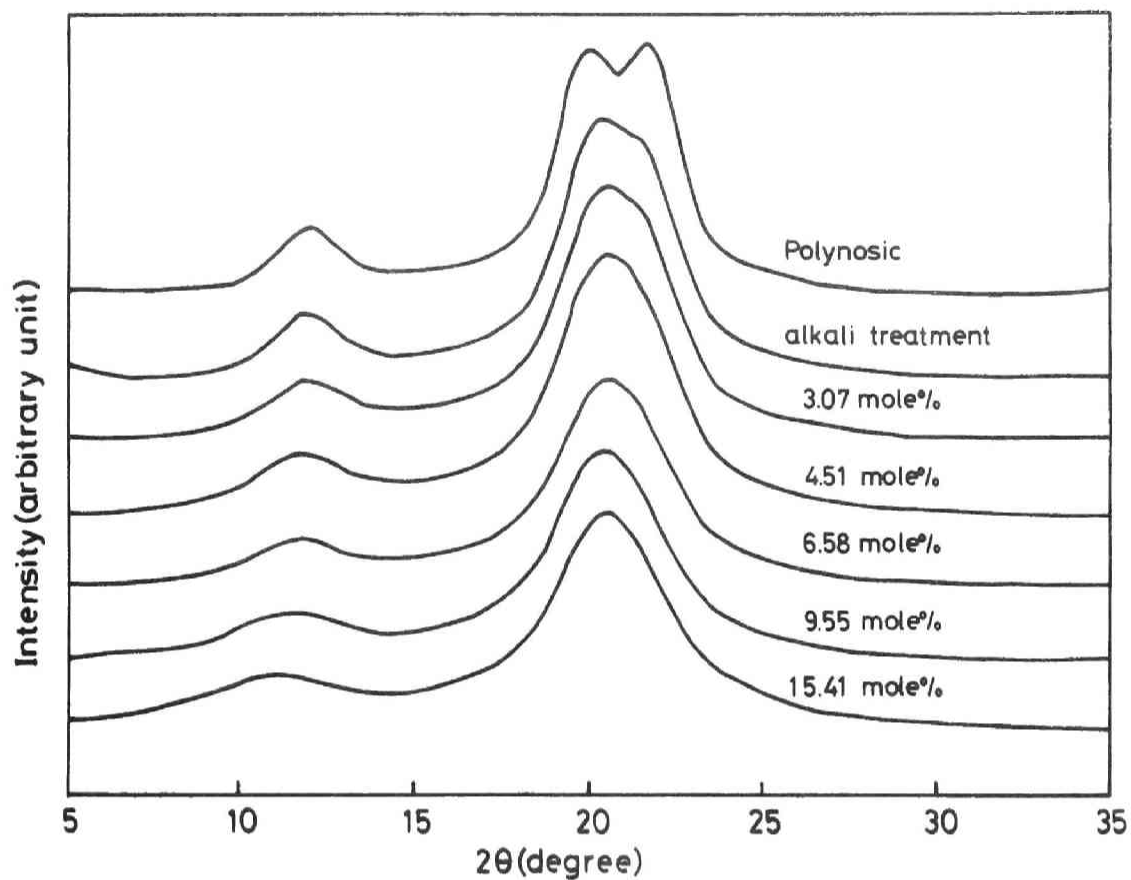Accessibility was designated in parentheses.

Figure 3. X-Ray diffractograms for polynosic fibers treated with alkali-acrylonitrile in the presence of ethanol.
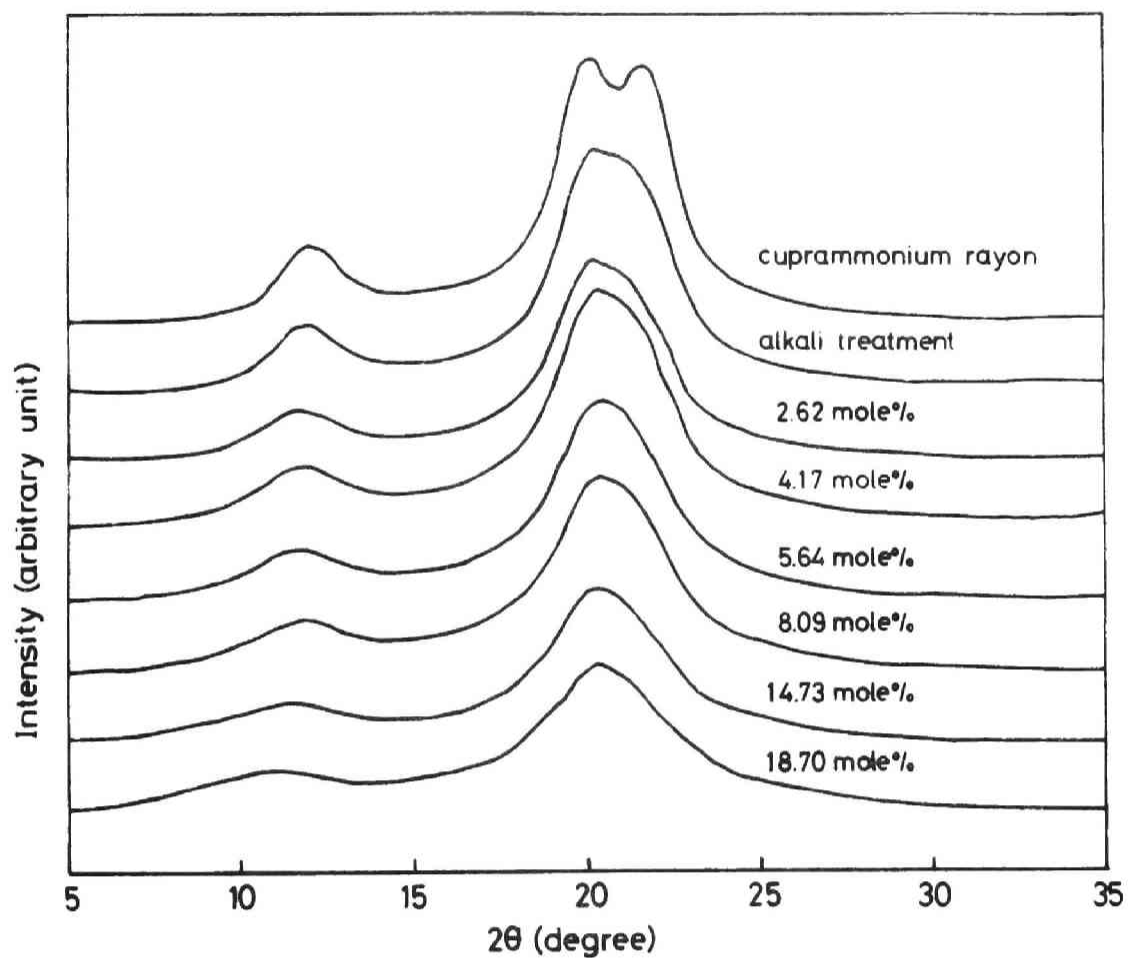
Figure 4.   X-Ray diffractograms for cuprammonium rayon
treated with alkali-acrylonitrile in the presence of ethanol.

Figure 5.   X-Ray diffractograms for cotton fibers treated
with alkali-acrylonitrile in the presence of ethanol.

