

Chemical Modification of Cotton Fiber by Alkali-Swelling and Substitution Reactions— Acetylation, Cyanoethylation, Benzoylation, and Oleoylation

WAICHIRO TSUJI, TOKIE NAKAO, KYOKO OHIGASHI, KINUYO
MAEGAWA, NORIKO KOBAYASHI, SATOMI SHUKRI, SADAOKO
KASAI and KYOKO MIYANAGA, *Faculty of Home Economics,
Mukogawa Women's University, Ikebiraki-cho, Nishinomiya-shi, Hyogo
Prefecture, Japan 663*

Synopsis

By impregnating cotton fiber with alkaline swelling agents and reacting with some chemical agents which can be substituted for the hydroxyl groups on cellulose molecules in the presence of alkali, highly accessible or decrystallized cotton fibers can be obtained. As the effective substitution reactions, acetylation by acetic anhydride and cyanoethylation by acrylonitrile were applied. The cotton fibers modified by these chemical treatments showed no decrease of tensile strength, and had moisture regain higher than the untreated cotton though the degrees of substitution were as high as 20–30 mol %. The resistance to heat or acid and the soil removal were improved. Dyeability for direct dye was increased, and dyeability for disperse or cationic dye was also given. Benzoylation and oleoylation were also investigated. Crease recovery of the cotton fabrics was somewhat improved and dyeability for disperse dye was given. The cotton fabrics oleoylated after decrystallizing by alkali-acrylonitrile treatment had moisture regain almost the same as the untreated cotton, while high water repellency was given.

INTRODUCTION

To obtain cotton fibers with new properties, we have carried out the researches for about 20 years on the chemical modification of cotton such as acetylation, cyanoethylation, and carboxymethylation.¹ One of them is the decrystallization of cotton or making cotton more accessible.²

The principle of our method of decrystallization is as follows. In the mercerization process cotton fiber is decrystallized when swollen with about 20% NaOH aqueous solution, but is recrystallized to a large extent during water washing and drying. If a small quantity of substituting group is introduced onto cellulose containing NaOH solution, the recrystallization during water washing and drying is remarkably prevented by the presence of the substituting residues. Thus, the permanently decrystallized, highly accessible cotton fibers are to be obtained. The same principle was afterward reported by Kulshreshtha and Dweltz³ using acetylation.

As the substitution reaction, those that substitute OH groups of cellulose molecules in the presence of alkali can be utilized. Hitherto, we have used for this object cyanoethylation,^{2,4,5} acetylation,^{6–8} or carbamoylethylation.^{7,8}

To obtain the decrystallization effect, a rather low degree of substitution (10 mol % or below) is effective. In the case of cyanoethylation the moisture

regain showed maximum value at the degree of substitution of about 8 mol %.⁴ If the degree of substitution is increased further, the specific properties which come from the substitution residue will be more remarkable. As the second stage of our research on the decrystallization of cotton, we intend to obtain cotton fibers which have both higher accessibility and the specific properties that come from the substituted groups. This is the object of this work.

EXPERIMENTAL

Method of Treatments

Cotton Cellulose. Scoured and bleached cotton fabric (plain weave, 126 × 62/in., 40 × 40's, 100 g/m², Unichika Co.) was used. Various treatments were carried out in slack state.

Mercerization. Cotton fabrics were immersed in 20% aqueous solution of NaOH at 20°C for 30 min. After being squeezed to about 100% pick up, they were rinsed with water for 30 min, immersed in 0.5% acetic acid for 30 min, rinsed again with water, and air-dried.

Treatment with Alkali and Acetic Anhydride (Acetylation). Cotton fabrics were immersed into 20% aqueous solution of NaOH at 20°C for 30 min, squeezed and reacted in the mixture of acetic anhydride and acetic acid, benzene, or trichlene at 30–40°C for 15–60 min.

Treatment with Alkali and Acrylonitrile (Cyanoethylation). Cotton fabrics were immersed into aqueous solution of NaOH or KOH, squeezed and reacted in acrylonitrile at 20–50°C for 30–60 min. Then, they were immersed in 0.5% acetic acid for 30 min, rinsed with water for 30 min, and air-dried.

