PARTIAL ACETYLATION *IN SITU* OF CELLULOSIC FABRIC AND ITS RESISTANCE TO MICROBIAL AND ACTINIC DEGRADATION

K.L. Maheshwari, U.S. Gupta, S.S. Nigam and N.D. Bhandari.
Defence Research Laboratory (Stores), Kanpur.

ABSTRACT

Partial acetylation *in situ* of cotton fabrics can be achieved satisfactorily when it is carried out using 0·03 per cent perchloric acid as the catalyst at a temperature not exceeding 30°C. Increase in concentration of perchloric acid or temperature adversely affects the tensile strength of the fabrics.

The acetylation of fabrics confers resistance to leaching. Scouring of the fabric prior to acetylation does not materially influence the extent of substitution of hydroxyl groups by acetyl ones. The acetylating mixture can be repeatedly used but fresh addition of the catalyst is necessary. With increase in the period of acetylation or in the quantity of catalyst, there is a progressive increase in acetic acid yield but the tensile strength of the fabric shows a corresponding decrease.

Partial acetylation affords protection against microbial attack when the acetyl content of the acetylated fabric is 14-15 per cent. The treatment does not however afford protection against degradation by artificial light, or sunlight or weathering.

INTRODUCTION

Cotton textiles are well known for their susceptibility to degradation by microorganisms[1] Doree[2] demonstrated that resistance to microbial attack can be imparted to cotton by altering the chemical structure of the cellulose molecule. The presence of one or more substituents in the anhydroglucose unit of the cellulose chain imparts such resistance. A large number of cellulose derivatives has been found to be resistant to fungal attack.[3,4,5] Goldthwait *et al*[6] showed that acetylated cotton with 30·0 per cent acetyl content or a degree of acetylation of 1·4 per anhydroglucose unit withstood soil burial for fifty weeks.

Investigations were undertaken to study whether the acetylation process can be used for conferring resistance to the treated fabric against microbial, actinic as well as weathering degradation. It was also desired to investigate the best method of acetylation without tendering the fabric.

EXPERIMENTAL

A. *Selection of a suitable catalyst.*—Preliminary experiments were carried out to select the most suitable method for acetylation of *dosootie* the cotton fabric of Indian tentage—in the presence of catalysts (such as pyridine, phosphoric acid and perchloric acid). Procedures tried for partial acetylation of the fabric were as follows:—

(*a*) *Dosootie* strips (10″ × 2½″) weighing 80 gms were steeped in 4N sodium hydroxide solution (500 cc) for 1 hour. The strips were washed free from alkali and steeped in pyridine for two days (giving two to three changes). The strips were then transferred to a mixture of acetic acid (400 c.c.) and pyridine (640 c.c.) shaken for 24 hrs, dried in shade and kept in an incubator at 37°C for 48 hours.

(*b*) *Dosootie* strips (10″×2½″) weighing 80 gms. were first dipped in acetic acid glacial (560 c.c.) for four hours at 37·8°C and then cooled to 21·1°C. To this bath was added a mixture of 250 c.c. of 85% acetic anhydride and 8·5 c.c. of phosphoric acid (cooled previously to 0°C). The fabric was kept for 4 hours and then washed and dried in shade.

(*c*) *Dosootie* strips (10″×2½″) weighing 18·5 gms were moistened so as to have 30% moisture content. These were then dipped in a solution of acetic anhydride (108 c.c.) in benzene (340 c.c.) and phosphoric acid (4·5 c.c.). The strips were kept immersed for a period of 17 hours at 37±2°C. These were then washed twice with benzene and twice with rectified spirit and dried in shade.

(*d*) *Dosootie* strips (10″×2½″) weighing 80 gms were soaked in glacial acetic acid (500 c.c.) for 4 hours and the extra acid was removed. Strips were then dipped for 4 hrs in a mixture of acetic anhydride (320 c.c.) benzene (480 c.c.) and traces of perchloric acid. Acetylated strips were then removed, washed and dried in shade.

(*e*) *Dosootie* strips (10″×2½″) were immersed in glacial acetic acid for 24 hours (fabric to acid ratio being 1 : 20). After draining off the extra acid the strips were transferred to the acetylating mixture composed of one part of acetic anhydride, four parts of glacial acetic acid, and perchloric acid (60·00%) 0·03 per cent of the total weight of the acetylating mixture. The mixture was maintained at 30±2°C for 45 minutes. Strips were then washed in tap water and dried in shade.