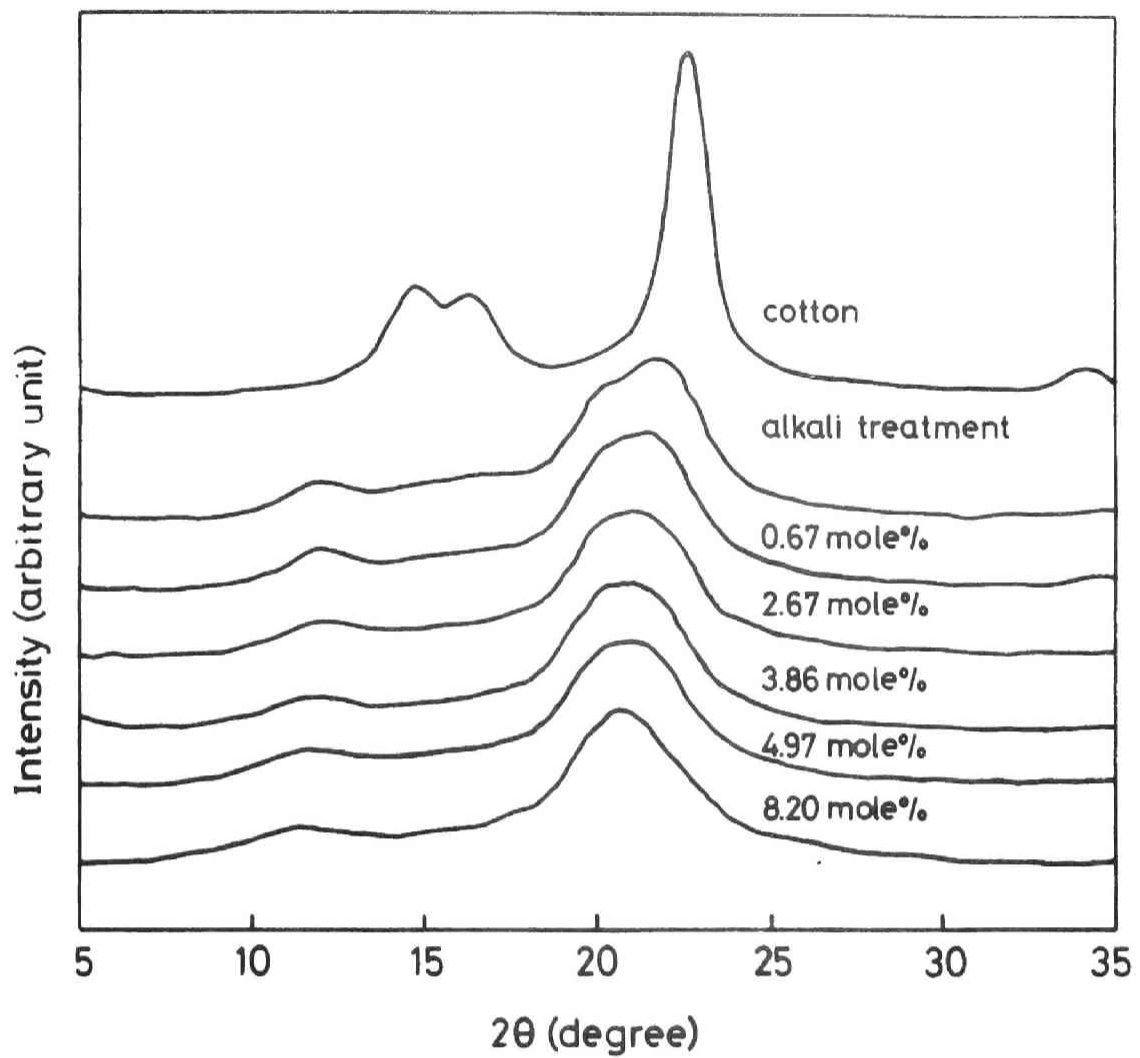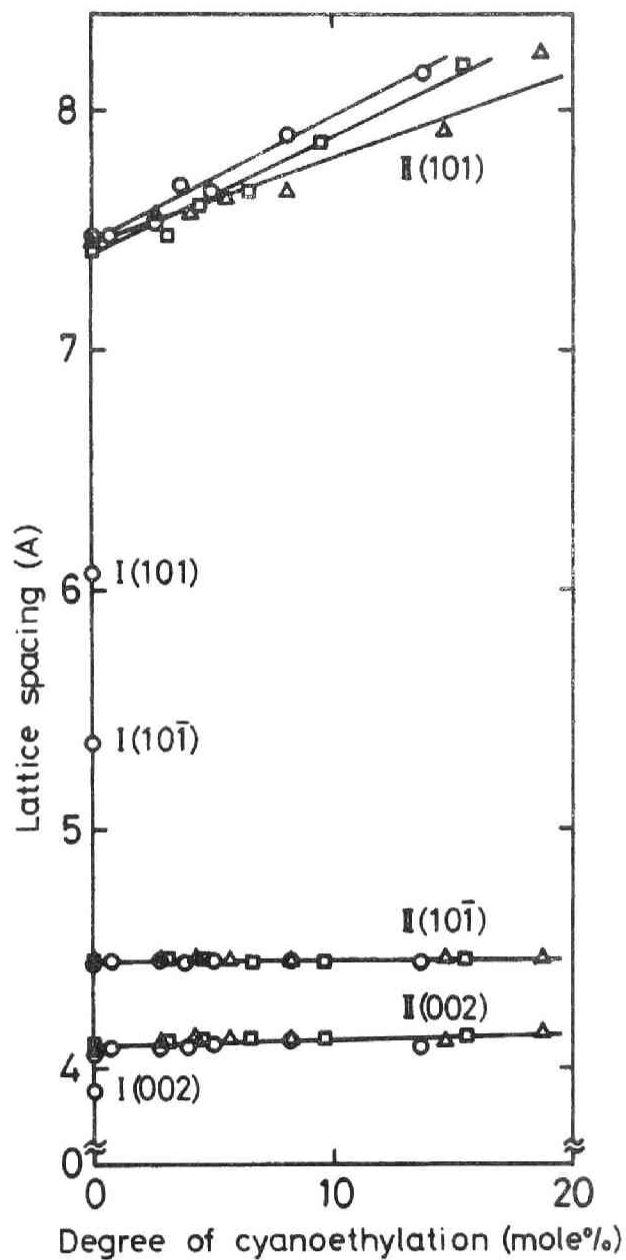Figure 6.   Lattice spacing vs. degree of cyanoethylation.
The values at zero degree of cyanoethylation represent the
values for samples immersed in alcoholic 5.4N NaOH.
(□) polynosic fiber, (△) cuprammonium rayon, (o) cotton fiber.

treated polynosic fiber, cuprammonium rayon and cotton fiber samples, respectively. All figures show that integral breadth of each crystalline plane increases as the cyano-ethylation proceeds.

Figures 10 and 11 show the relation between the cumulative intensity and the degree of cyanoethylation for polynosic fiber and cuprammonium rayon, respectively. Crystalline structure of regenerated cellulose is cellulose II. The intensity of ($10\bar{1}$) interference is stronger than that of (002) interference. By the treatment with 5.4N NaOH in a mixture of ethanol and water for 60 min at -5°C, the intensity of ($10\bar{1}$) interference is decreased. By introducing the cyanoethyl residues, the intensity of (002) interference decreases and that of ($10\bar{1}$) interference begins to decrease at 10 mole%, while that of (101) interference stays nearly unchanged.

Effect of boiling in water for 3 hr on the x-ray diffractograms of alkali-acrylonitrile treated cellulose in the presence of alcohol is shown in Figures 12 and 13 for polynosic fiber and cuprammonium rayon, respectively.

Figures 14 and 15 show the effect of boiling in water on cumulative intensity of polynosic fiber and cuprammonium rayon, respectively. Regenerated cellulose treated with 5.4N NaOH in a mixture of ethanol and water is recrystalliz-ed to the same order as original cellulose. But as the