Treatment with Alkali and Benzoylchloride (Benzoylation). Cotton fabrics were immersed into 20% aqueous solution of NaOH at 20°C for 30 min. After being squeezed, they were reacted in 10% benzene solution of benzoylchloride at 20°C for 30–90 min.

Treatment with Oleoylchloride (Oleoylation). Untreated or decrystallized cotton fabric was treated with dimethylformamide (DMF) solution of oleoylchloride at 40–60°C for 240–450 min. The decrystallized cotton fabric was prepared by impregnating cotton fabric with 20% NaOH aqueous solution and treating with acrylonitrile at room temperature (the degree of cyanoethylation was 3.68 mol %).

CHARACTERIZATION OF THE PRODUCTS

Degree of Acetylation. Acetyl contents A (%) were measured by the standard titration method. Then, the degree of substitution and acetylation were calculated by following formulae:

$$\text{degree of substitution DS} = 3.86 \times \frac{A}{1.02 - A}$$

$$\text{degree of acetylation (mol \%)} = \frac{\text{DS}}{3} \times 100$$

where mol % represents the percentage value of the substituted OH residues.

Degree of Cyanoethylation. Nitrogen contents N (%) were estimated by the semimicro Kjeldahl method. The degree of cyanoethylation was calculated using the following formula:

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

Degree of Benzoylation and Oleoylation. The values of the degree of substitution DS were calculated from the dry weights of the fabrics before and after treatment by the following formulae:

$$\text{degree of substitution DS} = \frac{w_1 - w_0}{w_0} \times \frac{162.08}{M_s - 1}$$

where w_0 , w_1 = dry weights of the fabrics before and after treatment (g) and M_s = molecular weight of the substituting group,

$$\text{degree of benzoylation or oleoylation (mol \%)} = \frac{\text{DS}}{3} \times 100$$

Moisture Regain. Sample fabrics were conditioned at 20°C, 65% RH for more than 24 h and weighed. Then, they were dried at 105°C for 1 h and weighed. Values of moisture regain were calculated by the following formula:

$$\text{moisture regain (\%)} = \frac{w_0 - w}{w} \times 100$$

where w_0 , w = weights of the fabrics before and after drying (g).

Density. Yarns taken from the sample fabrics were cut into small pieces and dried for 1 week in a desiccator containing P_2O_5 under vacuum. The densities were then measured by the floating method using a mixture of carbon tetrachloride and xylene.

Tensile Properties. Tensile strength and elongation at break of the warp yarns taken from the sample fabrics were determined using an Instron type tensile tester, Tensilon UTM-II-20.

Crease Recovery. Crease recovery was measured by Monsanto type tester using 1×4 cm test fabric of warp direction. 500 grams load was applied for 5 min, and the crease angle α was determined at 5 min after unloading. Crease recovery was calculated by the following formula:

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

where α = crease angle (deg).

Dyeing Properties. Dyes used and dyeing conditions are as follows:

Direct dye:

dye bath: Sumilight Supra Scarlet BNS concn	3% (to fiber weight)
anhydrous sodium sulfate	10%

anhydrous sodium carbonate	2%
nonionic surfactant Scourol 900	2 g/L
liquor ratio	100:1

Fabrics are immersed in the dye baths at room temperature, which are heated to 90°C during 30 min; then dyeing is continued for 30 min.

Disperse dye:

dye bath: Celliton Fast Red BB Type 8072 or	
Sumikaron Brilliant Blue S-BL	3%
nonionic dispersing agent Brij 35	50 mg/50 cc
liquor ratio	80:1

Fabrics are immersed in the dye baths at room temperature, which are heated to 90°C during about 40 min, and then dyeing is continued for 30 min.

