JOURNAL OF APPLIED POLYMER SCIENCE VOL. 13, PP. 1037-1048 (1969)

Reactivity of Cotton after Treatment in Alkaline and Acid Swelling Agents

J. O. WARWICKER and J. W. CLAYTON, *The Cotton Silk and Man-made Fibres Research Association, Shirley Institute, Manchester, England*

Synopsis

The reactivity of scoured Acala 4-42 cotton before and after treatment with alkaline and acid swelling agents has been assessed by a number of methods. It is shown that 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 a nonswelling or a swelling medium. Thus high intrafibrillar swelling can lead to a loss in reactivity of the treated cotton if the subsequent reaction takes place in a medium incapable of swelling the treated cotton, on the other hand, interfibrillar swelling can lead to an increase in reactivity in the same reaction mixture.

INTRODUCTION

It has recently been shown[1] that the degree of swelling of a cotton hair is no criterion for the manner in which the swelling has been achieved and cannot indicate the effect of the treatment on the morphology and fine structure of the cotton. Thus it is possible for the same degree of swelling to be achieved in two different concentrations of the same swelling reagent and the swelling to be interfibrillar in one concentration, and intrafibrillar, as well as interfibrillar, in the other. The reactivity of the resulting treated cotton may therefore be expected to be different towards other reagents according to the type of swelling achieved during the swelling treatment rather than according to the degree of swelling achieved. It is thus more important to relate the reactivity of cotton to the morphological and fine structural features of the treated cotton than to the degree of swelling attained during the treatment. This is even more important if the desired reaction is to take place in swollen cotton.

EXPERIMENTAL

Material

Mature Acala 4-42 cotton from the San Joaquin Valley (U.S.A.) was used. The sample used throughout was one that had been scoured in 1% caustic soda containing 1 ml/l. of Calsolene oil H.S. at 60°C, then treated for 3 hr in 1% caustic soda containing 0.15% castor oil soap under 35 lb/in.^{2} excess pressure. After treatment the cotton was washed thoroughly in distilled water and dried in the air.

Microscopical examination of the scoured cotton showed it to be free of cuticle (i.e., the outer pectinous layer) but the primary cellulose wall was intact.

Conditions of Swelling

Conditions of swelling are summarized in Table I. A 10-g portion of cotton was immersed in a liter of solution at 25°C. In the sulfuric acid treatments for 5 sec it was found more convenient to keep the same ratio of cotton to swelling liquid but to use small quantities at a time and to pour the whole into a large volume of water to terminate the reaction and to initiate the washing sequence. After caustic soda swelling, a wash in 0.2*N* acetic acid and after acid treatments a wash in 0.2*N* ammonium hydroxide was included in the washing sequence to ensure complete neutralization of the swelling agent: the fibers were then washed until free from all reagents and dried in the air.

The removal of EWNN after swelling required a treatment with glycerol to facilitate the removal of the iron tartrate complex from the structure followed by washing in water.

TABLE I

Swelling agent	Condition of Swelling
NaOH	30 min at the given concentration
EWNN[a]	30 min at the given concentration
H_2SO_4	One set 30 min at the given concentration
	One set 5 sec at the given concentration
H_3PO_4	30 min at given concentration
HNO_3	5 min at given concentration
$HClO_4$	5 min at given concentration

[a] Iron tartrate complex in 2*N* caustic soda containing free sodium tartrate.[1,2]

Moisture Sorption

Samples were first conditioned to 66% RH at 20°C in an evacuated chamber over a saturated solution of sodium nitrite containing an excess of the solid salt. The moist weight of the samples was determined and the subsequent dry weight found after drying to constant weight over P_2O_5 or by drying in an oven at 110°C, the latter was later found to give more consistent, results. The moisture regain is expressed as

$$\frac{\text{Weight of conditioned sample} - \text{Dry weight}}{\text{Dry weight}} \times 100 = \text{Moisture regain } \%$$

This can be also expressed as the number of molecules per anhydroglucose unit by multiplication by 162/1800.

