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Highly Accessible or Decrystallized Cotton by Chemical Methods

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Synopsis

To obtain highly accessible cotton by cyanoethylation with acrylonitrile after pretreatment with swelling agents, the effect of various swelling agents was examined. 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. It was found that the sodium hydroxide pretreatment or the dual pretreatment with either potassium hydroxide, ethylenediamine, or BTMOH, and sodium hydroxide prior to acrylonitrile treatment gave modified cottons having moisture regain as high as 14%. In such cases, maximum values of moisture regain were observed at the degrees of cyanoethylation of 5–8%.

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, recrystallizes 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 cellu-

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lose 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 our present research, more extensive treating conditions are examined using various swelling agents, and the structure and properties of the modified cotton are investigated.

It is expected that the decrystallized or highly accessible cotton may have some advantages relating to the decrease of mechanical strength of cotton fabric by intermolecular crosslinking.[9] The research on the crosslinking of such highly accessible cotton is now in progress.

EXPERIMENTAL

Cotton Cellulose. Scoured and bleached 40's cotton fabrics (plain weave, Toyo Spinning Co.).

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

Treatment with Alkali. Sample fabrics were immersed in an aqueous solution of alkali for 30 min at $-40 \sim 15°C$. Then, after being squeezed to about 100% pickup, 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 $-40 \sim 15°C$. Then, after being squeezed to about 100% pickup, the fabrics were immersed in acrylonitrile for $10 \sim 300$ min at $0 \sim 40°C$., squeezed to about 100% pickup, 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% pickup, 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 500 mg) 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 cyanoethylated OH residues against OH residues of cellulose.

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

Alkali	Normality, N	Moisture regain, %		CN deg.,[d] mole-%
		Alk.[b]	Alk.–AN[c]	
—	—	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.

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 of 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 5.7N for LiOH, NaOH, and KOH, respectively. The effect of the temperature of NaOH pretreatment on the moisture regain was examined by lowering the immersion temperature, but no significant effect was observed, as is shown in Table II. Sodium hydroxide solution, 3N, was used, because it has been reported[10] that cotton shows a maximum degree of swelling at this concentration at 0°C.

Table III shows the results when methanol or ethanol was added to NaOH aqueous solutions. It was anticipated that NaOH might increase the mois-

TABLE II
Effect of Immersion in NaOH Aqueous Solutions at Low Temperature

NaOH treatment			Moisture regain, %		CN deg., mole-%
Normality, 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 Alcohols Added to NaOH Aqueous Solution

	Moisture regain, %		CN deg., mole-%
NaOH solvent[a]	Alk.[b]	Alk.–AN[c]	
—	7.8[d]	—	—
Water	11.0	14.0	7.5
Ethanol–water (30/70 vol.)	—	13.4	5.0
Methanol–water (30/70 vol.)	—	13.4	4.1

[a] Concentration of NaOH is 5.4N.
[b] Alkali treatment.
[c] AN treatment after alkali treatment.
[d] Original cotton fabric.

TABLE IV
Effect of DMSO on Acrylonitrile Treatment[a]

AN treatment				
DMSO/AN vol. ratio	Temp., °C	Time, min	Moisture regain, %	CN deg., mole-%
—	—	—	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.

ture regain by being dissolved in alcohol, but the degree of cyanoethylation of the resulting fabric was somewhat reduced. Such results may be attributed to a side reaction of acrylonitrile with alcohol.

Table IV 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 ac-

TABLE V
Effect of Time and Temperature on Acrylonitrile Treatment

AN treatment[a]			
Temp., °C	Time, min	Moisture regain, %	CN deg., mole-%
—	—	7.8	—
—	—	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 5.4*N* NaOH aqueous solution for 30 min at 15° C.
[b] Original cotton fabric.
[c] Alkali treatment alone.
[d] Pretreated with 5.4*N* NaOH aqueous solution for 30 min at 0° C.

rylonitrile for 60 min, the fabric became yellow and the degree of cyanoethylation did not increase.

Table V shows the effect of time and temperature on acrylonitrile treatments. As shown in Figures 1 and 2 and Table V, 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 effects of the treatment of cotton with various swelling agents were examined. Results obtained are shown in Table VI. 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 employed.