Dye uptake: Values of dye uptake were estimated from the dye concentrations in dye bath before and after dyeing using the following formula:

$$\text{dye uptake (\%)} = \frac{c_1 - c_2}{c_1} \times 100$$

where c_1, c_2 = dye concentrations before and after dyeing. Dye concentrations were determined from the values of light absorption at wave length of maximum absorption measured by the spectrophotometer, Hidachi Type 101.

Color fastness:

Washing: Tests were carried out in a launder-ometer at 40°C for 30 min according to JIS L-0844 A-1 method using 5 g/L aqueous solution of Marseille soap.

Light: Sample fabrics were irradiated with carbon arc for various hours using a weather-ometer without water shower, referring to JIS L-842.

Results of the color fastness tests were expressed by five grade numbers.

Soiling and Soil Removal. Sample fabrics (5 × 5 cm) were conditioned at 65% RH in a desiccator containing aqueous solution of sulfuric acid, and immersed at room temperature for 1 min into the following soiling liquor:

carbon black	0.002 g
beef tallow	0.1 g
liquid paraffin	0.3 g
carbon tetrachloride	80 g

After conditioning in a 65% RH desiccator for 2 weeks, the soiled fabrics were washed with 0.3% aqueous solution of Marseilles soap in a launder-ometer at 40°C for 30 min at 42 rpm. Light reflections of the unsoiled, soiled, and washed fabrics were measured at a 550 nm wave length using a Shimadzu UV-200 Spectrophotometer. Then the degree of soiling and soil removal were calculated using the following formulae:

$$\text{soiling (\%)} = \frac{R_0 - R_s}{R_0} \times 100$$

$$\text{soil removal (\%)} = \frac{R_w - R_s}{R_0 - R_s} \times 100$$

where R_0 , R_s , R_w = reflections of the unsoiled, soiled and washed fabrics at 550 ηm . Test methods of other properties will be described in the appropriate sections.

RESULTS AND DISCUSSION

Treatment with Sodium Hydroxide and Acetic Anhydride (Acetylation)

It has been reported by Sakurada et al.⁹ that alkali cellulose could be acetylated with acetic anhydride. In the present research, cotton fabrics impregnated with 20% aqueous solution of sodium hydroxide were acetylated in the bath containing acetic anhydride and a diluent, such as acetic acid, benzene, or trichlene. The degrees of acetylation of the treated fabrics are shown in Table I. The reaction rates are large in the following order: benzene > trichlene > acetic acid. If NaOH was washed out by water before acetylation, the degrees of acetylation were only 0.5–2 mol %.

Cotton fabrics were then treated in some selected conditions, and the properties of the treated fabrics were estimated. Values of moisture regain, specific gravity, and tensile properties are shown in Table II. Data are also shown in the table for the fabric acetylated by the ordinary fibrous acetylation method (9-2-2), in which cotton fabrics, pretreated with acetic acid,

TABLE I
Chemical Treatment of Cotton Fabrics by the Mixture of Acetic Anhydride and Diluent after being Impregnated with 20% Aqueous Solution of Sodium Hydroxide

Diluent	Acetic anhydride (vol %)	Temp (°C)	Time (min)	Degree of acetylation (mol %)
Acetic acid	90.9	30	60	14.0
			15	23.4
			30	28.6
Benzene	95.2	40	60	26.5
			15	25.2
			30	23.9
Trichlene	90.9	40	60	26.6
			15	18.8
			30	17.9
Trichlene	95.2	40	60	25.7
			15	18.9
			30	22.0
			60	23.3

TABLE II
Some Properties of the Cotton Fabrics Acetylated after Alkali Impregnation^a

Sample no.	Diluent	Acetic anhydride (vol %)	Temp (°C)	Time (min)	Degree of acetylation (mol %)	Density	Moisture regain (%)	Warp tensile	
								Strength (g)	Elongation (%)
0	Untreated	—	—	—	—	1.54	6.0	251	8.1
1	Mercerized ^b	—	22	30	—	—	9.4	247	11.6
2-1-1	Acetic acid	90.9	30	60	14.0	1.47	—	—	—
4-2-3	Benzene	95.2	40	60	27.1	1.48	8.6	265	13.4
5-2-1	Trichlene	90.9	40	15	18.7	1.47	8.8	255	12.7
5-1-2				30	17.9	—	9.0	249	12.9
5-1-3				60	25.7	—	8.0	266	13.4
9-2-2 ^c	Trichlene	15.0	25	30	29.4	1.41	4.4	—	—

^a Immersed in 20% NaOH, and in acetylation bath after squeezing.