-131-
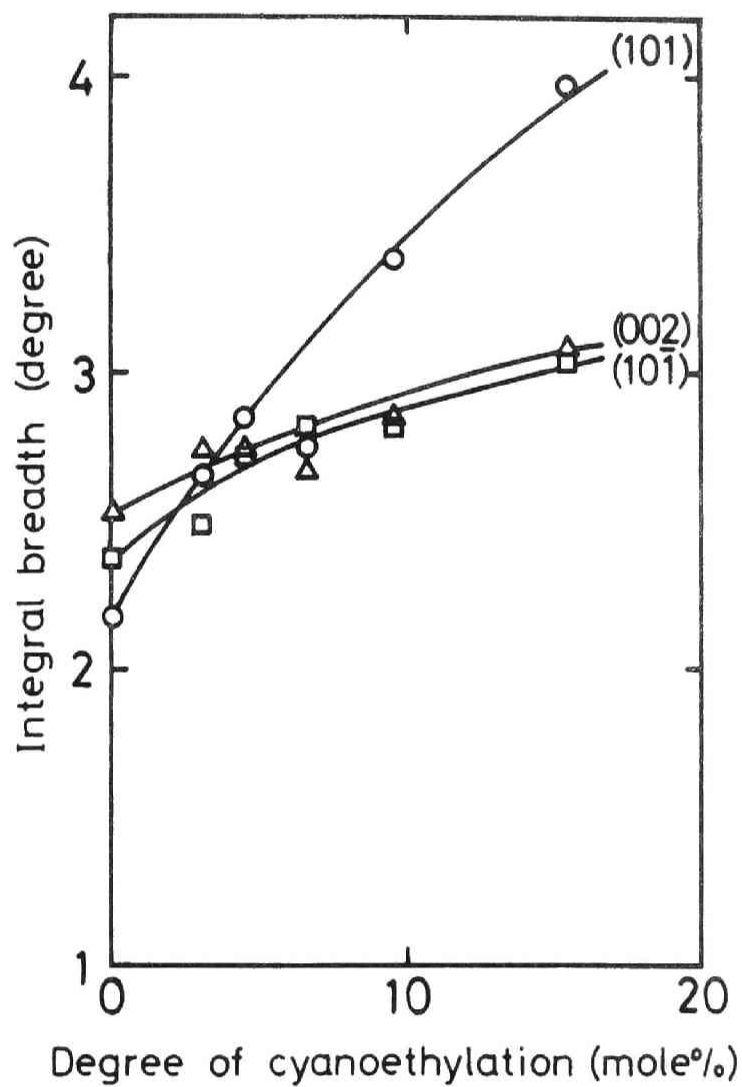
Figure 7.   Integral breadth vs. degree of cyanoethylation
for polynosic fibers.
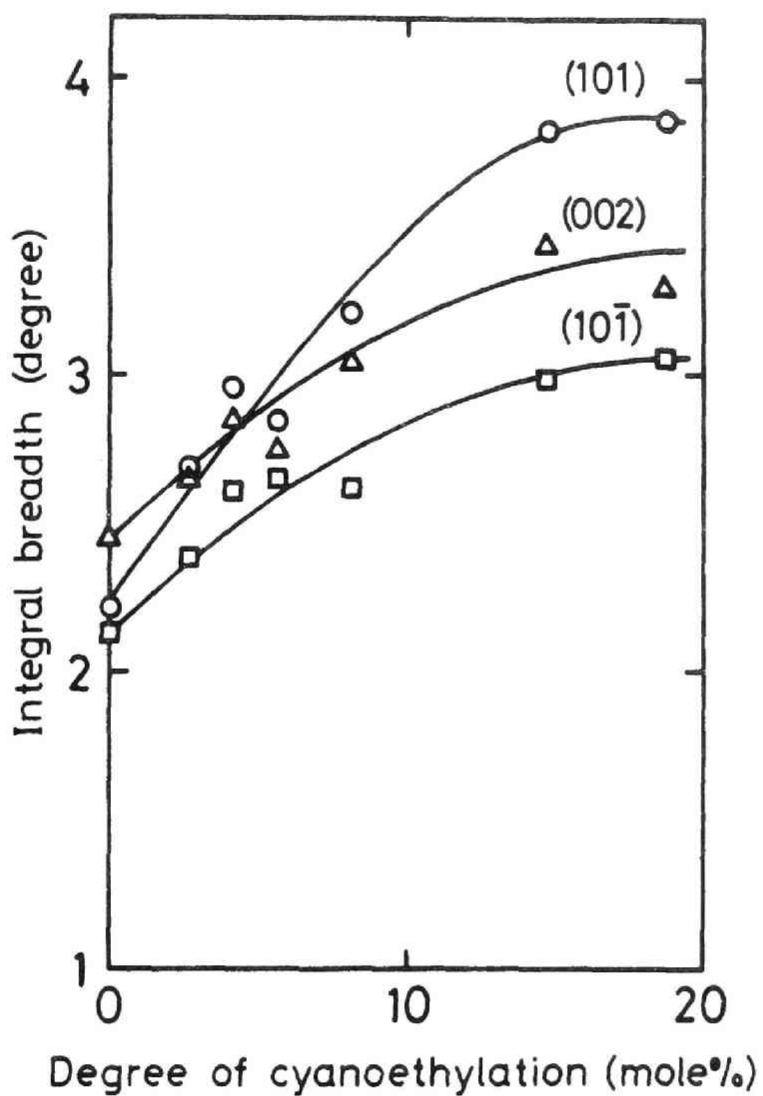
Figure 8.   Integral breadth vs. degree of cyanoethylation for cuprammonium rayon.
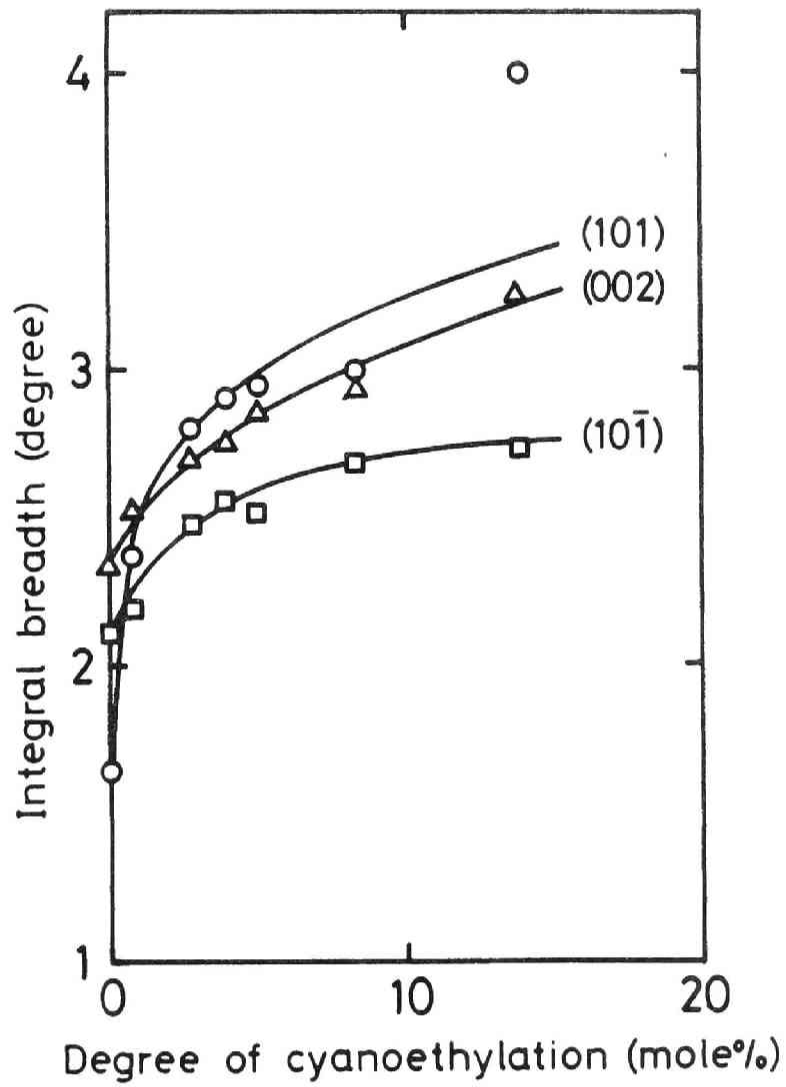
Figure 9.   Integral breadth vs. degree of cyanoethylation for cotton fibers.
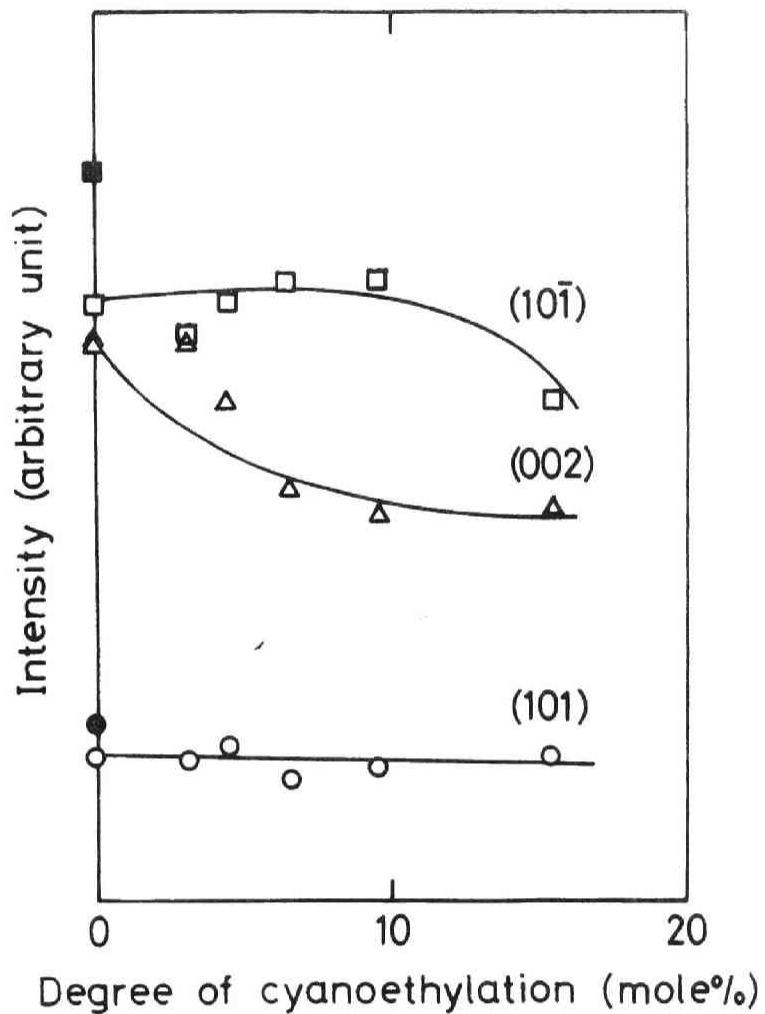
Figure 10.   Cumulative intensity vs. degree of cyano-
ethylation for polynosic fibers.   (●)(■)(▲); original fibers.
Symbols (o), (□) and (Δ) at zero degree of cyanoethylation
represent the values for samples prepared with alcoholic
sodium hydroxide.
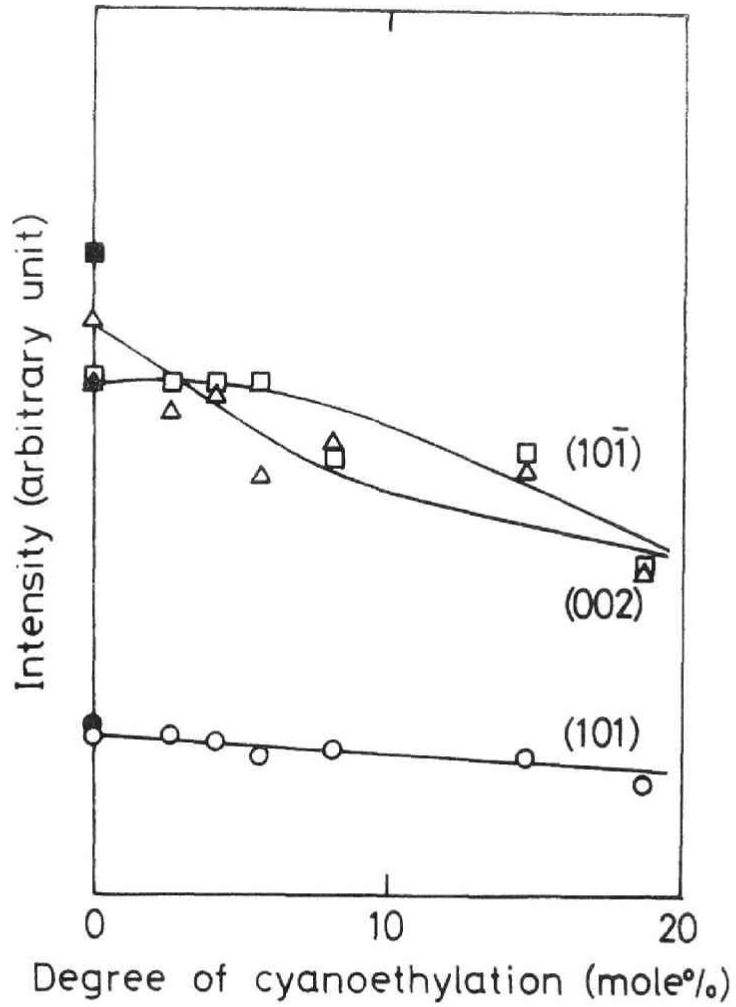
Figure 11.   Cumulative intensity vs. degree of cyano-
ethylation for cuprammonium rayon. (●)(■)(▲); original
fibers. Symbols (o), (□) and (△) at zero degree of cyano-
ethylation represent the values for samples prepared with
alcoholic sodium hydroxide.