The breaking strength[7] and the acetyl content[8] of the above acetylated fabrics were determined. The results are summarised in Table 1.

Table 1

Breaking Strength and acetic acid yield of variously acetylated dosootie

Treatment	Breaking Strength in lbs.	Acetic Acid Yield Percentage
As described in (*a*)	178	9·6
As described in (*b*)	166	2·7
As described in (*c*)	173	3·00
As described in (*d*)	168	0·90
As described in (*e*)	159	16·9
Untreated *Dosootie*	161	Nil

The data in Table 1 show that the desired substitution of acetyl groups in the cellulose molecule can be best obtained by using perchloric acid as catalyst by the procedure described at (*e*) above.

B. *Selection of the suitable quantity of perchloric acid as a catalyst for use in partiall acetylation of the fabric*—The effect of the various quantities of the catalyst on partial acetylation of the fabric was studied by adding the catalyst in varying proportions in the acetylating mixture (prepared as given in para A(*e*) earlier). The temperature of the mixture was maintained at 35°C during the treatment (45 minutes). The fabrics were then washed and dried. The resistance of the acetylated fabrics to soil burial was studied. Acetyl content as well as breaking strength were also determined. The results are given in Table 2.

TABLE 2

EFFECT OF DIFFERENT CONCENTRATIONS OF PERCHLORIC ACID ON ACETIC ACID YIELD, BREAKING STRENGTH OF THE TREATED FABRIC AND ITS RESISTANCE TO SOIL BURIAL

Perchloric Acid (60·00 per cent) Percentage on the Total weight of the Acetylating mixture	Initial Breaking Strength in lbs.	Percentage Loss due to treatment in Breaking Strength	Acetic Acid Yield Percentage	Breaking Strength in lbs. ofter Soil Burial	Percentage Loss in Breaking Strength due to Soil Burial Test	Acetic Acid Yield Percentage after Soil Burial
0·05	129	32	28·2	126	2·5	27·2
0·03	134	29	21·2	133	No less	18·6
0·01	164	13	0·3	80	51	8·7
0·005	170	10·5	4·2	18	89·4	1·8
0·003	195	3·2 (Gain)	2·0	13	93·3	Nil
Control (untreated)..	189	Nil	0·1	Nil	100·00	Nil

The results in Table 2 show that the degree of acetylation based on acetyl content increases with increase in the concentration of the catalyst. There is however a progressive loss in breaking strength of the fabric with increasing quantity of the catalyst.

The resistance of the acetylated fabric to microbial deterioration increases with the degree of acetylation. When the concentration of the catalyst is 0·03 per cent of the weight of the acetylating mixture or more, the fabric does not show any appreciable loss in breaking strength under soil burial test.

C. *Effect of* (*i*) *scouring prior to acetylation,* (*ii*) *temperature during acetylation and* (*iii*) *leaching on acetylated fabric*—Investigations were carried out to examine the effect of (*i*) scouring (*ii*) temperature during acetylation and (*iii*) leaching after acetylation on *dosootie.* The fabric was scoured by two methods (*a*) boiling with 1·00 per cent sodium hydroxide solution for 24 hours (8 hours daily for three consecutive days) and (*b*) boiling with 2·00 per cent sodium hydroxide solution for four hours only. Acetylation was investigated separately at 20°C and 30°C. The quantity of the catalyst (perchloric acid 60·00 per cent) and the period of treatment were 0·03 per cent on the weight of the acetylating mixture and 45 minutes respectively in all cases. Leachig was carried out as per details given in Appendix C of the Indian Standards Specification[9]. Acetyl content was deter mined before and after leaching. The results are summarised in Table 3.

Table 3

Effect Of Scouring Temperature And Leaching On Acetic Acid Yield.