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 5.4*N* NaOH at 15°C for 30 min. The cotton fabrics, after being squeezed to about 100% pickup, were then treated with acrylonitrile at 20°C for 30 min. Results obtained are shown in Table VII. The effect of acrylonitrile treatment in increasing the moisture regain is notable, suggesting 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 treatment might give effective results, but any significant

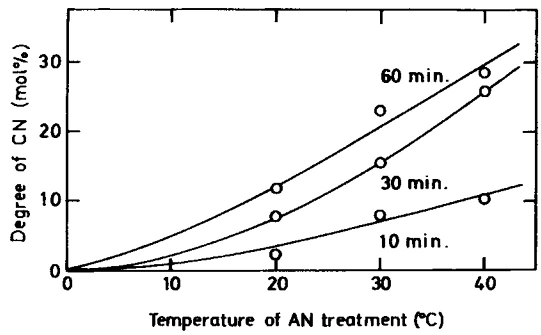

Fig. 1. Relation between degree of cyanoethylation and time and temperature of acrylonitrile treatment.

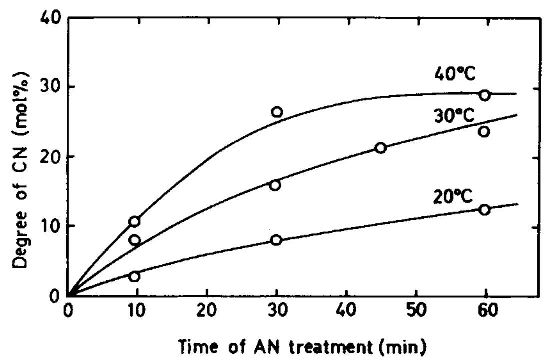

Fig. 2. Relation between degree of cyanoethylation and time and temperature of acrylonitrile treatment.

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

Betrabet et al.[11] 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.[12,13] 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 ob-

TABLE VI
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
	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.

TABLE VII
Dual Pretreatment of Cotton with Various Swelling Agents and NaOH Before Acrylonitrile Treatment

Swelling agent	Concn., %	Temp.,[a] °C	Temp. NaOH,[b] °C	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 5.4*N* 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.

TABLE VIII
Dual Pretreatment of Cotton with BTMOH and NaOH Before Acrylonitrile Treatment

BTMOH				Moisture regain, %			
Concn., %	Temp., °C	Time, min	Washing	BTMOH[a]	BTMOH–NaOH[b]	BTMOH–NaOH–AN[c]	CN deg., mole-%
5.4*N* 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	acetone, water	—	—	13.2	4.3
34.4% BTMOH	20	30	acetone, water	—	—	13.1	4.3
–14% EtOH	20	2100	acetone, water	—	—	13.9	7.5

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

TABLE IX
Dual Pretreatments of Cotton with Liquid Ammonia and NaOH Before Acrylonitrile Treatment

Liq. NH_3 treatment	5.4*N* 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.

served. 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 VIII. 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 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

TABLE X
Moisture Regain of Cotton Fabrics[a] Treated with Acrylonitrile after Pretreatment with NaOH or KOH

AN treatment at 20° C, min	2.2*N* NaOH[c] CN deg., mole-%	2.2*N* NaOH[c] M.R.,[b] %	5.4*N* NaOH[c] CN deg., mole-%	5.4*N* NaOH[c] M.R.,[b] %	8.2*N* NaOH[c] CN deg., mole-%	8.2*N* NaOH[c] M.R.,[b] %
None (NaOH alone)	—	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
	2.2*N* KOH[c]		5.4*N* KOH[c]		8.2*N* KOH[c]	
None (KOH alone)	—	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 XI
Moisture Regain of Cotton Fabrics Treated with Acrylonitrile after Dual Pretreatment with Either BTMOH or Ethylenediamine, and NaOH

AN treatment, min	35% BTMOH[a] CN deg., mole-%	35% BTMOH[a] M.R., %	Ethylenediamine[b] CN deg., mole-%	Ethylenediamine[b] 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 5.4*N* 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 5.4*N* NaOH for 30 min at 15° C, squeezed, and treated with acrylonitrile at 20° C.

fabrics, but did not exceed the value obtained by pretreatment with 5.4*N* NaOH alone.