^b 20% NaOH.

^c Ordinary fibrous acetylation by sulfoacetic acid.

were acetylated in the mixture of acetic anhydride, trichlene, and acidic catalyst, such as sulfuric acid in the form of sulfoacetic acid ($\text{HOOC}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$), the volume ratio of sulfoacetic acid to trichlene being 15:85.

As shown in Table II, the decrease of density and increase of moisture regain were obtained as a result of these treatments, which suggested decrystallization had occurred. The fabrics having a degree of acetylation as high as 27 mol % showed moisture regain higher than the untreated cotton. On the other hand, the fabric acetylated by the ordinary method without NaOH impregnation, showed a much lower moisture regain. Tensile strengths of the warp yarns taken from the treated fabrics had not decreased by these treatments. To examine the effect on heat and acid resistances, the sample fabrics were heated for 10 h at 150°C in air, or immersed in 30% H_2SO_4 at 40°C for 1 h. The tensile strength of the warp yarns were then measured. As shown in Table III, the heat and acid resistances were increased by these treatments. Crease recovery was not increased by these treatments, and dimensional stability to water was not improved very much.

Dyeabilities for direct and disperse dyes are shown in Table IV. The cotton fabric acetylated by the ordinary method using acidic catalyst and ordinary cellulose acetate fabric cannot be dyed with direct dye, while cotton fabrics alkali-treated and acetylated can be dyed with direct dye deeper than mercerized cotton though the degree of acetylation reaches 20 mol %. Moreover, they can also be fairly well dyed with disperse dye. Color fastness to laundering was excellent for a direct dye, but was poor for a disperse dye.

Soil removal was remarkably improved by these treatments as shown in Table V.

Treatment with Metal Hydroxides and Acrylonitrile (Cyanoethylation)

Many studies have been carried out by us^{2,4,5} on the treatment of cotton with alkali-acrylonitrile, but the properties of the treated cotton of high degree of cyanoethylation have not been examined. In the present work sample fabrics having the degree of cyanoethylation of 10–32 mol % were prepared using NaOH and KOH. Various properties of the treated cotton fabrics were examined. The conditions of the treatment and moisture regain and tensile strength of the warp yarn of the treated fabrics are shown in Table VI.

KOH appears to give a higher reaction rate of cyanoethylation than NaOH. It was recognized that the moisture regain of the treated fabric having the degree of cyanoethylation as high as 32 mol % was higher than that of the untreated cotton. Tensile strength of the warp yarn did not decrease by these treatments, but it was noted that the wet tensile strength of the treated cotton having a degree of cyanoethylation of 12–20 mol % decreased considerably.

Crease recovery of the fabrics was not improved by this treatment as in the case of NaOH-acetylation. Heat and acid resistances were improved, but light resistance was almost the same as the untreated cotton (Table VII).

TABLE III
Heat and Acid Resistance

Sample no.	Degree of acetylation (mol %)	Tensile strength of warp yarns					
		Untreated (g)	Acid-treated ^a		Heat-treated ^b		
			Strength (g)	Retention (%)	Strength (g)	Retention (%)	
0	Untreated	251	142	56.5	191	76.2	
1	Mercerized	247	165	66.9	229	92.5	
5-1-2	17.9	249	212	85.2	243	97.4	
5-1-3	25.7	266	197	74.0	251	94.4	

^a 30% H₂SO₄, 40°C, 1 h.

^b 150°C air, 10 h.