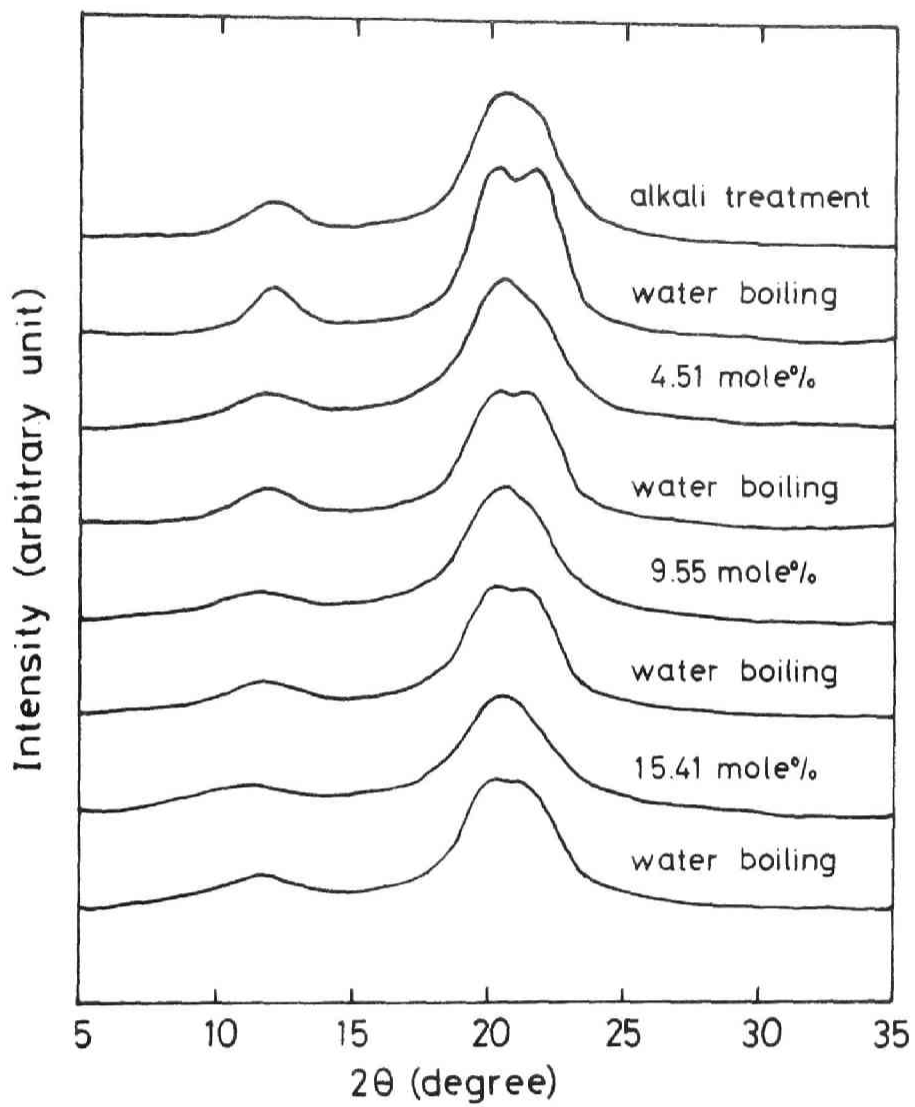
Figure 12. Effect of boiling in water for 3 hr on the
x-ray diffractograms of alkali-acrylonitrile treated
polynosic fibers in the presence of alcohol.
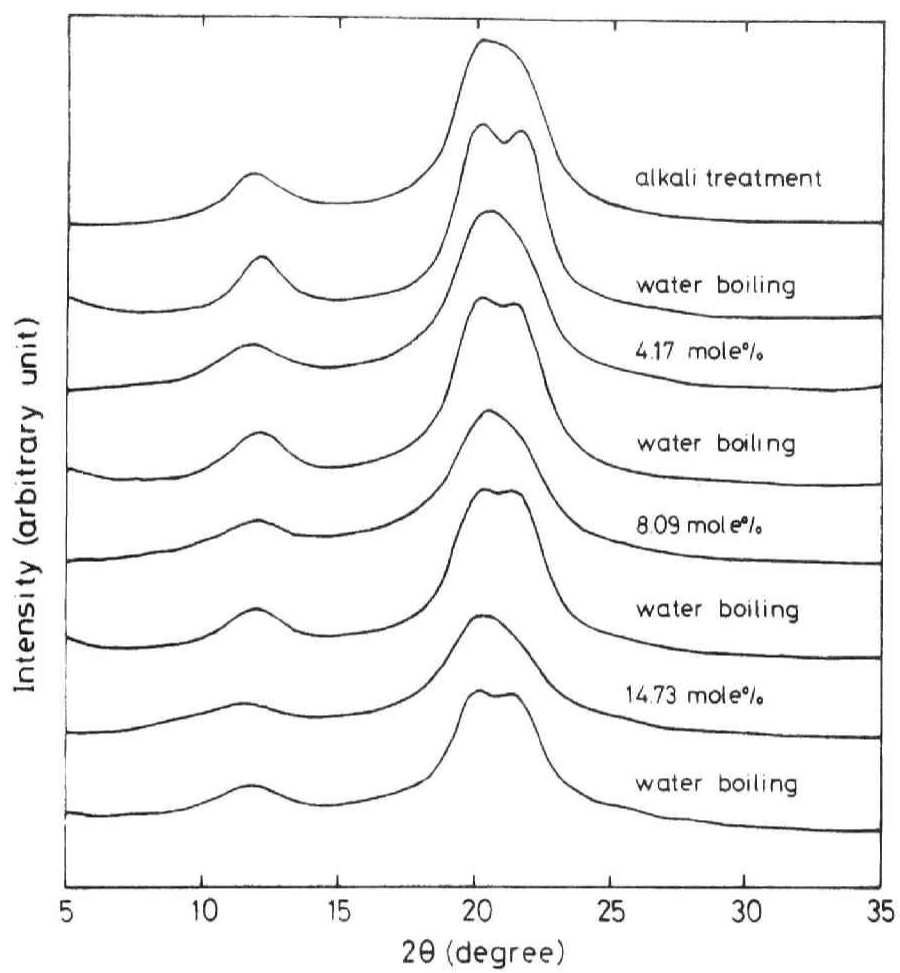
Figure 13.   Effect of boiling in water for 3 hr on the
x-ray diffractograms of alkali-acrylonitrile treated
cuprammonium rayon in the presence of alcohol.
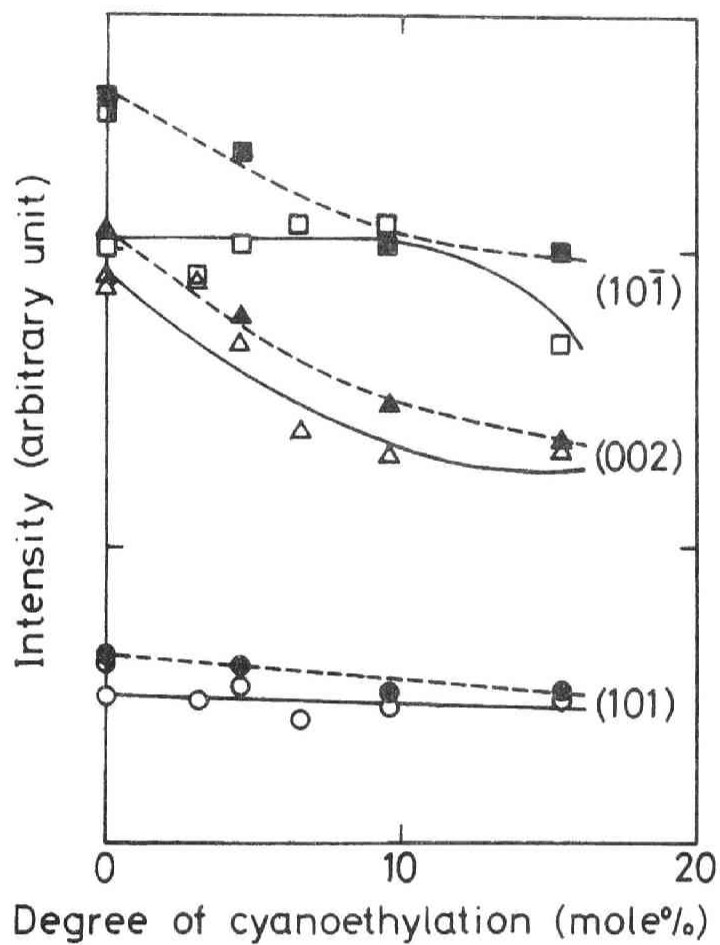
Figure 14.   Effect of boiling in water for 3 hr on
cumulative intensity of polynosic fibers.
(●) (101) plane, (■) (10$\bar{1}$) plane, (▲) (002) plane for
original fiber. (○), (□), (△); before boiling: (●), (■),
(▲); after boiling.
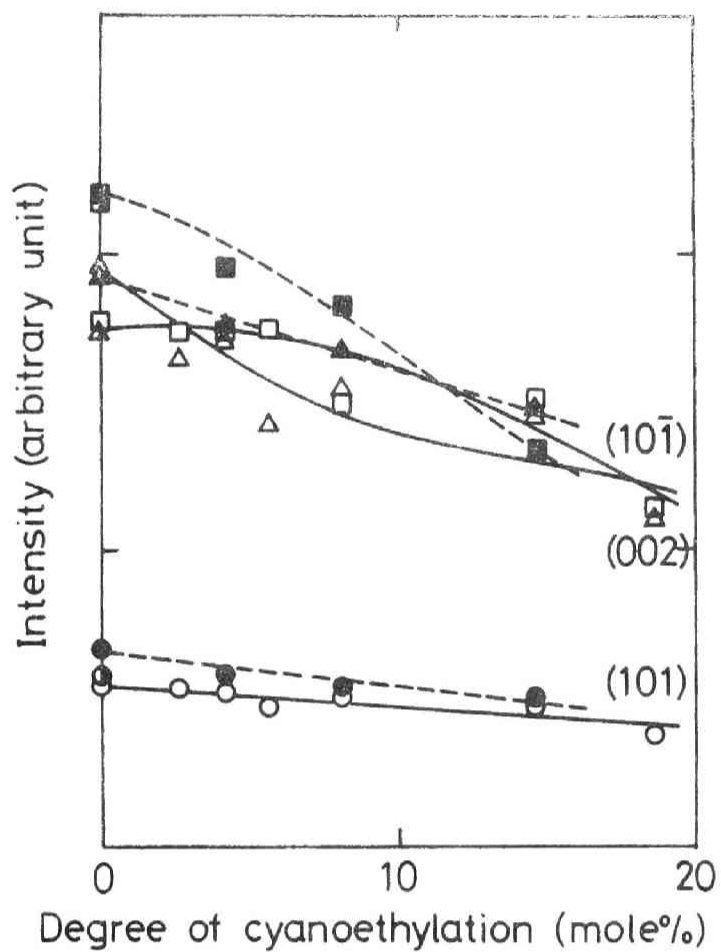
Figure 15.   Effect of boiling in water for 3 hr on
cumulative intensity of cuprammonium rayon.
(●) (101) plane, (■) (10$\bar{1}$) plane, (▲) (002) plane for
original fiber. (o), (□), (△); before boiling: (●), (■),
(▲); after boiling.