	Treatment	Leached/Unleached	Initial		After Soil Burial		
			Breaking Strength in Lbs.	Acetic Acid Yield Percentage	Breaking Strength in lbs.	Percentage Loss in Breaking Strength	Acetic Acid Yield Percentage
Acetylated at 20°C	Acetylated after Scouring with 2·00% NaOH Solution for 4 Hours.	Leached ..	163	14·4	159	Nil	10·8
		Unleached ..	155	17·1	160	Nil	13·7
	Acetylated after Scouring with 1·00% NaOH Solution for 24 Hours.	Leached ..	157	10·9	84	46·5	7·13
		Unleached ..	157	8·5	98	37·5	8·19
	Unscoured Fabrics Acetylated.	Leached ..	168	15·3	163	Nil	9·7
		Unleached ..	156	15·1	158	Nil	12·6
	Unscoured and Unacetylated	Leached ..	170	Nil	23	86·4	Nil
		Unleached ..	162	Nil	43	73·4	Nil
Acetylated 30°C	Acetylated after Scouring with 2·00% NaOH Solution for 4 Hours.	Leached ..	156	18·1	153	Nil	18·8
		Unleached ..	153	15·6	149	Nil	19·90
	Acetylated after Scouring with 1·00% NaOH Solution for 24 Hours.	Leached ..	161	8·4	55	65·2	5·60
		Unleached ..	153	7·9	69	54·9	7·2
	Acetylated without scouring.	Leached ..	162	18·4	163	Nil	18·8
		Unleached ..	159	16·9	160	Nil	19·9
	Unscoured and Unacetylated.	Leached ..	176	Nil	19	89·2	Nil
		Unleached ..	168	Nil	37	77·9	Nil

The results in Table 3 show that scouring of the fabric prior to acetylation with 2·0% NaOH solution for four hours accelerate substitution of acetyl group while scouring with 1·0% NaOH solution for 24 hours brings about retardation.

It has been observed in Table 2 that when the quantity of perchloric acid (60·00%) was 0·03 per cent and the temperature of acetylating mixture was 35°C, there was a considerable loss in breaking strength of the acetylated fabric. The loss in breaking strength is considerably reduced when acetylation is carried at 30° or 20°C (Table 3). Acetylation whether carried at 30°C or 20°C does not materially affect the acetyl content or the breaking strength of the acetylated fabric.

D. *Effect of the repeated use of the acetylating mixture with and without the addition of fresh catalyst and increase in period of treatment on the breaking strength and the acetic acid of the acetylated fabric.*—It was of interest to examine the possibility of acetylation with the used acetylating mixture. The effect of the following factors was studied (*a*) addition of fresh catalyst (*b*) increase in the period of treatments and (*c*) increase in the quantity of the catalyst. Acetylations were carried out at 25—30°C. The results are summarised in Table 4.

TABLE 4

EFFECT OF REPEATED USE OF ACETYLATING MIXTURE, INCREASE IN PERIOD OF TREATMENT, CONCENTRATION OF CATALYST ON THE ACETIC ACID YIELD AND BREAKING STRENGTH OF THE ACETYLATED FABRICS

Percentage of the Catalyst	Period of the treatment in Minutes	Acetylating Mixture							
		Fresh		Once Used		Twice used		Thrice used	
		% Loss in Breaking Strength	% Acetic Acid Yield	% Loss in Breaking Strength	% Acetic Acid Yield	% Loss in Breaking Strength	% Acetic Acid Yield	% Loss in Breaking Strength	% Acetic Acid Yield
0·03	45	4·0	15·7	5·5	15·4	19·7	13·7	16·0	12·8
0·03	90	10·0	22·2	11·7	22·3	32·7	19·0	33·0	14·1
0·03	135	14·0	25·1	13·0	23·6	38·2	21·9	45·0	12·8
0·06	45	10·0	20·3	19·7	20·1	22·2	21·5	30·0	12·1
0·10	45	13·0	28·2	20·3	23·6	43·8	22·3	55·0	14·4

Acetylation when carried with once used mixture without fresh addition of the catalyst, the acetic acid yield of the acetylated fabric was 2·35 per cent only.

It will be observed from Table 4 that the acetyl content of the acetylated fabric is very low when the treatment is carried out with once used acetylating mixture without the fresh addition of the catalyst. However, with fresh additions of the catalyst, acetyl content increases. Acetyl content also increases with increase in the period of acetylation.

When the same acetylating mixture is used repeatedly with the fresh additions of catalyst, the fabric so acetylated shows progressively increasing loss in the breaking strength with the increase in the number of acetylations. Increase in the period of acetylation (using the same mixture with fresh additions of catalyst) also has an adverse effect on the breaking strength of the fabric. The acetyl content gradually goes on decreasing with the repeated use of the acetylating mixture even with fresh additions of the catalyst.