According to Valentine[3] quoting values of Gibbons,[4] the accessibility of the cellulose can be derived if it is accepted that 1.53 moles of water per anhydroglucose unit (AGU) are sorbed by completely accessible cellulose. So that accessibility can be defined as:

$$\text{Accessibility to water vapor, \%} = \text{moles/AGU} \times 100/1.53$$

Water Retention

Samples of treated cotton were soaked in water for 1 hr at 25°C, then centrifuged for 7 min in closed tubes fitted with a sintered disk at a speed of 3800 rpm, which was found to correspond to a relative centrifugal force of 1300. The cotton was then weighed in the tube, dried for 3 hr at 110°C and the dry weight determined, from which the water retention per cent of the dry weight could be readily calculated. The sample was then resoaked in water and the water retention redetermined for the sample that had been dried in an oven; this gave some indication of the collapse of the fine structure on oven-drying.

Acetylation

Before determining the acetyl value all samples were conditioned to 66% RH unless otherwise stated. A 2-g cotton sample was then acetylated in 50/50 (v/v) pyridine/acetic anhydride at 25°C for 24 hr. After acetylation, the acetyl content was determined by hydrolysis of the sample in 0.4*N* sodium hydroxide, acidification with 0.4*N* sulfuric acid, and the excess acid determined by back-titration with 0.1*N* sodium hydroxide.

The acetyl value is expressed as the acetyl content (as a percentage) achieved by the sample after 24 hr of reaction, i.e.,

$$\frac{\text{Weight of acetyl (CH}_3\text{CO—) groups after 24 hr of reaction}}{\text{Weight of acetylated sample}} \times 100$$

Acid Hydrolysis

A 1.0-g sample was immersed in 1.0*N* hydrochloric acid and refluxed for 1 hr. The loss in weight was determined, and the intrinsic viscosity of the residue in cuprammonium hydroxide at 20°C was found for each sample calculated according to the methods given by Calvert and Clibbens.[5] The degree of polymerization (DP) of the residues, often known as the leveling-off degree of polymerization (LODP) was determined from the relation

$$\text{DP} = 175[\eta]$$

where $[\eta]$ is the intrinsic viscosity, which was found by Cumberbirch to be more accurate than the usual relation

$$[\eta] = K(\text{DP})^{\alpha}$$

where α and K are constants, for cellulosic samples of low molecular weight. The simplified relation was found by Cumberbirch[6] from experiments with cellulose fractions of low molecular weight the DP of which, were determined by accurate osmotic pressure measurements and the intrinsic viscosity found from viscosity measurements.

RESULTS AND DISCUSSION

To gain a greater understanding of the results it is necessary to know the type of swelling that took place during the swelling treatment. This information[1] can be classified into interfibrillar swelling, where no penetration of the fibrils takes place and the fibrils move apart, and intrafibrillar swelling where penetration of the fibrils also takes place. It is conceivable to have intrafibrillar swelling without any interfibrillar swelling, and indeed such swelling might reduce the interfibrillar spaces and lead to a compacting of the morphological structure. These processes clearly alter the overall morphology and the fine structure of the cotton and lead to modified properties that profoundly affect the reactivity of the cotton to different reagents.

In Tables II and III are the results for moisture sorption on samples treated in alkaline and acid swelling agents. It will be seen from these results that no swelling agent has produced a greater accessibility to water vapor than 86% (70% sulfuric acid for 5 sec) as against 46% for the control. It is known from previous data[1] that interfibrillar swelling alone takes place in concentrations less than 3*N* NaOH, 100 g/l. EWN, 62.5% H_2SO_4, 82% H_3PO_4, 61% HNO_3, and 60% $HClO_4$, whereas above these concentrations intrafibrillar swelling, as well as other processes, can also take place. From these data it is seen that accessibilities greater than 55% are not generally achieved without intrafibrillar swelling taking place. It would seem, therefore, that intrafibrillar swelling must cause extra internal surfaces to be exposed in the treated samples, and one