Recently, Vigo et al.[14] 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%

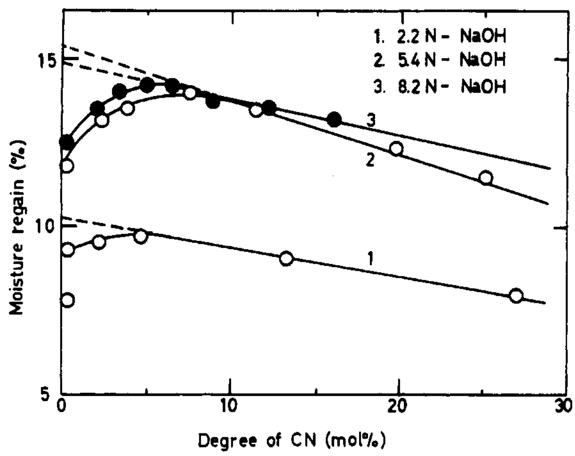

Fig. 3. Relation between moisture regain and degree of cyanoethylation of cotton fabrics treated with acrylonitrile at 20°C for different periods of time after pretreatment with NaOH of different concentrations.

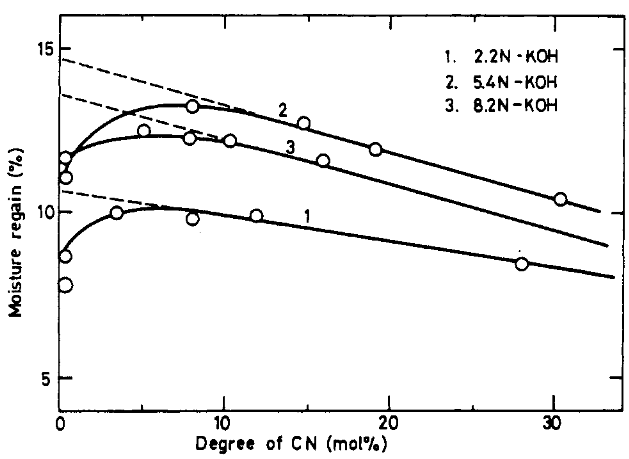

Fig. 4. Relation between moisture regain and degree of cyanoethylation of cotton fabrics treated with acrylonitrile after pretreatment with KOH.

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 5.4*N* NaOH at 15°C for 30 min, followed by treatment with acrylonitrile.

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

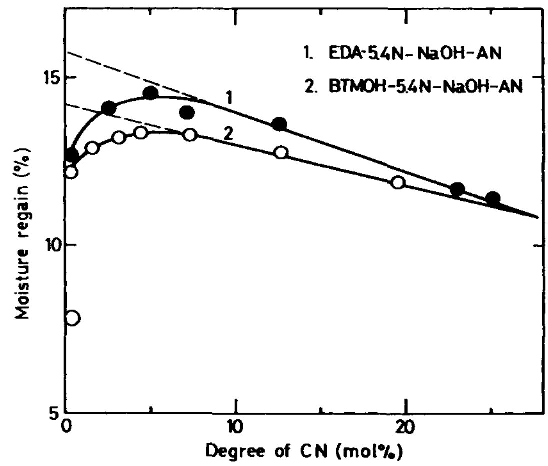

Fig. 5. Relation between moisture regain and degree of cyanoethylation of cotton fabrics treated with acrylonitrile after dual pretreatments with either 35% BTMOH or ethylenediamine and NaOH.

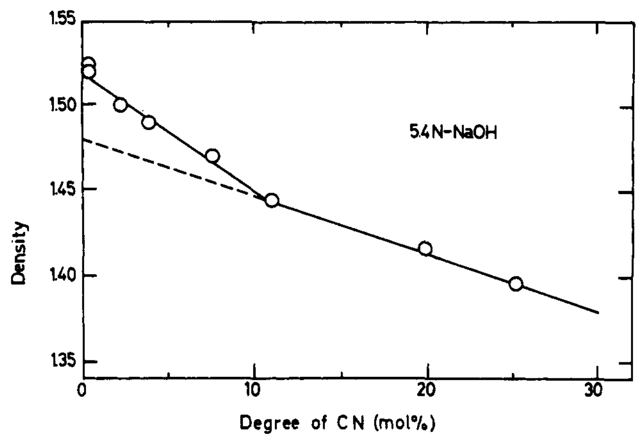

Fig. 6. Relation between density and degree of cyanoethylation of cotton fabrics treated with acrylonitrile at 20°C for different periods of time after pretreatment with 5.4*N* NaOH.