TABLE IV
Dyeability and Color Fastness for Laundering

Dye	Sample no.	Degree of acetylation (mol %)	Dye uptake (%)	Color fastness for laundering		
				Discoloration	Staining	
					Cotton	Wool
Direct ^a	0	Untreated	11.0	5	2-3	4-5
	1	Mercerized	20.3	5	2-3	5
	4-1-3	26.6	21.7	5	3-4	5
	5-1-1	18.8	26.0	5	3	5
	9-2-1 ^b	22.5	2.7	4	3-4	5
	Acetate	76.7	1.7	1	3	5
Disperse ^c	0	Untreated	12.1	1	4-5	4-5
	1	Mercerized	15.8	1	4	4-5
	4-2-3	27.1	16.8	1	3-4	3-4
	5-2-1	18.7	16.3	2	3-4	3
	9-2-1 ^b	22.5	46.6	5	4	4
	Acetate	76.7	29.2	5	4-5	4-5

^a Sumilight Super Scarlet BNS concn.

^b Ordinary fibrous acetylation by sulfoacetic acid.

^c Celliton Fast Red BB Type 8072.

TABLE V
Soiling and Soil Removal

Sample no.	Degree of acetylation (mol %)	Soiling (%)	Soil removal (%)
0	Untreated	66.2	30.7
1	Mercerized	65.5	31.3
6-1-3	23.3	66.8	57.8
9-1-1 ^a	26.2	54.5	71.8

^a Ordinary fibrous acetylation by sulfoacetic acid.

The treated cotton fabrics having the degree of cyanoethylation of 11-19 mol % showed dye uptake of direct dye higher than mercerized cotton. They also showed dye uptake of cationic dye similar to acrylic fiber (Table VIII). Color fastness to light was excellent in all cases, but fastness to laundering was poor in the case of cationic dyeing except 3-5-1 and acrylic fiber.

Treatment with Sodium Hydroxide and Benzoyl Chloride (Benzoylation)

On the benzoylation of cotton some researches have been carried out to improve the resistance to weathering¹⁰ and dyeability with disperse dye.¹¹ In these researches, cotton fabrics impregnated with NaOH were treated with benzoyl chloride, while in the present research 10% benzene solution of benzoyl chloride was used for the treatment. Benzoylation proceeded at room temperature. The results obtained are shown in Table IX. Specific gravity and moisture regain were somewhat decreased. Tensile strength of

TABLE VI
Some Properties of the Alkali-Acrylonitrile-Treated Cotton Fabrics^a

Sample no.	Pretreatment	Acrylonitrile		Degree of cyanoethylation (mol %)	Moisture regain (%)	Warp tensile strength		
		Temp (°C)	Time (min)			Dry (g)	Wet (g)	Wet/Dry (%)
0	Untreated	—	—	—	6.4	233	230	98.7
1	Mercerized	—	—	—	7.9	243	253	104.1
2-6-1	25% NaOH	40	60	10.5	9.4	235	237	100.9
2-7-1		50	60	15.1	10.2	244	170	69.7
3-1-1	2.5N KOH	20	30	11.7	7.9	238	188	79.0
3-4-1	5.4N KOH	20	30	19.2	8.2	235	213	90.6
3-5-1		40	30	32.8	9.6	256	256	100.0

^a Alkali pretreated at room temperature for 30 min, and then squeezed and treated with acrylonitrile.

TABLE VII
Heat, Acid, and Light Resistances

Sample no.	Pretreatment	Acrylonitrile		Degree of cyanoethylation (mol %)	Warp tensile strength (g)			
		Temp (°C)	Time (min)		Untreated	Heat ^a	Acid ^b	Light ^c
0	Untreated	—	—	—	233	156	70	139
1	Mercerized	—	—	—	243	207	165	—
3-1-1	2.5 <i>N</i> KOH	20	30	11.7	238	215	—	154
3-4-1	5.4 <i>N</i> KOH	20	30	19.2	235	258	113	—
3-5-1	5.4 <i>N</i> KOH	40	30	32.8	256	231	133	139

^a 150°C air, 10 h.

^b 30% sulfuric acid, 40°C, 60 min.