cyanoethylation proceeds, intensity of each crystal plane decreases and prevention of recrystallization by cyanoethyl residues is obvious.

Figures 16 and 17 show integral breadth before and after boiling in water for treated polynosic and cuprammoniun rayon samples, respectively. After boiling in water, the integral breadths of $(10\bar{1})$ and (002) planes decrease, especially in treated cuprammonium rayon samples.

Fine structure of regenerated cellulose is quite different from that of native cellulose as already described. For example, crystal size is small, degree of crystallinity and degree of polymerization are low. So different behavior was expected on alkali-acrylonitrile treatment. But the influence of cyanoethyl residue on the crystalline structure of regenerated cellulose seems to be identical with that of cotton described in chapter 5. Moreover these alkali-acrylonitrile treated regenerated cellulose samples easily recrystallize in the region of a lower degree of cyanoethylation.

Cellulose I can be transformed into cellulose II by mercerizing. It is considered that this transfer results from the transformational change of the cellulose chain from the cell I type ("bent") to the cell II type ("bent and twisted") (4,5). This transformation affects the crystalline structure of NaOH-acrylonitrile treated cotton.

-141-
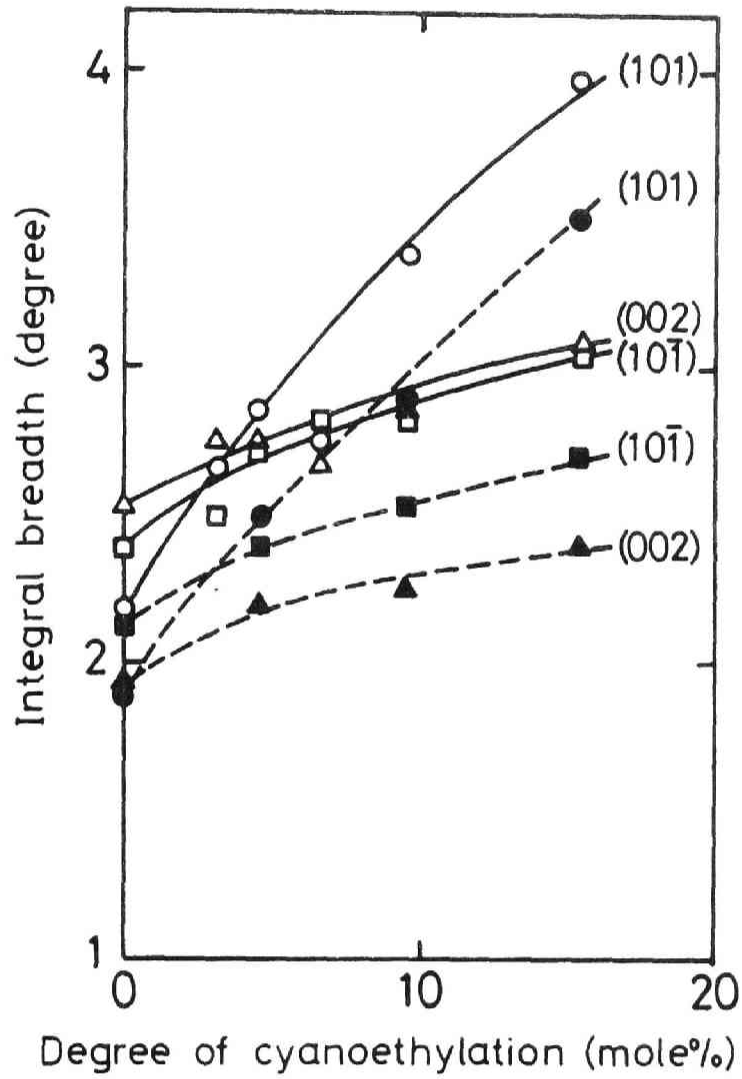
Figure 16.   Effect of boiling in water on integral
breadth of polynosic fibers.   (o), (□), (△); before boiling:
(●), (■), (▲); after boiling.
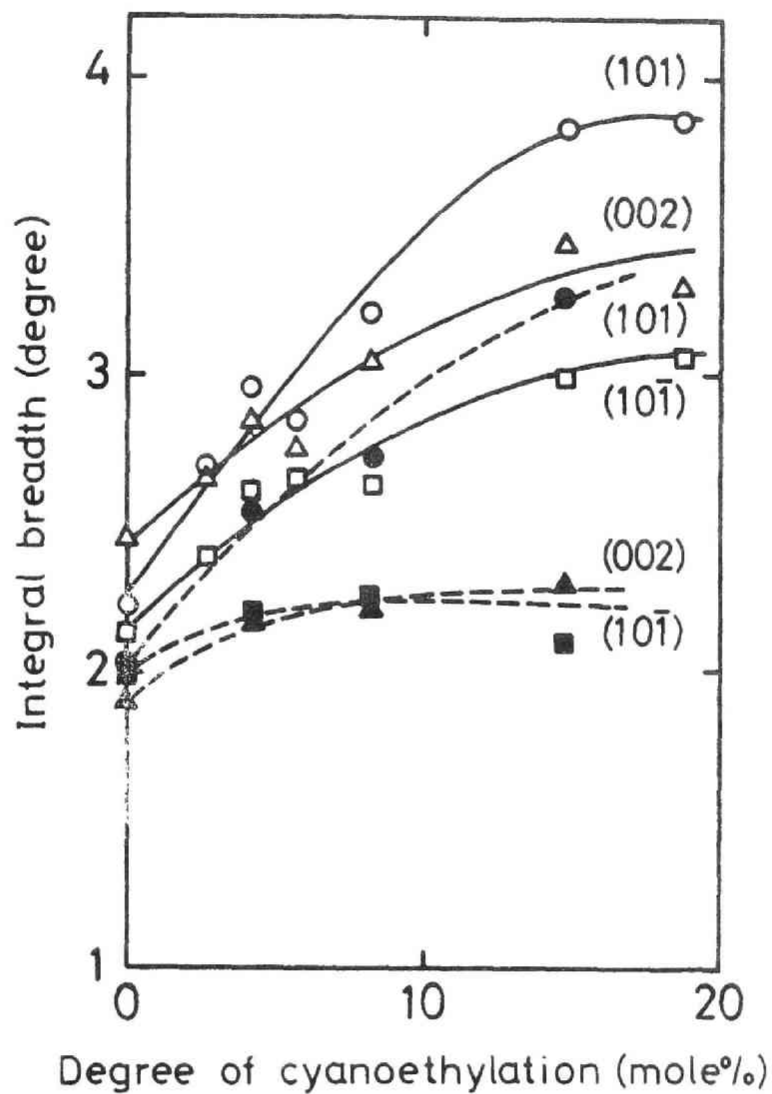
Figure 17.   Effect of boiling in water on integral
breadth of cuprammonium rayon. (o), (□), (△); before
boiling: (●), (■), (▲); after boiling.

Kato and Yamada (6) investigated several types of cellulosic rayons by means of acid hydrolysis combined with alkali swelling. The alkali swelling resulted in an increase of the leveling-off DP and elongation of crystalline particles obtained by the subsequent hydrolysis, probably due to molecular rearrangement which has occurred in intercrystalline regions, while the yield of hydrolysis residue remained almost unaltered. Whereas, the alkali treatment of native cellulose resulted in a decrease of the LODP and subdivision of crystallites.

This behavior is one of the reason why structural change of regenerated cellulose is not so much as was expected. But if the structure of amorphous regions can be investigated, an index of structural features inherent to each kind of cellulose fibers may be obtained.

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Chapter 7

Influence of the Decrystallization by Alkali and
Acrylonitrile Treatments on the Properties of
the Cotton Fabrics with or without Crosslinking

INTRODUCTION

As already decribed in chapters 2 and 3, highly
accessible or decrystallized cotton could be obtained by
cyanoethylation with acrylonitrile after pretreatment with
swelling agent such as sodium hydroxide. The investigation
by x-ray diffraction on the fine structure of the cotton
thus decrystallized was also described in chapter 3. In
this chapter, cotton fabrics with or without crosslinking
were treated with acrylonitrile after impregnation with
5.4N aqueous solution of sodium hydroxide, and some physical
properties of the treated cotton fabrics were examined. In
this process a small quantity of cyanoethyl residue was
introduced onto cellulose molecules to prevent recrystal-
lization during water rinse and drying. Crosslinking was
given to cotton fabrics before or after the decrystalliza-
tion process, using conventional crosslinking agents.

As is well-known, the deterioration of the mechanical
properties of cotton, such as tensile strength and abrasion

resistance, caused by the crosslinking finishing, is a serious problem in wash-and-wear finishing of cotton fabrics.

When intermolecular crosslinkings are given to cotton cellulose chains in amorphous region, the mobility of molecular segments is so greatly restricted that decrease of tensile strength may be caused. Therefore, if the degree of crystallinity is decreased or the accessibility is increased, the tensile stress is distributed more uniformly and decrease of tensile strength of cotton by crosslinking may be minimized (1).

EXPERIMENTAL

Sample. Scoured and bleached 40's cotton fabric (plain weave) supplied by Toyo Spinning Co. was used.

Treatment with Alkali. Sample fabrics were immersed in 5.4 N aqueous solution of sodium hydroxide for 30 min at 15°C without tension. Then after being squeezed to about 100% pick up, they were washed with water, immersed in 0.2% acetic acid, washed again with water and air dried.

Treatment with Alkali and Acrylonitrile. Sample fabrics were immersed in 5.4N aqueous sodium hydroxide solutions for 30 min at 15°C. After being squeezed to about 100% wet pick up, they were immersed in acrylonitrile at 20°C,

squeezed to about 100% wet pick up, immersed in 0.2% acetic acid, washed with water, and air dried. Fabrics were treated without tension.

Moisture Regain. After vacuum-drying for 3 hr at room temperature, sample fabrics were conditioned at 20°C and 65% R.H. until a constant weight was reached, and weighed. Then, the samples were weighed after drying for 24 hr at 40°C in high vacuum. The moisture regain was calculated from the weights before and after drying.