TABLE II
Acala 4-42 Scoured Cotton Treated with Alkaline Swelling Agents at 25°C

Sodium Hydroxide				EWNN			
NaOH concn, *N*	Regain, %	Moisture sorption, moles H_2O/C_6	Accessibility, %	EWN concn, g/l.[a]	Regain, %	Moisture sorption, moles H_2O/C_6	Accessibility, %
0	7.82	0.704	46.0	0	7.73	0.696	45.5
1.0	7.88	0.709	46.3	20	6.86	0.617	40.3
2.0	7.65	0.689	45.0	50	7.02	0.632	41.3
3.0	8.75	0.788	51.5	60	6.92	0.623	40.7
3.25	9.03	0.813	53.1	70	7.30	0.657	42.9
3.50	9.37	0.843	55.1	80	7.34	0.661	43.2
4.0	10.32	0.929	60.7	100	7.15	0.644	42.1
5.0	11.11	1.000	65.4	150	11.08	0.997	65.2
10.0	11.88	1.069	69.9	200	12.40	1.116	72.9

[a] Iron tartrate complex concentration

TABLE III
Moisture Sorption of Acala 4-42 Scoured Cotton Treated with Acid Swelling Agents at 25°C

Swelling agent	Swelling agent concn, wt-%	Regain, %	Moisture sorption, H_2O/moles C_6	Accessibility, %
H_2SO_4	0	7.8	0.702	45.9
(30 min)	58	7.6	0.684	44.7
	59	7.8	0.702	45.9
	60	8.1	0.729	47.6
	61	8.9	0.801	52.4
	62	8.6	0.774	50.6
	62.5	9.2	0.828	54.1
H_2SO_4	0	7.73	0.696	45.5
(5 sec)	60	8.19	0.737	48.2
	62	8.58	0.772	50.5
	64	8.95	0.806	52.7
	66	11.35	1.022	66.8
	68	12.57	1.131	73.9
	70	14.55	1.310	85.6
	72	14.24	1.282	83.8
	74	13.90	1.251	81.8
H_3PO_4	0	7.8	0.702	45.9
	70	7.8	0.702	45.9
	75	7.8	0.702	45.9
	80	9.4	0.846	55.3
	81	10.1	0.909	59.4
	82	12.3	1.107	72.4
HNO_3	0	7.73	0.696	45.5
	61.2	9.9	0.891	58.2
	65.4	11.5	1.035	67.6
	68.8	12.4	1.116	72.9
	72.0	13.6	1.224	80.0
	76.0	13.15	1.179	77.0
	80.0	12.5	1.125	73.5
$HClO_4$	62	14.31	1.288	84

simple mechanism whereby this can be achieved is by the splitting of the fibrils during the intrafibrillar swelling process.

Consideration of the retention of liquid water (Tables IV and V) reveals a somewhat similar pattern of events although there are anomalies. In general when only interfibrillar swelling has taken place only a comparatively small increase in water retention is attained, except with a sample treated with 82% phosphoric acid, which became hard and horny after treatment. It is suspected that the high water retention shown by the sample treated in 82% phosphoric acid may be partly caused by the capillary retention of water between fibres in the horny mass. Intrafibrillar swelling leads in general to a much greater capacity for the retention

TABLE IV
Water Retention of Acala 4-42 Scoured Cotton Treated with Alkaline Swelling Agents at 25°C