^c Sunlight exposure, 200 h.

TABLE VIII
Dyeability

Dye	Sample no.	Degree of cyanoethylation (mol %)	Dye uptake (%)
Direct ^a	0	Untreated	10.0
	1	Mercerized	15.4
	3-1-1	11.7	44.0
	3-4-1	19.2	23.3
	3-5-1	32.8	7.7
	4	Acrylic ^b	6.3
Cationic ^c	0	Untreated	17.8
	1	Mercerized	20.7
	3-1-1	11.7	22.3
	3-4-1	19.2	27.2
	3-5-1	32.8	37.0
	4	Acrylic ^b	26.8

^a Sumilight Supra Scarlet BNS concn.

^b Exlan made by Nippon Exlan Ind.

^c Sumiacryl Red F GTL.

the warp yarns and crease recovery were somewhat increased. Other properties, such as dyeability and water repellency of the treated fabrics are shown in the following tables together with the properties of the oleoylated cotton.

Treatment with Oleoyl Chloride (Oleoylation)

As oleoylation did not proceed if the cotton fabrics impregnated with 20% aqueous solution of NaOH were treated with the dimethyl formamide (DMF) solution of oleoyl chloride, the cotton fabrics decrystallized by the treatment with acrylonitrile, after impregnation with 20% aqueous solution of NaOH, were treated with DMF solution of oleoyl chloride (AO in Table X). For comparison, the untreated cotton fabrics were treated with DMF solution of oleoyl chloride (O in Table X). Results obtained are shown in Table X together with some properties.

Oleoylation of the decrystallized cotton proceeded faster than for the untreated cotton. Specific gravities were decreased by these processes. Moisture regains were much decreased when the untreated cotton fabrics were oleoylated, but were rather increased if the decrystallized cotton fabrics were oleoylated in the same way. Tensile strengths of the warp yarns were decreased because the acid scavenger such as pyridine was not used, but it was noted that the decrease of warp tensile strengths were much reduced if the decrystallized cotton fabrics were oleoylated. In the case of oleoylation, the crease recoveries were somewhat increased.

Results of the dyeing tests are shown in Table XI. In all cases, the dye uptakes of direct dye were much decreased. Those of disperse dye were as high as cellulose acetate fabric, though the color fastness for laundering was poor.

TABLE IX
Benzoylation of Cotton Fabrics

Sample no.	Treatment	Temp (°C)	Time (min)	Degree of benzoylation (mol %)	Moisture regain (%)	Specific gravity	Warp tensile		Crease recovery (%)
							Strength (g)	Elongation (%)	
0	Untreated	—	—	—	5.5	1.52	235	7.4	47.6
1	Mercerized	—	—	—	8.8	—	245	13.0	49.3
BZO-8	20% NaOH,		30	14.0	4.5	—	253	11.5	—
BZO-11	10% benzene	20	60	16.0	4.6	—	254	13.9	53.5
BZO-13	solution of		90	16.3	4.6	—	276	13.1	—
BZO-14	benzoyl chloride		90	17.2	4.8	1.37	216	12.9	—

TABLE X
Oleoylation of the Untreated and the Decrystallized^a Cotton Fabrics

Sample no.	Concn of DMF solution of oleoyl chloride (mol)	Temp (°C)	Time (min)	Degree of oleoylation (mol %)	Moisture regain (%)	Specific gravity	Warp tensile			Crease recovery (%)
							Strength (g)	Elongation (%)	—	
0	Untreated	—	—	—	5.5	1.52	235	7.4	47.6	—
1	Mercerized	—	—	—	8.8	—	245	13.0	49.3	—
O-5				5.4	2.5	—	88	4.9	—	—
O-6	0.4	40	450	5.5	2.7	—	118	5.4	68.4	—
O-7				5.5	2.3	1.39	—	—	—	—
O-13	0.3	60	240	4.5	3.5	—	55	4.2	—	—
AO-2 ^a	0.3	40	240	5.9	6.3	1.30	203	11.3	50.9	—
AO-3 ^a	0.4	40	240	8.7	5.6	1.34	179	11.1	52.6	—
AO-4 ^a	0.3	50	240	8.9	—	—	—	—	—	—

^a Cotton fabrics decrystallized by treatment with acrylonitrile after impregnating with 20% NaOH were oleoylated (degree of cyanoethylation: 3.7 mol %).