Resin Treatment. Dimethylol ethyleneurea (DMEU) (Sumitex Resin 901) and trimethylolmelamine (TMM)(Sumitex Resin M3) were used as crosslinking agents and Sumitex Accelerator KX and ACX were used as catalysts. Sample fabrics were padded with the solution of resin and catalyst, to 80% wet pick up. Drying and curing were performed at 80°C for 30 min and 150°C for 5 min, respectively. After curing, the fabric samples were immersed in 0.3% solution of soap at 50°C, then rinsed with water at 50°C, and dried.

Resin Add-on. The add-on of crosslinking agent is determined as follows. The resin-treated sample dried at 40°C in high vacuum was weighed (W_0), then immersed in an aqueous solution containing 0.25% 'Maruseru' soap and 0.25% anhydrous sodium carbonate for 5 min at 90°C, rinsed throughly in hot water, dried at 40°C in high vacuum, and weighed (W_1). The sample was next immersed in 0.25% hydro-

chloric acid for 60 min at 90°C, rinsed throughly in hot
water, dried at 40°C in high vacuum, and weighed (W_2).
Resin add-on was calculated from the following formulae:

$$\text{Unfixed resin (\%)} = \frac{W_0 - W_1}{W_2} \times 100$$

$$\text{Fixed resin (\%)} = \frac{W_1 - W_2}{W_2} \times 100$$

Total resin add-on (%) = Unfixed resin (%) + Fixed resin (%)

Tensile Properties of Warp Yarns.   Tensile strength and
elongation of the warp yarns taken from fabrics were
measured by a Tensilon UTM Type III. Specimen length was
30 mm. The extension speed was 10 mm/min.

Crease Recovery.   The crease recovery of fabric (4 cm x
1 cm: the longer dimension was along the warp direction)
was measured using a Monsanto type tester. 500g weight was
applied for 5 min and the crease angle ($\alpha°$) was measured
at 5 min after unloading. Crease recovery was calculated
by the following formula.

$$\text{Crease recovery (\%)} = \frac{\alpha}{180} \times 100$$

Abrasion Resistance.   Flex- and edge-abrasion resistances
were measured with a custom type fabric abrasion tester.

RESULTS AND DISCUSSION

The physical properties of cotton fabrics treated with
alkali and acrylonitrile are shown in Tables I and II.
Table II includes the results on the resin-treated fabrics.

The cotton fabrics decrystallized by the alkali-acrylo-
nitrile treatment give no change in tensile strength of
warp yarn, but exhibit an increase in elongation. It is
notable that abrasion resistance of fabrics is increased
in order of decrystallized > mercerized > untreated, though
the mercerized or decrystallized fabric is somewhat thicker
than original fabric. This improvement of abrasion resist-
ance of the decrystallized cotton fabric may be advantageous
in reducing the decrease in abrasion resistance by cross-
linking.

Kullmann et al. (2) examined the effects of the cross-
linking with DMEU on several modified cotton fabrics, such
as carboxymethylated, carboxyethylated, hydroxyethylated
and methylated cottons. The treating solution used by them
contained 8% DMEU, 0.5% zinc nitrate hexahydrate, and 0.05%
acetic acid. For cyanoethylation of cottons, Kullmann et
al. used 2 % sodium hydroxide and reacted with acrylonitrile
at 55-60°C.

In this experiment, cotton fabrics were impregnated
with 5.4N NaOH soution and immersed into acrylonitrile at

TABLE I

Physical Properties of Decrystallized Cotton

| Sample | Thickness mm | Warp Tensile Properties | | Abrasion Resistance, cycle | |
		Strength, g	Elongation %	Flex-	Edge-
Original cotton	0.228	267	6.5	688	1289
Mercerized cotton[a]	0.282	265	8.7	736	1763
Decrystallized cotton[b]	0.315	260	9.3	792	2937

a   Immersed in 5.4N NaOH for 30 min at 15°C.
b   Immersed in 5.4N NaOH for 30 min at 15°C and treated with acrylonitrile for
    30 min at 20°C. Degree of cyanoethylation, 3.8-4.6 mole%.

20°C. As shown in Table II, the crosslinking treatment was applied to the fabrics with various degrees of cyanoethyl-ation, i.e., 1.9, 5.6 and 9.4 mole%. The treating solution included 10% DMEU and 15% KX.

The dry crease recovery of the cotton fabric treated with alkali-acrylonitrile without further crosslinking is lower than that of the untreated or mercerized fabric. Contrary, the wet crease recovery value is increased by decrystallization. As shown in Table II, the dry crease recovery value of the crosslinked fabric decreases and the wet value increases as the cyanoethylation proceeds. As the degree of substitution increases, the tensile strength seems to decrease, but the elongation does not change significantly and the moisture regain increases. The increased accessibility may be due to disruption of the hydrogen bonds. The presence of the cyanoethyl groups prevents reformation of hydrogen bonds on drying, which can occur to some extent with mercerized cotton.

The influence of drying after the alkali-acrylonitrile treatment on the resin finishing was examined. The fabrics treated with alkali-acrylonitrile were preserved in water until the resin treatment. It was expected that both wet crease recovery and resin add-on would increase. But the results shown in Table II were not in accord with this expectation.

TABLE II

Properties of Resin-Treated Cotton Fabrics[a]

Sample	Shrinkage % Warp×Filling	Crease Recovery % Dry	Wet	Resin Add-on %	Fixed Resin %	Tensile Properties Strength g	Elongation %	Moisture Regain %
No Resin								
Control	—	39	37	—	—	267	6.5	7.8
Mercerized[b]	17×5	39	50	—	—	265	8.7	11.1
Decrystallized[c] CN-3.9 mole%	27×12	22	56	—	—	260	9.3	12.1
Resin treatment (10% DMEU)[a]								
Mercerized[b]	22×7	71	70	5.8	5.8	116	5.0	8.5
Decrystallized[c] CN-1.9 mole%	24×6	73	82	6.0	5.8	105	6.3	10.0
5.6 mole%	28×9	64	75	6.9	6.8	79	6.5	10.7
9.4 mole%	35×13	64	86	7.3	6.5	80	7.1	10.8
Mercerized[d]	22×5	74	74	7.3	7.3	104	9.5	8.3
Decrystallized[d] CN-1.9 mole%	24×5	66	69	5.9	5.8	93	4.9	9.5
5.6 mole%	29×10	63	81	6.5	6.2	90	4.8	10.1
9.4 mole%	33×12	56	82	6.6	6.2	78	5.8	11.1

a Catalyst; Sumitex accelerator KX 15%.   All treatment is in slack state.
b Immersed in 5.4N NaOH for 30 min at 15°C.
c Immersed in 5.4N NaOH for 30 min at 15°C and treated with acrylonitrile at 20°C.
d Not dried before resin treatment.

Moisture regain of the decrystallized cotton fabrics
is higher than original and mercerized fabrics as shown in
chapters 2 and 3 and also in Table II. They retain high
moisture regain as shown in Table II even after crosslinking.

Resin add-on is altered using the treating solution
containing 5, 10 and 17% DMEU, and the results are shown
in Table III. The decrystallized cotton fabrics give lower
dry crease recovery than original and mercerized cotton
at the same resin add-on.

But wet crease recovery of the decrystallized cotton
fabrics are nearly equal to those of original cotton.

The minimum crease recovery required for good tumble-
dry wash-wear behavior was reported to be 70% (3). DMEU
solution of 7-8% is required for the decrystallized cotton
fabric to obtain dry crease recovery of 70%.

At the same resin add-on, the tensile strength of the
warp yarn of original cotton fabric is higher than
mercerized or decrystallized cotton. On the other hand, the
elongation increases in the following order:
decrystallized cotton > mercerized cotton > original cotton.

Properties of the resin-treated cotton fabrics having
the same degree of dry crease recovery are shown in Table
IV. To compensate the disruption of bonds due to decrystal-
lization, higher resin add-on was required to obtain the
same degree of crease recovery as original cotton. Larger

TABLE III

Cross-linking of NaOH-AN Treated Fabrics with Various Concentration of DMEU

Sample Pre-Treatment	DMEU, %	Shrinkage % W×F	Crease Recovery % Dry	Wet	Resin Add-on %	Fixed Resin %	Tensile Properties Strength g	Elongation %	Moisture Regain %
Control	No	—	39	37	—	—	267	6.5	7.8
Mercerized[a]	resin	17×5	39	50	—	—	265	8.7	11.1
Decrystallized[c] CN-3.9 mole%		27×12	22	56	—	—	260	9.3	12.1
Control	5	2×-5	76	75	—	3.4	163	3.3	6.3
Mercerized[a]		16×1	75	68	—	3.0	142	5.4	9.3
Mercerized[b]		16×1	63	69	—	3.4	143	5.3	9.9
Decrystallized[c]		18×2	57	79	—	4.1	133	7.2	11.4
Control	10	3×-4	83	80	6.8	6.2	136	2.5	5.4
Mercerized[a]		15×2	77	68	5.5	5.5	102	4.9	8.3
Mercerized[b]		15×2	77	75	6.3	6.2	99	4.7	8.7
Decrystallized[c]		26×12	67	82	6.9	6.5	94	7.6	9.8
Control	17	1×-5	91	85	15.1	13.8	124	2.3	5.2
Mercerized[a]		15×2	89	79	10.9	10.3	78	4.3	7.2
Mercerized[b]		15×2	80	79	11.0	10.3	81	4.9	7.8
Decrystallized[c]		18×2	84	81	12.1	11.5	73	7.5	9.4

a Immersed in 5.4N NaOH for 30 min at 15°C.
b Not dried before resin treatment.
c Immersed in 5.4N NaOH for 30 min at 15°C and treated with acrylonitrile at 20°C. Degree of cyanoethylation is 5-6 mole%.

TABLE IV

Properties of Resin-Treated Cotton Fabrics
Having Same Degree of Dry Crease Recovery

Sample		Crease Recovery %		Resin Add-on %	Fixed Resin %	Tensile Properties		Moisture Regain %
Pre-Treatment	DMEU,%	Dry	Wet			Strength g	Elongation %	
Untreated	10	82	77	8.3	6.9	142	2.5	5.3
Mercerized[a]	17	89	79	10.9	10.3	78	4.3	7.2
Decrystallized[b]	17	84	81	12.1	11.5	73	7.5	9.4
Untreated	5	76	75	3.4	3.4	163	3.3	6.3
Mercerized[a]	10	77	68	5.5	5.5	102	4.9	8.3
Decrystallized[b]	10	67	82	6.9	6.5	94	7.6	9.8

a   Immersed in 5.4N NaOH for 30 min at 15°C.
b   Immersed in 5.4N NaOH for 30 min at 15°C and treated with acrylonitrile
    for 30 min at 20°C. Degree of cyanoethylation, 5-6 mole%.

loss in the tensile strength was caused, but the elongation remained at high value. If the decrystallized fabric is stretched and the resin treatment is applied, then the decrease in tensile strength may be reduced.