E. *Effect of ultraviolet light on acetylated fabric*—To examine the effectiveness of acetylation against actinic degradation, the acetylated *dosootie* was exposed to ultraviolet light from a mercury arc lamp* kept at a distance of 30·0 cms for 48·0 hours both before and after leaching. The results are summarised in Table 5. The lamp emits a powerful spectrum from a 2,200A° in the ultraviolet to 20,000A° in the infra red region, with light spectral lines at 2,536A° and 4,538A°. The fabric was placed directly under the lamp at a distance of 30 cms. Rise in temperature of the fabric was prevented by cooling with a continuous blast of cold air. The temperature was maintained at 31±1°C.

It is seen from Table 5 that scoured as well as unscoured acetylated fabrics registered a high loss (72—76 per cent) in breaking strength after exposure to mercury arc lamp while the untreated fabric showed only a loss of 38—43 per cent. Thus partial acetylation apart from conferring protection appears to accelerate degradation by ultraviolet light.

* This lamp manufactured by Hanovia Ltd. Slough England.

TABLE 5

EFFECT OF ULTRA-VIOLET LIGHT FROM A MERCURY ARC LAMP ON ACETYLATED DOSOOTIE

Treatment	Leached						Unleached					
	Unexposed			Exposed			Unexposed			Exposed		
	B.S. in lbs.	Copper Number	A.Y.	Percentage Loss in B.S.	Copper Number	A.Y.	B.S. in lbs.	Copper Number	A.Y.	Percentage Loss in B.S.	Copper Number	A.Y.
Unscoured *Dosootie* Not acetylated.	164	0·28	Nil	42	1·62	Nil	166	0·42	Nil	38	1·68	Nil
Unscoured *Dosootie* Acetylated	162	0·51	11·10	72	4·74	10·20	165	0·58	11·3	72	4·83	10·8
Unscoured *Dosootie* Not acetylated.	155	0·07	Nil	43	2·19	Nil	153	0·07	Nil	40	1·68	Nil
Scoured *Dosootie* Acetylated.	160	0·26	10·7	76	6·91	10·00	163	0·21	10·8	72	7·38	10·4

Legend: B.S.=Breaking Strength. A.Y.—Acetic Acid Yield percentage.

Copper Number was Determined according to the method of Clibbens and Geake [10].

F. *Effect of weathering on partially acetylated fabrics*—For confirmation of the laboratory findings, randomised out door exposure trials of acetylated *dosootie* were carried out at Kanpur (Lat. 26° 2B 'N, Long. 80° 22' E, altitude 416 ft. m.s.l.) representing hot-dry climate for a period of eight months. Wooden frames with fabrics mounted on them were exposed on steel racks at four feet above ground at an angle of 45° facing south in the D.R.L.(S) exposure yard. Samples were withdrawn every two months and were tested for breaking strength, copper number and acetyl content. The results are given in Table 6.

The results given in Table 6 show that partial acetylation does not confer any protection against outdoor weathering. Both treated as well as untreated samples showed nearly the same degree of loss in breaking strength after eight months of exposure to weathering. Acetic acid yield showed gradual decline with the increase in the period of exposure. Copper number increased with increase in the period of exposure.

DISCUSSION

Selection of a suitable catalyst and process of acetylation—Out of the various methods described in literature for the acetylation of cotton cellulose, those making use of pyridine [11] phosphoric acid [11,12] and perchloric acid [13,14] as catalysts were primarily selected for acetylating *dosootie*. The results presented in Table 1 show that the method followed by Cooper *et al* [14] with a little modification in the quantity of perchloric acid (60·00%) gives satisfactory substitution (measured in terms of acetyl content).

Effect of the quantity of perchloric acid used as catalyst in acetylating mixture on the acetyl content and breaking strength of the treated fabric—Cooper *et al* [14] have made use of 0·10 per cent perchloric acid (60·00 per cent) on the weight of the acetylating mixture at 18°C and obtained an acetyl content of 21-22 per cent. The results presented in Table 2 indicate that higher the quantity of catalyst, the higher is the acetyl content and loss in breaking strength of the acetylated fabric at 35°C. A concentration of 0·03 per cent of