trile without the pretreatment with NaOH, cyanoethylation 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 5.4*N* NaOH. In these treated cotton fabrics of various degrees of cyanoethylation, the moisture regain was measured (Tables X and XI). The relations between the moisture regain and the degree of cyanoethylation are shown in Figures 3, 4, and 5. 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

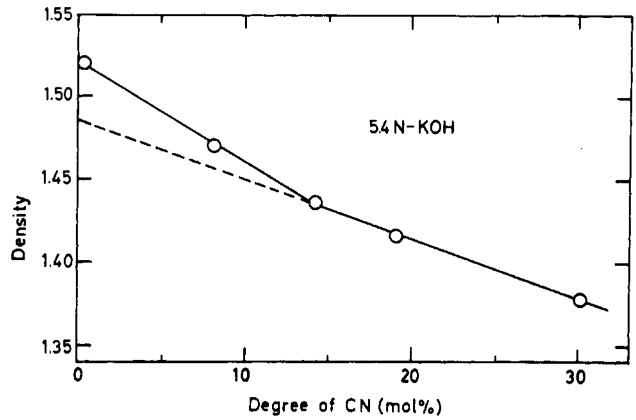

Fig. 7. Relation between density and degree of cyanoethylation of cotton fabrics treated with acrylonitrile after pretreatment with 5.4*N* KOH.

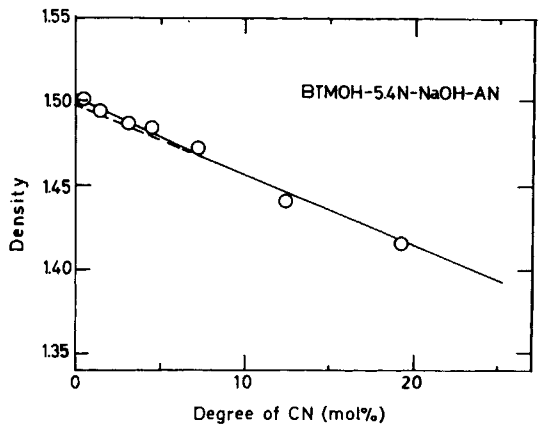

Fig. 8. Relation between density and degree of cyanoethylation of cotton fabrics treated with acrylonitrile after dual pretreatments with 35% BTMOH and 5.4*N* NaOH.

moisture regain occurs as a result of balance of the increase in accessibility and the blocking effect of cyanoethyl residues. It is noted that the straight lines at higher degrees of cyanoethylation 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 presumed to show the values of the treated cottons when the 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 5.4*N* NaOH or KOH and the dual treatment with the 35% BTMOH or ethylenediamine and 5.4*N* 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[15] for the disordered cellulose prepared by regeneration of cellulose derivatives in a nonaqueous medium.

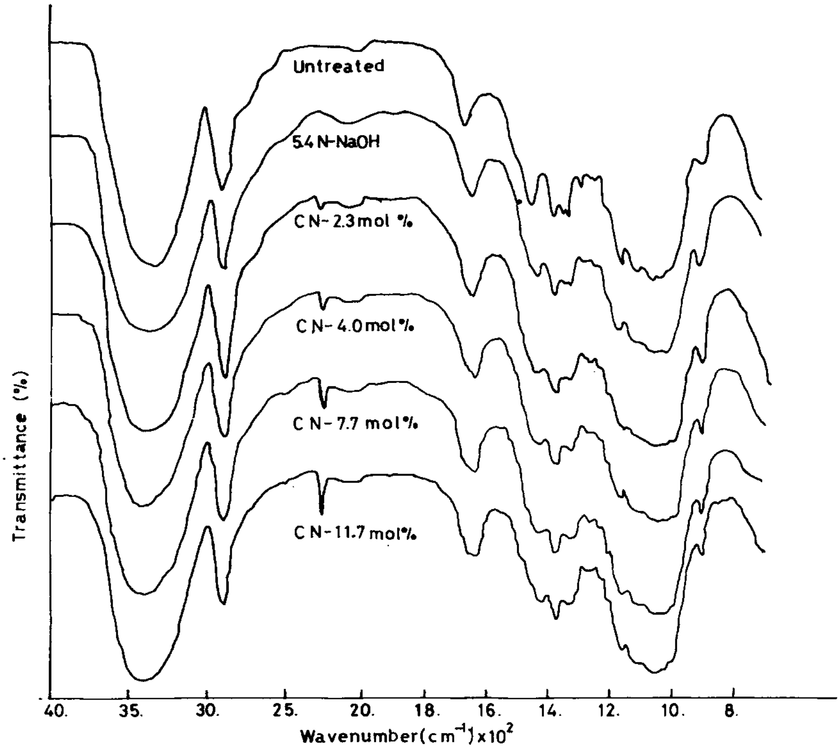

Fig. 9. Infrared spectra of cottons having different degrees of cyanoethylation prepared by treatments with 5.4*N* NaOH and acrylonitrile.