Sodium hydroxide				EWNN		
	Water retention, %				Water retention, %	
Concn, N	Never dry	Air-dry	Oven-dry	Concn, g/l.	Air-dry	Oven-dry
0	49		49	0	47	45
1.0	53		44	50	50	48
2.0	60		46	100	48	46
2.5	64		48	150	76	65
3.1	73		51	200	66	61
3.5	86		57			
4.1	90		59			
5.2	94		58			
6.3	95		61			
7.6	97		61			
8.7	102		60			
10.2	97		60			
5.0		69	58			

of water but the sample treated with 80% nitric acid has a lower water retention than any sample examined. It is known[1] from other data that this sample has suffered partial nitration during the swelling process and it is therefore probable that this is the cause of the drop in water retention despite the opening up of the structure by intrafibrillar swelling. Further examination of the results shows that oven drying of a sample that has been swollen interfibrillarly produces a water retention not much different from that of the control. In this case it would seem that any advantage gained from the swelling treatment is not retained after oven drying, and can be explained by the re-formation of hydrogen bonds broken during the swelling treatment. On the other hand samples in which a high water retention has been achieved via an intrafibrillar swelling process, retain some of the extra capacity for water even on drying in the oven. The nature of the final morphology and fine structure of these samples is clearly different from those of the control, whereas in samples in which interfibrillar swelling has taken place only a small modification of the morphology and fine structure seems to have been achieved.

Examination of the results for acetylation however, reveal quite a different situation with regard to the reactivity of the treated cotton. It should be noted that the acetylation reaction is carried out in pyridine that is not capable of swelling cotton to the same extent as water, and furthermore, cannot penetrate the crystal structure of cotton, so that pyridine is classed as a nonswelling agent for cotton. Acetylation of samples that had undergone interfibrillar swelling is as good as, and in many cases better than that of the control (Tables VI and VII) when carried out on air-dried and conditioned samples. Samples that had

TABLE V
Water Retention of Acala 4-42 Scoured Cotton Treated with Acid Swelling Agents at 25°C

Swelling agent	Swelling agent concn, wt-%	Water retention, % Air dry	Water retention, % Oven dry
H_2SO_4	0	47	45
(5 sec)	60	48	47
	62	50	47
	64	58	53
	66	105	68
	68	124	76
	70	126	70
	72	130	64
	74	138	69
H_3PO_4	0	47	45
	70	47	45
	75	50	46
	80	84	72
	81	114	82
	82	123	89
HNO_3	0	47	45
	61.2	53	52
	65.4	59	56
	68.8	62	58
	72	73	56
	76	62	53
	80	39	33
$HClO_4$	62	74	65

undergone intrafibrillar swelling, washed, air-dried and conditioned show a dramatic fall in acetylation over that of the control. On the other hand, if intrafibrillar swelling is followed by washing, solvent exchange to pyridine, and then acetylation, then there is a dramatic rise in acetylation. Results with 5*N* caustic soda as the swelling agent emphasize these changes. Thus if swelling is followed by washing, solvent exchange to pyridine, and acetylation, an acetyl value of 16.9% is given. If the solvent exchange process is carried out with methanol followed by benzene and the sample air dried before acetylation then an acetyl value is given of 4.6%. However, if after washing the sample is air-dried and conditioned before acetylation, an acetyl value of only 0.6% is given. Clearly this is not the result of chemical or crystallographic changes in the sample, but due entirely to morphological and fine structural changes. Intrafibrillar swelling, accompanied also by interfibrillar swelling, leads to much more open structures, while water is present or can be replaced by other solvents; if no agent is present to preserve this open structure, however, then intrafibrillar swelling leads to a compacting of the structure on drying. Unless, therefore, sufficient swelling takes place during the desired reaction, and

TABLE VI
Acetyl Content of Acala 4-42 Scoured Cotton Treated in Alkaline Swelling Agents at 25°C