TABLE XI
Dyeability and Color Fastness to Laundering^a

Sample no.	Degree of substitution, (mol %)	Direct dye ^b		Disperse dye ^c	
		Uptake (%)	Fastness ^a	Uptake (%)	Fastness ^a
0	Untreated	19.3	4-5	13.4	3-4
1	Mercerized	26.3	5	12.9	3-4
BZO-11	16.0	7.7	5	24.7	4
O-5	5.4	5.0	4-5	22.4	2
AO-4	8.9	6.3	5	28.4	2
Acetate	76.7	3.7	1	22.4	5

^a Laundering: 5 g/L Marseilles soap, 42 rpm, 40°C, 30 min.

^b Sumilight Supra Scarlet BNS conc.

^c Sumikaron Brilliant Blue S-BL.

Soiling was somewhat decreased by these treatments, as shown in Table XII. But soil removal was decreased in the case of oleoylation, perhaps due to the oleophilicity for oily soil.

To examine the wettability or repellency to water and oily liquid of the treated fabrics, the following tests were carried out according to the water absorption test method JIS L 1004-1978. For comparison, Qiana and polyester spun fabric were tested. The test method and the results obtained are shown in Table XIII.

The benzoylated cotton fabric shows less water absorption velocity than the untreated cotton fabric. All oleoylated cotton fabrics show high water repellency. It is interesting that the cotton fabrics oleoylated after being decrystallized (AO-2, -3) show either high water vapor absorption (moisture regain, Table IX) or high water repellency. On the case of liquid paraffin, it was somewhat difficult to obtain accurate test results, but it seemed that the oleoylated cotton, Qiana, and polyester fabrics had the highest absorption velocity; then the benzoylated cotton came next and the cotton fabrics oleoylated after being decrystallized had less absorption velocity.

The apparent contact angles of water on the fabrics were calculated by the following formula taking photographs of the water droplets on the fabrics immediately after dropping.

$$\tan(\theta_D/2) = h(D/2)$$

TABLE XII
Soiling and Soil Removal

Sample no.	Degree of substitution (mol %)	Soiling (%)	Soil removal (%)
0	Untreated	66.2	30.7
1	Mercerized	67.4	31.3
BZO-13	16.3	53.8	30.4
O-13	4.5	52.6	15.8

TABLE XIII
Wettability or Repellency for Water and Liquid Paraffin

Sample no.	Degree of substitution (mol %)	Water			Liquid paraffin		
		Dropping ^a (s)	Wicking ^b (mm)	Sinking ^c (s)	Dropping ^a (s)	Wicking ^b (mm)	Sinking ^c (s)
0	Untreated	~0	36.0	1.5	31.3	8.3	40
1	Mercerized	2.7	36.0	1556	42.5	6.1	155
BZO-14	17.2	562	11.0	x ^d	44.4	7.2	52
O-7	5.5	x ^d	0.3	x	26.0	6.6	30
AO-2	5.9	x	0.1	x	61.6	5.9	137
AO-3	8.7	x	0.3	x	59.5	5.9	210
Qiana	—	127	8.5	x	27.1	5.5	351
Polyester	—	x	1.2	x	24.5	5.1	59

^a Time required until the droplet placed on the fabric is absorbed and the reflection of light from the droplet disappears.

^b Height of liquid sucked up during 1 min through the lower end of the strip of fabric immersed vertically in the liquid.

^c Time required until the small piece of fabric floated on the liquid surface begins to sink.

^d x marks show that no change occurred during 1 h on the droplet or sinking test.