TABLE 6

EFFECT OF WEATHERING ON ACETYLATED DOSOOTIE

Treatments	Period of Weathering													
	Initial			2 Months			4 Months		6 Months			8 Months		
	B.S.	Copper Number	A.Y.	% Loss In B.S.	Copper Number	A.Y.	%Loss in B.S.	Copper Number	%Loss in B.S.	Copper Number	A.Y.	%Loss in B.S.	Copper Number	A.Y.
Unscoured *Dosootie* (Not acetylated).	165	0·42	Nil	15·7	1·35	Nil	25·4	1·88	43·0	2·39	Nil	58·0	2·55	Nil
Unscoured *Dosootie* Acetylated.	163	0·58	11·3	15·3	1·41	11·05	18·4	2·00	39·9	2·51	2·26	55·0	2·87	1·61
Scoured *Dosootie* (Scouring Done with 1% NaOH for 24 Hours.)	169	0·07	Nil	9·5	0·92	Nil	20·1	1·17	39·0	1.89	Nil	56·0	2·78	Ni
Scoured *Dosootie* Acetylated.	163	0·21	10·8	9·8	1·18	10·7	14·1	1·41	34·9	2·34	1·58	62·0	2·43	1·16

Legend = B.S.—Breaking Strength A.Y.—Acetic Acid Yield Percentage.
Acetic Acid Yield of Samples Drawn after 4 months was not determined.

perchloric acid on the weight of the acetylating mixture is however found satisfactory in terms of acetyl content, breaking strength and the resistance of the acetylated fabric to micro-organisms in soil burial test.

Effect of scouring prior to acetylation, temperature during acetylation and leaching on acetylated fabric—According to Coopper *et al* [14] the presence of noncellulosic materials in the cotton fibre, interferes with the reaction. They have suggested desizing to be done by boiling with 2·0 per cent caustic soda solution for four hours to remove starch and other impurities. In the experiments reported in the paper (Table 6) scouring was done in two ways (*i*) boiling the fabric with 1·0 per cent caustic soda solution for 24 hours (8 hours daily for three consecutive days) and (*ii*) boiling with 2·0 per cent caustic soda solution for four hours only. After thorough washings the scoured as well as unscoured fabrics were acetylated at 20° and 30°C for 45 minutes. The acetyl content of the fabric scoured with 2·0 per cent caustic soda solution and that of unscoured fabric were not much different. The fabric scoured with 1·0 per cent caustic soda solution when acetylated gave less acetyl content. The breaking strength of the acetylated fabrics in the three cases was more or less the same. Acetylated fabrics with an acetyl content of the

order of 14·0 per cent or more withstood soil burial test. Acetylation whether carried at 20° or 30°C had no material effect on the substitution of acetyl groups or breaking strength of the acetylated fabric. Leaching does not affect the acetyl content, breaking strength and the resistance of the acetylated fabric to soil burial.

Effect of repeated use of the acetylating mixture with and without the addition of fresh catalyst and increase in the period of treatment on the acetyl content and breaking strength of the acetylated fabric—With the fresh addition of the catalyst perchloric acid and the acetic anhydride the acetylating mixture has been reused by Cooper *et al*[14]. The results given in Table (4) indicate that without fresh addition of the catalyst, the acetyl content is very much lowered. The acetyl content, with fresh additions of the catalyst, though satisfactory, gradually goes on decreasing, if the mixture is used for a number of times. The loss in breaking strength of the fabric acetylated goes on increasing with the use of the acetylating mixture for a number of times with fresh additions of the catalyst. With increase in the period of treatment or quantity of perchloric acid, there is an increase in acetyl content and the loss in breaking strength.

Effect of ultraviolet light and weathering on acetylated fabric—The effect of exposure to dry heat on acetylated fabrics in an oven at 130° and 160° C has been studied by Cooper *et al.*[14] They have observed that the acetylated cotton would require more than seven times as long to become weakened to half strength at 160°C. The results presented in Table 5 show that acetylated *dosootie* when exposed to ultraviolet light (from an Hanovia Mercury Arc Lamp for a period of 48 hrs) from a distance of 30 cms undergoes greater deterioration (72—76 per cent) as compared to the nonacetylated dosootie (38—43 per cent). The copper number data also confirm this finding.

During weathering for a period of 8 months in hot dry climate of Kanpur, it was observed (Table 6) that the acetylated as well as nonacetylated *dosootie* suffer more or less the same loss in breaking strength. Copper number figures also confirm that the loss in acetylated as well as nonacetylated dosootie is more or less the same after 8 months weathering.

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