Sodium hydroxide				EWNN			
		Acid hydrolysis				Acid hydrolysis	
NaOH concn, N	Acetyl content A, (never dry), %[a,b]	Loss, %	LODP	EWN concn, g/l.	Acetyl content A, (conditioned), %	Loss, %	LODP
0	7.8	3.2	140	0	7.6	3.2	140
1.0	7.7	3.5	140				
2.0	8.7	3.2	138	50	8.0	4.7	141
2.5	8.9	4.1	137				
3.1	11.7	4.5	125	100	7.7	4.1	145
3.5	14.8	5.6	107				
4.1	15.9	5.8	97	150	10.3	7.6	118
5.2	16.9	6.4	92				
6.3	16.8	7.2	87	200	0.9	8.2	86
7.6	17.8	6.4	84				
8.7	17.9	7.0	80				
10.2	18.2	—	79				

[a] Percentage acetyl content after 24 hr scoured cotton conditioned at 66% R.H., A = 7.6%; scoured cotton + $5N$ NaOH, washed solvent exchanged via methanol and benzene and dried, $A = 4.6\%$; scoured cotton + $5N$ NaOH washed air dried and conditioned, $A = 0.6\%$.

[b] Solvent exchanged to pyridine before acetylation.

TABLE VII
Acala 4-42 Scoured Cotton Treated in Acid Swelling Agents at 25°C

Swelling agent	Swelling agent concn, wt-%	*A* (conditioned), %	Acid hydrolysis	
			Loss, %	LODP
H_2SO_4	0	7.6	3.2	140
(30 min)	58	9.5	4.1	—
	59	9.7	3.3	141
	60	10.6	3.8	144
	61	13.1	4.7	144
	62	15.0	5.6	137
	62.5	16.1	7.0	136
H_2SO_4	0	7.6	3.2	140
(5 sec)	60	7.8	3.5	148
	62	8.0	3.8	132
	64	10.6	3.9	137
	66	6.5	6.3	95
	68	4.0	7.9	87
	70	2.8	10.5	68
	72	2.9	10.2	56
H_3PO_4	0	7.6	3.2	140
	70	7.4	4.9	147
	75	7.7	5.2	143
	80	12.6	6.0	162
	81	17.5	5.6	137
	82	18.6	7.0	116
HNO_3	0	7.6	3.2	140
	61.2	8.6	4.4	136
	65.4	8.7	7.9	112
	68.8	2.3	8.0	79
	72.0	4.8	14.1	60
	76.0	23.9	19.1	47
	80.0	24.0	—	
$HClO_4$	62	0.9	12.2	54

water is often sufficient to produce such swelling, treatment of cotton with a swelling agent that produces intrafibrillar swelling can lead to a structure of virtually no reactivity. The difficulty of the acetylation of cellulose materials that had been highly swollen in caustic soda has long been known in the cellulose acetate industry, but does not seem to have been appreciated by chemists attempting other reactions on cotton. There is an apparent anomaly in the results for samples treated in 76 and 80% nitric acid. However, nitration has accompanied the swelling reaction, and the dried structure contains fractions of nitrocellulose that can be swollen by pyridine, thus opening up the rest of the structure to the acetylation reaction.

The reactivity of the treated samples to acid hydrolysis with hydrochloric acid further illustrates the difference in reactivity brought about by interfibrillar or intrafibrillar swelling. If only interfibrillar swelling had taken place, then the loss in weight on acid hydrolysis was 3–5% except for those samples treated with 62.5% sulfuric acid and 82% phosphoric acid, samples treated in swelling agents that are at a concentration near to the threshold at which intrafibrillar swelling is possible, and which might contain some material that had been interfibrillarly swollen. Samples that had undergone intrafibrillar swelling showed a higher loss in weight on acid hydrolysis consistent with a higher accessibility to water vapor. This is clearly brought out by the correlation of loss in weight on acid hydrolysis with accessibility to water vapor (Fig. 1), which in turn is related to the type of swelling as discussed above. Two results have been omitted from the graph because they are from samples in which appreciable nitration has taken place and therefore other factors are operative in the moisture sorption. Although there is a scatter of results, the results for the leveling-off degree of polymerization (LODP) for the residue of acid hydrolysis also fit a straight line (Fig. 2), correlating them with the accessibility to water vapor and hence to the type of swelling that the sample had undergone. The regression lines calculated statistically for these data are:

$$Y = 0.1668X - 3.895$$

where Y is the loss in weight and X the accessibility and

$$Z = -2.0202X + 236.55$$

where Z is the LODP. The first equation predicts that for zero loss in weight the accessibility is 23%. This appears to be different from that predicted by a similar plot given by Jeffries et al.,[7] but the difference is apparent only because of the different conditions used in the acid hydrolysis experiments. Jeffries et al.[7] used the loss in weight values for the whole of the easily hydrolizable fraction in $6N$ hydrochloric acid, whereas here the loss in weight refers to the fraction lost in a fixed time in $1.0N$ hydrochloric acid. Consideration of the two methods shows that in those materials in which high losses are found in 1 hr in $1.0N$ hydrochloric acid the corresponding loss in weight found by extrapolation with the method of

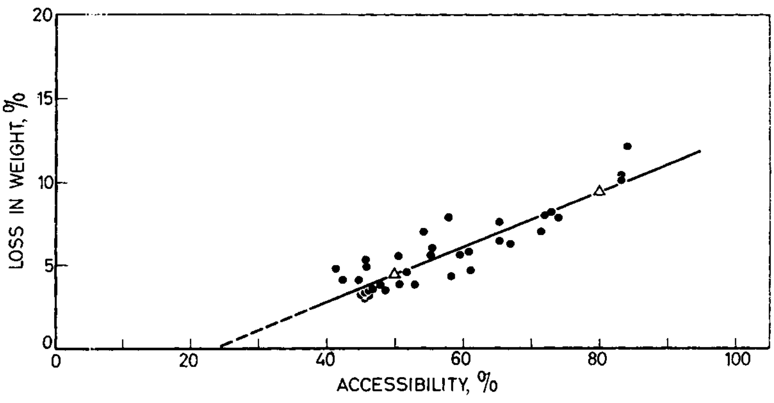

Fig. 1. Correlation between the loss in weight on acid hydrolysis and the accessibility of the treated cotton to water vapor.

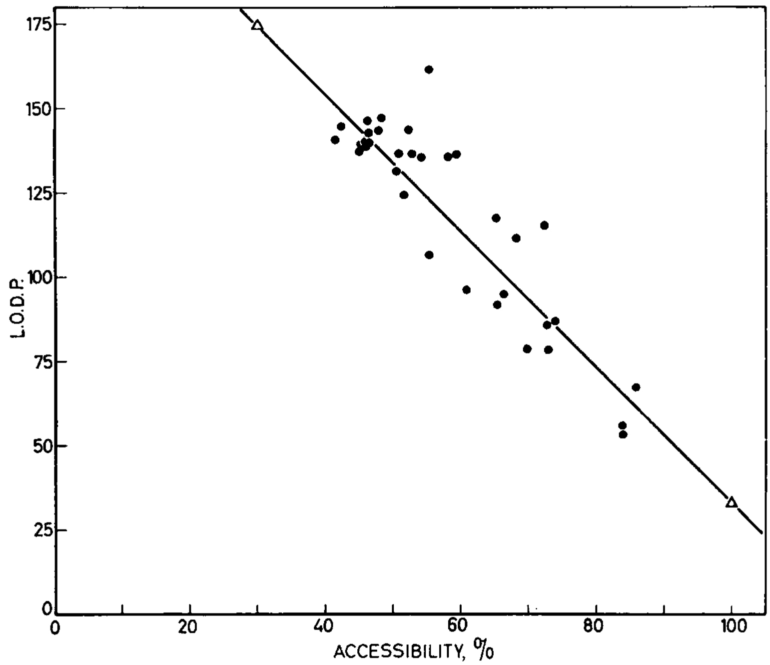

Fig. 2. Correlation between the leveling-off degree of polymerization (LODP) of the residue after acid hydrolysis and the accessibility of the treated cotton to water vapor.