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 cyanoethylation by the ordinary method using 3–5% NaOH will be as low as 4–5%.

Density of Cotton Having Various Degrees of Cyanoethylation

Densities of some samples of the treated cotton described in Tables X and XI were measured. The results obtained are shown in Figures 6, 7, and 8. Each density–cyanoethyl content curve fell into two parts: an initial linear portion followed by a second linear portion. The densities obtained by extrapolating the second linear portion to the ordinate axis are presumed to show the values of treated cottons when the blocking effect of the cyanoethyl residues is eliminated. These values correspond to the potential accessibility described above.

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

Treatment at 15° C, min		CN deg.,	Moisture		Infrared ratio	X-Ray crystallinity index, %	
5.4*N* NaOH	AN, 20° C	mole-%	regain, %	F_{am},[a]	$a_{1372}\text{cm}^{-1}/a_{2900}\text{cm}^{-1}$	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.[17]

[b] $\% \text{ Crystallinity} = \frac{I_{002} - I_{am}}{I_{002}} \times 100.$[18]

[c] Correlation method of Wakelin et al.[19] - 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.

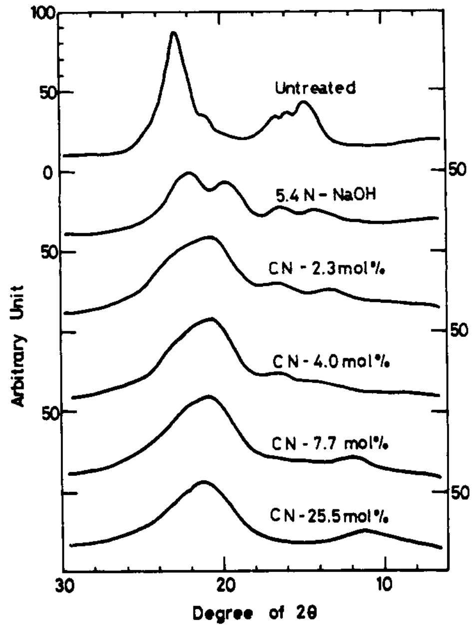

Fig. 10. X-Ray diffractrograms of cottons having various degrees of cyanoethylation prepared by treatments with 5.4*N* NaOH and acrylonitrile.

Preliminary Examination of the Fiber Structure by Infrared Spectra and X-Ray Diffraction

Infrared spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer by the use of the KBr pellet technique (Fig. 9). Fibrous samples were cut into small pieces by a Wiley mill and with scissors before mixing with the KBr.

Evidence for the existence of the cyanoethyl residues introduced onto cellulose molecules by NaOH and acrylonitrile treatment is shown by the C–N stretching band at 2240 cm^{-1} (Fig. 9).

As a measure of the crystallinity, an infrared crystallinity ratio a_{1372} cm^{-1}/a_{2900} cm^{-1} was adopted according to Nelson and O'Connor.[16] Results obtained are shown in Table XII together with the amorphous fraction F_{am} (i.e., accessibility) calculated from the moisture regain by Valentine's relation[17] $F_{am} = S.R./2.60$, where $S.R.$ is the sorption ratio (the ratio of the moisture sorption of the experimental sample to that of the standard cotton at the same relative humidity). In Table XII, x-ray crystallinity indices are also shown, which were calculated graphically from the infrared crystallinity ratios using the linear relation proposed by Nelson and O'Connor.[16]

Finally, x-ray diffractograms of the NaOH and acrylonitrile-treated cottons are shown in Figure 10. Although the fine structure of these modified cotton fibers should be examined in more detail hereafter, the results of the preliminary examination described above show that the crystallinity of cotton fibers can be considerably decreased by these chemical methods.

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