The crosslinking with DMEU solution for alkali-acrylonitrile treated cotton in slack state did not improve the tensile strength. As pointed out by Kullamann et al. (2), the effect of substitution of hydroxyl groups of cellulose on the reactivity toward DMEU may be dependent on the nature of the substituent and the swellability of the etherified fiber. In other words, if the substituent is inert to DMEU, the reactivity toward DMEU decreases. Besides, the efficiency of crosslinking may be decreased by the distended cellulose structure. The most reactive site on cellulose molecule is first occupied with substituent group. When the decrystallization and crosslinking treatment is performed, it is desirable to take into account these circumstances.

The crosslinking treatment for the NaOH-acrylonitrile treated fabrics was also carried out using 10% TMM and Sumitex Accelerator ACX. The results were compared with those for samples treated with 10% DMEU in Table V. For the crosslinked samples with TMM, the crease recovery and the loss in tensile strength are smaller, and the elongation and moisture regain are higher than those with DMEU.

TABLE V

Cross-linking of NaOH-AN Treated Fabrics with DMEU and TMM

Sample		Crease Recovery %		Resin Add-on %	Fixed Resin %	Tensile Properties		Moisture Regain %
Pre-Treatment	Resin	Dry	Wet			Strength g	Elongation %	
Untreated	No Resin	39	37	—	—	267	6.5	7.8
Mercerized[a]		39	50	—	—	265	8.7	11.1
Decrystallized[c] CN-3.9 mole%		22	56	—	—	260	9.3	12.1
Mercerized[a]	TMM[d] 10%	66	63	5.7	5.2	183	5.7	8.6
Mercerized[b]		57	61	6.5	6.0	168	5.1	9.0
Decrystallized[c] CN-1.9 mole%		47	70	6.2	5.8	178	5.9	10.2
CN-5.6 mole%		47	73	6.9	5.9	173	6.3	11.1
Untreated	DMEU[e] 10%	83	80	6.8	6.2	136	2.5	5.4
Mercerized[a]		77	68	5.5	5.5	102	4.9	8.3
Mercerized[b]		77	75	6.3	6.2	99	4.7	8.7
Decrystallized[c] CN-5.0 mole%		67	82	6.9	6.5	94	7.6	9.8

a   Immersed in 5.4N NaOH for 30 min at 15°C.
b   Not dried before resin treatment.
c   Immersed in 5.4N NaOH for 30 min at 15°C and treated with acrylonitrile at 20°C.
d   Catalyst; ACX 10%.
e   Catalyst; KX 15%.

Finally the cotton fabrics treated with DMEU were subjected to alkali-acrylonitrile treatment. Results obtained are shown in Table VI.

Plotz (4) reported that, when the cotton fabrics applied with a crease-resistant finish were subjected to the prolonged contact with 20% sodium hydroxide solution, the dry crease recovery and the water resistance imparted by the finish disappeared almost completely, whereas the wet crease recovery was hardly affected by this treatment.

As shown in Table VI, a large loss in dry crease recovery of the fabrics treated with 10% DMEU is caused by the treatment with alkali-acrylonitrile. Tensile strength and elongation of the crosslinked fabrics are increased by the alkali-acrylonitrile treatment. In addition, the moisture regain increases to a value higher than 10%. In the case of 17% DMEU solution, the influence of NaOH-acrylonitrile treatment on the resin treated cotton fabrics is less than that with 10% DMEU solution. But the tensile strength, elongation and moisture regain of treated fabrics are larger than those of the crosslinked control fabric. The tensile stress distribution suppressed by the rigid and brittle joints introduced by crosslinking agents is relaxed by the NaOH-acrylonitrile treatment. This leads to a more flexible structure and to restoration of tensile strength.

TABLE VI

Influence of NaOH-AN Treatment on Resin-Treated Cotton Fabrics

| Sample | | Crease Recovery % | | Resin Add-on % | Fixed Resin % | Tensile Properties | | Moisture Regain % |
Resin Treatment	NaOH-AN Treatment[a]	Dry	Wet			Strength g	Elongation %	
No Resin	—	39	37	—	—	267	6.5	7.8
	NaOH 30 min	39	50	—	—	265	8.7	11.1
	NaOH 30 min AN 30 min	22	56	—	—	260	9.3	12.1
DMEU 10%	—	82	77	8.3	6.9	142	2.5	5.3
	NaOH 15 min	76	74	8.1	5.7	152	4.4	6.3
	NaOH 30 min	54	59	7.9	4.7	191	4.3	7.2
	NaOH 15 min AN 30 min	60	63	8.9	8.5	191	6.3	9.8
	NaOH 30 min AN 30 min	48	60	9.3	8.8	161	6.2	11.8
DMEU 17%	—	86	83	14.0	11.4	137	2.3	5.2
	NaOH 15 min	79	85	13.4	11.2	144	2.4	5.0
	NaOH 30 min	81	79	11.9	9.9	143	2.2	5.0
	NaOH 15 min AN 30 min	72	70	12.6	10.1	158	3.2	7.7
	NaOH 30 min AN 30 min	63	70	12.8	9.5	164	3.8	7.9

a Immersed in 5.4N NaOH at 15°C and treated with acrylonitrile at 20°C.

As shown above, the decrystallization by the NaOH-acrylonitrile treatment did not contribute to the prevention of the decrease of tensile strength of cotton by cross-linking, though it increased the abrasion resistance of cotton fabrics. It is noted that the decrystallized cotton fabrics showed a low dry crease recovery, though its wet crease recovery was increased. The decrystallized cotton fabrics showed considerably higher stiffness than untreated or mercerized cotton fabric. It is presumed that this high stiffness of decrystallized cotton fabrics causes a decrease in the dry crease recovery. Relating to this problem, it seems interesting that a possibility was found to obtain high accessible cotton fabrics which retained the softness of original cotton fabric by treating with NaOH and acrylo-nitrile in the presence of ethanol as described in chapter 5.

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Chapter 8

Summary

In this dissertation, the methods of swelling and decrystallization of cellulose samples, and the structural change and the properties of treated cellulose samples were investigated.

As cellulose samples, native cotton, and regenerated cellulose, such as polynosic and cuprammonium rayon fibers, were used.

The principle of this method was to impregnate cotton with swelling agents, such as alkali metal hydroxides, and then to react it with acrylonitrile. In this reaction, a small quantity of cyanoethyl residues was introduced onto cellulose chains in the amorphous regions. The introduction was promoted by alkaline swelling. This procedure is called "alkali and acrylonitrile treatment" hereafter.

In chapter 1, the historical background and the object of this dissertation were described. The content of each chapter was also summarized.

In chapter 2, the effect of the swelling agents was examined to obtain highly accessible cotton fabric by alkali and acrylonitrile treatment. Swelling agents, such as

lithium hydroxide, sodium hydroxide, potassium hydroxide, ethylamine, triethylamine, ethylenediamine, piperazine, benzyltrimethylammonium hydroxide (BTMOH), urea, dimethyl sulfoxide, dimethylformamide, zinc chloride, and liquid ammonia, were examined. In cyanoethylation alkali metal hydroxides were needed as catalysts, so each swelling agent described above was combined with sodium hydroxide. Cotton fabrics pretreated with ethylenediamine and BTMOH had as high moisture regain as cotton fabrics pretreated with alkali metal hydroxides (*ca.* 11%). So the sodium hydroxide-acrylonitrile treatment, potassium hydroxide-acrylonitrile treatment, ethylenediamine-sodium hydroxide-acrylonitrile treatment, and BTMOH-sodium hydroxide-acrylonitrile treatment were examined in detail. It seemed that these treated cottons had similar effect in making the cotton highly accessible. It was observed that the moisture regain of treated cotton increased by acrylonitrile treatment compared with single treatment with swelling agents. These modified cottons gave moisture regain as high as 14%. The moisture regain of various swelling agents before acrylonitrile treatment was 8.2-11.7 %. In such cases maximum values of moisture regain were observed at the degrees of cyanoethylation of 5-8 mole%.

The influence of various swelling agents on moisture regain of treated cotton fabric was not so sensitive as

was to be expected. For example, BTMOH has a powerful swelling ability for cellulose. It was expected that BTMOH-NaOH-acrylonitrile treatment might give effective result, but any significant effect was not obtained as compared with NaOH-acrylonitrile treatment. Swelling behavior might be influenced by the fabric construction. In this connection, the cotton fibers were treated with alkali-acrylonitrile in chapter 4. But from the standpoint of chemical modification of cotton, the treatment in fabric form is important. It is interesting that highly accessible cotton could be obtained by introducing a small quantity of cyanoethyl residues with respect to post-treatment such as intermolecular crosslinking and graft polymerization.

The density of such treated cotton decreased with an increase of cyanoethylation. This behavior is attributable to the decrystallization and cyanoethyl residues itself.

In chapter 3, the crystalline structure of decrystallized cotton, prepared by partial cyanoethylation with use of sodium hydroxide aqueous solution and acrylonitrile was examined by x-ray and infrared spectra in connection with such fabric properties as moisture regain. The most practical method was chosen among methods described in chapter 2. It was found that the increase of moisture regain in the region of the lower degree of cyanoethylation was well related to the decrease in the crystallinity of cotton.

The infrared absorption ratio, $a_{1372}cm^{-1}/a_{2900}cm^{-1}$ had a linear relation with the crystallinity obtained by x-ray analysis.