Jeffries et al.[7] would be higher because the straight portion of their curves would not be attained, whereas the difference between the values predicted by the two methods for samples showing low weight losses would be small. If these effects on the values of the weight loss for a given accessibility are taken into account then it is seen that the steeper straight line given by Jeffries et al.[7] is not contradicted by the present results. The reason for the use of the simpler method of acid hydrolysis used in the present work was to have an easily determinable parameter indicating the reactivity of the sample to acid. It is, however, clear that acid hydrolysis data do correlate with accessibility to water vapor, and therefore the use of such data for estimations of so-called crystallinity or the use of LODP data as a means of estimating crystallite size as found in the literature,[8] must be treated with great caution.

It has been shown in a previous paper[1] that the degree of swelling is not a criterion for the type of swelling that has taken place by placing cotton in a given reagent. A further deduction arising from the results in this paper is that the degree of swelling achieved is not a criterion to the reactivity of cotton after treatment with swelling agents. It should be further emphasized that the reactivity can also be influenced by the way in which the swollen cotton is washed free from the reagent and dried. In general, solvent-exchange processes are likely to influence the reactivity of cotton that receives a swelling treatment involving intrafibrillar swelling more than those only swollen interfibrillarly, but some effect is found with the latter also. If reactions are carried out while the cotton is still swollen and placed in the reaction mixture via solvent exchange, then the reactivity is likely to be a function both of the degree of swelling and the type of swelling. It should be pointed out that the swelling reactions studied in this paper in which intrafibrillar swelling plays a prominent role are such that interfibrillar swelling also takes place. There are other swelling agents, not studied here, that cause intrafibrillar swelling with little or no interfibrillar swelling and the cotton treated with these reagents can be expected to react differently from the cotton treated as described here. Such reagents as liquid ammonia and the amines may fit into this class, and even solvent-exchange processes may not be successful with such swelling agents if the succession of solvents cannot replace the reagent located in the structure of the fibrils. Such reagents are being studied, and results with them will be reported later.

SUMMARY AND CONCLUSIONS

The reactivity of cotton treated with swelling agents depends on the type of swelling achieved during the process and not only on the degree of swelling.

The reactivity of the treated cotton further depends on whether the subsequent reactions take place in a medium that can swell the treated cotton or not. If interfibrillar swelling took place during the swelling treatment then some increase in reactivity to all reagents is found. If, however, intrafibrillar swelling also took place a reaction from a swelling medium (e.g., water) is improved but there is a dramatic loss in reactivity towards a reaction in a nonswelling solvent (e.g., acetylation from pyridine) unless a compensating factor is present such as nitration.

The loss in weight on acid hydrolysis and the leveling-off degree of polymerization of the residue correlate with the accessibility of the sample to water vapor.

This work was carried out under a P.L. 480 grant from the United States Department of Agriculture (Project No. UR-E29-(20)-65, Grant No. FG-UK-139).

References

1. J. O. Warwicker, *J. Appl. Polym. Sci.*, in press.
2. G. Jayme and W. Bergmann, *Reyon Zellwolle*, **34**, No. 127 (1956).
3. L. Valentine, *Text. Res. J.*, **24**, 670 (1954).
4. G. C. Gibbons, *J. Text. Inst.*, **44**, T201 (1953); *Shirley Inst. Mem.*, **26**, 59 (1952).
5. M. A. Calvert and D. A. Clibbens, *Shirley Inst. Mem.*, **45**, 1 (1951).
6. R. J. E. Cumberbirch, unpublished data.
7. R. Jeffries, J. G. Roberts, and R. N. Robinson, *Text. Res. J.*, **38**, 234 (1968).
8. J. O. Warwicker, R. Jeffries, R. L. Colbran, and R. N. Robinson, *Shirley Institute Pamphlet No. 93* (1966).

Received November 29, 1968