TABLE XIV
Apparent Contact Angle θ_D of Water on the Fabrics

Sample no.	Degree of substitution (mol %)	D^a (mm)	h^b (mm)	θ_D^c
0	Untreated	6.3	11	(38.5) ^c
1	Mercerized	4.5	23	(91.3) ^c
BZO-14	17.2	5.2	30	98.2
O-7	5.5	3.3	29	120.7
AO-2	5.9	2.5	25	98.6
AO-3	8.7	2.5	25	101.3
Qiana	—	2.8	28	108.9
Polyester	—	2.6	26	112.1

^a D = the length of the base of droplet.

^b h = the height of droplet.

^c Contact angle values of the untreated and mercerized cotton fabrics are uncertain, as the droplets of water disappear within a few seconds after dropping.

where θ_D = apparent contact angle on fabrics, h = the height of droplet, and D = the length of base of droplet. As shown in Table XIV, the oleoylated cotton fabric shows the highest contact angle, polyester, and Qiana follow it, and the cotton fabric oleoylated after being decrystallized and the benzooylated cotton show less values. Droplets of liquid paraffin were observed to disappear within 1 min, and so accurate estimation of contact angle was difficult.

The investigations on the fine structure of some modified cotton fibers by X-ray and infrared spectroscopy are reported in other papers.^{12,13} The outline of this work were presented at the 1980 Annual Meeting of the Society of Fiber Science and Technology, Japan.¹⁴

References

1. I. Sakurada, W. Tsuji, et al., *Res. Reps. Jpn. Cotton Tech. Inst.* Nos. 14, 20, 34, 49, (1956, 1957, 1959, 1961).
2. W. Tsuji, and M. Imai, *Annu. Rep. Res. Inst. Chem. Fibers, Kyoto Univ.*, **20**, 9 (1963); *Bull. Inst. Chem. Res., Kyoto Univ.*, **44**, 183 (1966).
3. A. K. Kulshreshtha and N. E. Dweltz, *J. Appl. Polym. Sci.*, **21**, 2085 (1977).
4. W. Tsuji, A. Hirai, and M. Hosono, *J. Appl. Polym. Sci.*, **20**, 2837 (1976); *Sen-i Gakkaishi (J. Soc. Fiber Sci. Tech., Jpn.)*, **34**, T-6, T-82 (1978).
5. W. Tsuji, C. Kubo, Y. Yamada, and T. Nakao, *Bull. Mukogawa Women's Univ. (Clothing Sci.)*, **26**, 59 (1978).
6. W. Tsuji, S. Okamura, et al., *Res. Rep. Jpn. Cotton Tech. Inst.* No. 20, 89 (1957).
7. W. Tsuji, K. Tsukamoto, T. Nakamine, and T. Nakao, *Bull. Mukogawa Women's Univ. (Clothing Sci.)*, **26**, 65 (1978).
8. W. Tsuji, Abstracts of Papers, ACS/CSJ Chemical Congress, Honolulu, Hawaii, Apr. 1979, Cell. 157; W. Tsuji, T. Nakao, H. Miyazaki, M. Murata, et al., *Bull. Mukogawa Women's Univ. (Clothing Sci.)*, **31**, 1 (1983).
9. I. Sakurada et al., *Cellulose Ind. (Jpn.)*, **4**, 304 (1928); *J. Soc. Ind. Chem. (Jpn.)*, **37**, 1484 (1934).
10. J. C. Arthur, Jr., et al., *Text. Res. J.*, **35**, 1116 (1965).
11. Shikishima Spinning Co., Japan Kokai Tokkyo, Showa 51-99185, Sep. 1, 1976.

12. A. Hirai, W. Tsuji, R. Kitamaru, and M. Hosono, *J. Appl. Polym. Sci.*, **20**, 3365 (1976).
13. W. Tsuji, T. Nakao, and T. Okuno, *Bull. Mukogawa Women's Univ. (Clothing Sci.)*, **31**, 11 (1983).
14. W. Tsuji and T. Nakao, Annual Meeting of the Society of Fiber Science and Technology, Japan, June 1980.

Received November 1, 1983

Accepted December 16, 1985