The swelling and decrystallization of cotton were investigated by many workers as described in chapter 1. But their discussion was only qualitative. In this chapter, the structure of cellulose of various degrees of cyanoethylation (1.05-15.5 mole%) was examined by x-ray analysis. With increasing cyanoethyl residues, broadening of x-ray profile was observed. But x-ray profile could be resolved into six Gaussian curves, (101), (10$\bar{1}$) and (002) of cellulose I, and (101), (10$\bar{1}$) and (002) of cellulose II. Thus, the influence of cyanoethyl residue on crystalline structure of treated cotton was clarified.

The intensities of cellulose I peaks decreased rapidly, on the other hand intensities of the (002) plane decreased less rapidly as the substitution increased.

From the peaks of the resolved curves, lattice spacings, dimension and cross-sectional area of unit cell were determined with respect to the cellulose II structure. The lattice spacing of (101) plane of cellulose II increased with increasing cyanoethyl content [7.37-8.00 A at 1.05-15.5 mole%], while those of the (10$\bar{1}$) and (002) planes nearly unchanged [4.46-4.47 A for the (10$\bar{1}$) and 4.06-4.13 A for the (002)]. With increasing cyanoethyl content, a and

c of the unit cell increased [8.17-8.71 A for a and 9.18-9.68 A for c], while b remained constant [10.34 A] and β decreased [62.2-58.4°]. Integral breadths of the (101) and (002) reflections increased as the cyanoethylation proceeded [1.90-3.07° for (101) and 2.36-3.17° for (002)], while that of the (101) reflection nearly unchanged [1.91-2.17° at 1.05-15.5 mole%].

From these data, it was suggested that the distension and disorder of the unit cell arise primarily in the direction perpendicular to the (101) crystal plane with increasing cyanoethyl content.

In chapter 4, the crystalline structure and the moisture regain of cotton fibers by alkali-acrylonitrile treatment were examined in comparison with results on the cotton fabrics. Cotton was treated by the same conditions as described in chapter 3; i.e., immersed in 5.4N NaOH aqueous solution for 30 min at 15°C and then treated with acrylonitrile at 20°C (method 1). The moisture regain of treated cotton in fiber form was nearly equal to that of treated cotton in fabric form.

X-Ray equatorial scannings showed that if the cotton fibers were treated only with the alkali solution (mercerized cotton), presence of the crystalline form of cellulose I was detected in addition to that of cellulose II, but the crystalline form of the alkali-acrylonitrile treated fibers

was fully that of cellulose II. But lattice spacing of (101) plane of cellulose II for fibers was less increased compared with that of fabric. Integral breadth of the (101) reflection increased as the cyanoethylaton proceeded, while those of the (10$\bar{1}$) and (002) reflections stayed nearly unchanged. The change of x-ray profile of cotton fiber was somewhat smaller than that of cotton fabric. The reaction rate for the fibers was greater than that for the fabrics. So the cyanoethylation might be taken place mainly on fiber surface and the distribution of cyanoethyl group might be nonuniform.

In order to delay the reaction of cyanoethylation while keeping the swollen state, alkali-acrylonitrile treatment was carried out at a lower temperature. Furthermore it was expected that time of immersing in alkali solution could affect the decrystallization. Taking into account these facts, cotton immersed in 5.4N NaOH for 60 min at -5°C was treated with acrylonitrile at 0°C (method 2). The moisture regain of cotton fibers with sodium hydroxide pretreatment for 60 min at -5°C was greater than that of cotton fibers for 30 min at 15°C [13.0% vs. 11.4%]. The change of crystalline structure of cotton fibers prepared by method 2 was greater than that of cotton fibers prepared by method 1. In the case of fabric, however, marked difference was not observed in moisture regain and crystalline

-168-

structure between methods 1 and 2. Influence of alkali-pretreatment was not so sensitive as the case of fibers on account of fabric construction.

In chapter 5, cotton was cyanoethylated after pretreatment with 5.4N NaOH in a mixture of ethanol and water, and the structure of cotton thus obtained was examined in comparison with the results on the cyanoethylation with 5.4N NaOH aqueous solution. X-Ray pattern of cotton treated with 5.4N NaOH in a mixture of ethanol and water (volume ratio 30:70) was quite different from that of cotton treated with 5.4N NaOH aqueous solution. Complete mercerization was obtained when treated with 5.4N NaOH aqueous solution for 60 min at -5°C. Whereas, some cellulose I content and broadening of x-ray profile were observed when treated with alcoholic 5.4N NaOH for 60 min at -5°C. X-Ray analysis revealed that cumulative intensity of the ($10\bar{1}$) interference was much weaker than that of the (002) interference when cotton treated with 5.4N NaOH in a mixture of ethanol and water, while those of the ($10\bar{1}$) and (002) interferences were about the same when treated with 5.4N NaOH aqueous solution. Moreover, integral breadths of the ($10\bar{1}$) and (002) planes of cotton treated with alcoholic sodium hydroxide were greater than those of cotton treated with sodium hydroxide solution. With respect to NaOH-water system, integral breadth of (101) plane of cellulose II increased with

increasing the cyanoethyl content, while those of (10$\bar{1}$) and (002) planes stayed nearly unchanged. On the other hand, with respect to NaOH-alcohol-water system, integral breadths of (10$\bar{1}$) and (002) planes as well as that of (101) plane increased as the cyanoethylation proceeded. The memory of cellulose I structure was pronounced by adding alcohol to 5.4N sodium hydroxide. For example, the intensity of (002) plane was stronger than that of (10$\bar{1}$) plane in the region of the lower degree of cyanoethylation.

To clarify the difference between alkali treated cotton and alkali-acrylonitrile treated cotton, these treated cotton fibers were boiled in water for 3 hr. Each intensity of cellulose I and II interferences increased for samples only pretreated with NaOH-ethanol-water after boiling in water. Whereas, diffraction of cellulose I disappeared at a few degree of cyanoethylation and as the cyanoethylation proceeded the recrystallization was prevented after boiling in water.

When the cyanoethylation with 5.4N NaOH in a mixture of ethanol and water (volume ratio 30:70) was applied to cotton fabric as well as fibers, the same tendency in the structural change was observed except that strong peaks of (101), (10$\bar{1}$) and (002) diffractions of cellulose I remained. After cyanoethylation with NaOH-ethanol-water system, it was necessary to immerse the treated cotton in 1% acetic

acid in a mixture of ethanol and water. Because after cyanoethylation, cotton immersed in 1% acetic acid aqueous solution swelled to a great extent and partially disappeared fibrous form. Cotton fabric treated with alcoholic system retained the softness and the value of dry crease recovery of original cotton fabric, while cotton fabric treated with NaOH aqueous solution system had high stiffness and low crease recovery. Cyanoethylated cotton with NaOH-ethanol-water system gave no change in tensile stength of warp yarn, but exhibited an increase in elongation and had high moisture regain.

In chapter 6, regenerated celluloses such as polynosic and cuprammonium rayon were cyanoethylated after pretreatment with 5.4N NaOH in a mixture of ethanol and water (volume ratio 30:70) and crystalline structure thus obtained was investigated. Fine structure of regenerated cellulose is quite different from that of native cellulose. So different behavior was expected on alkali-acrylonitrile treatment.

As regenerated cellulose was dissolved in 5.4N NaOH aqueous solution, it was necessary to add ethanol to 5.4N NaOH aqueous solution. As moisture regain of original regenerated cellulose was higher than that of cotton, the moisture regain of cyanoethylated cellulose was high [17.5% at 14.7 mole%]. But the rate of reaction in the region of

the lower degree of cyanoethylation of regenerated cellulose was nearly equal to that of cotton. Moreover the influence of cyanoethyl residue on the crystalline structure of regenerated cellulose seemed to be identical with that of cotton described in chapter 5. However, regenerated cellulose is cellulose II, so intensity of ($10\bar{1}$) plane is stronger than that of (002) plane. The difference in crystalline structure between regenerated cellulose and cotton was clarified by boiling in water.

In chapter 7, cotton fabrics with or without cross-linking were treated with acrylonitrile after impregnation with 5.4N aqueous sodium hydroxide solution and some physical properties of the treated cotton fabrics were examined. The cotton fabrics decrystallized by the alkali-acrylonitrile treatment gave no change in tensile strength of warp yarn, but exhibited an increase in elongation. The abrasion resistance of cotton fabrics was increased by the treatment and fairly high moisture regain was obtained. However, the dry crease recovery of the cotton fabric treated with alkali-acrylonitrile was lower than that of the untreated or mercerized fabric. Crosslinking was given to cotton fabrics after the decrystallization process, using conventional crosslinking agents. Dimethylol ethyleneurea and trimethylolmelamine were used as crosslinking agents. Higher resin add-on was required to obtain the same degree

of crease recovery as original cotton.

Cotton fabrics treated with DMEU were subjected to
alkali-acrylonitrile treatment. A small loss in dry crease
recovery of the fabrics treated with 17% DMEU was caused by
the treatment with alkali-acrylonitrile. But the tensile
strength, elongation and moisture regain of treated fabric
were increased by the alkali-acrylonitrile treatment.

List of Publications

[1] "Highly Accessible or Decrystallized Cotton by Chemical Methods", J. Appl. Polym. Sci., 20, 2837 (1976). (presented in Chapter 2).

[2] "Structure of Decrystallized Cotton in Fabrics Prepared by Alkali and Acrylonitrile Treatments", J. Appl. Polym. Sci., 20,   (1976). (presented in Chapter 3).

[3] "Structure of Decrystallized Cotton Prepared in Fiber Form by Alkali and Acrylonitrile Treatments", Sen-i Gakkaishi, submitted. (presented in Chapter 4).

[4] "Crystalline Structure of Polynosic, Cuprammonium Rayon and Cotton Fibers Treated with Alkali and Acrylonitrile", Preprint of the Annual Meeting of the Society of Fiber Science and Technology, Japan (June 18, 1976). (presented in Chapters 5 and 6).

[5] "Effect of Ethanol on Alkali and Acrylonitrile Treatments for Cellulose Fibers", Preprint of the Semi-Annual Meeting of the Society of Fiber Science and Technology,

Japan (November 19, 1976). (presented in Chapters 5
and 6).

[6] "Properties of Decrystallized Cotton Prepared by Alkali-
Acrylonitrile Treatment", Sen-i Gakkaishi, submitted.
(presented in Chapter 7).

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