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Studies on the Fibrous Acetylation of Cotton. I.

Liquid Phase Acetylation*

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Cotton cloth was acetylated to various degree of acetylation by liquid phase method. Various catalysts and diluents were used, and their effects on the velocity of acetylation, the stability of the acetylation bath and the fiber property were compared. It was shown that sulfuric acid was most favorable as catalyst if used in the form of sulfo acetic acid.

When cotton cloth pre-treated with acetic acid was immersed in the acetic anhydride solution of sulfuric acid (this solution was pre-heated at 95°C for 5 min.) and was heated at 40–50°C in air after squeezed with rolls to about 70% pick up, it could be acetylated continuously in short time (1–1.5 min) up to the degree of acetylation of 20–25% without any loss of strength (semi-liquid phase method or so-called padding method).

INTRODUCTION

In recent years, the fibrous acetylation of cotton has been actively studied in U. S. A. In Japan a systematic study of this problem was started by Sakurada¹⁾ about thirty years ago, which has been developed to the later studies of the fibrous acetylation of viscose rayon staple^{2),3)}. The results of these studies are now being applied to the production of the acetate fiber called Alon in Toho Rayon Co., which is made by the fibrous acetylation of high tenacity viscose rayon staple by gaseous phase method.

As described above, studies of the fibrous acetylation of cotton have been reported in U. S. A. in some papers, but the detail on the properties of the acetylated cotton and the effect of the acetylation method have not been sufficiently studied.

On the chemical reaction of fibrous acetylation Sakurada and Sakaguchi have reported their research in some papers⁴⁾. Referring to their research, we carried out the following research mainly from the industrial standpoint on the various conditions of the liquid phase acetylation and the effect on the properties of the acetylated cotton.

EXPERIMENTAL AND DISCUSSION

1. General View of the Effect of Various Catalyst and Diluent on the Liquid Phase Fibrous Acetylation of Cotton

* This work was reported in more detail partly with Y. Sakaguchi and F. Kimura in the *Journal of the Society of Textile and Cellulose Industries, Japan*, 16, 1020, 1026 (1960).

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In general method of the liquid phase fibrous acetylation, cotton fiber is immersed in glacial acetic acid and then acetylated in the acetylation bath liquor composed of acetic anhydride, catalyst and diluent. From the previous results⁴⁾, the effect of various diluents and catalysts on the liquid phase fibrous acetylation can be compared as shown in Table 1. With re-

Table 1. The qualitative comparison of the effect of various diluents and catalysts on the liquid phase fibrous acetylation of cotton.

Diluent	Trichlene		Benzene		Acetic acid	
	Sulfuric acid	Perchloric acid	Sulfuric acid	Perchloric acid	Sulfuric acid	Perchloric acid
Catalyst	Sulfuric acid	Perchloric acid	Sulfuric acid	Perchloric acid	Sulfuric acid	Perchloric acid
Reaction velocity	Medium	Largest	Medium	Large	Small	Medium
Effect of the concentration of acetic anhydride on the acetylation	Smallest	Medium	Small	Medium	Small	Medium
Stability of the acetylation bath	Stable	Unstable	Stable	Unstable	Stable	Almost stable
Fiber damage	None	Slightly	None	Slightly	Somewhat large	Large

gard to the diluent, the order of the reaction velocity is as follows :

trichlene > benzene » acetic acid

When acetic acid is used, the shrinkage and the strength loss of fiber become considerable as the acetylation progresses. Benzene is inflammable. Trichlene is not inflammable, comparatively low cost, and gives the highest reaction velocity, so it seems to be most advantageous to use it from the industrial standpoint.

As to the catalyst, perchloric acid seems to give higher reaction velocity than does sulfuric acid. But as shown later, sulfuric acid gives satisfactorily high reaction velocity if it is used in the form of sulfoacetic acid, and gives more stable acetylation bath than perchloric acid does, so it seems to be more favorable to use sulfuric acid as catalyst. The effect of the various condition of acetylation will be discussed in more detail in the following.

2. The Effects of the Methods of Acetylation and the Stability of the Acetylation Bath

The results obtained by using various kinds of catalyst are described in the following. In all cases the cotton cloth was pre-treated with glacial acetic at 25°C for about 1 hr. The cotton cloth used in this work is scoured and bleached 30's calico (not mercerized), which was furnished by the Toyo Spinning Co.

a. **Sulfuric acid catalyst.** When sulfuric acid is used as the catalyst, fiber will suffer remarkable damage if sulfuric acid remains in free form in the acetylation bath. So in this work sulfuric acid was mixed at first with acetic anhydride and heated to 95°C. Sulfuric acid was converted to

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sulfoacetic acid ($\text{HO}_2\text{S}\cdot\text{CH}_2\text{COOH}$) in this process. After cooling the diluent was added. In this case the time of heating of the mixture of sulfuric acid and acetic anhydride has some influences upon the acetylation power and stability of acetylation bath. Some examples are shown in Table 2.

Table 2. Relation between the velocity of acetylation and the heating time of the mixture of sulfuric acid and acetic anhydride.

Composition of mixture ^{a)}		Time of heating at 95°C (min.)	0	10	30	120	
H_2SO_4 (c.c.)	$(\text{CH}_3\text{CO})_2\text{O}$ (c.c.)						
1	99	Degree of ^{b)} acetylation	3 hr ^{c)}	39.2	45.4	46.5	40.8
		(mole %) ^{d)}	16 hr	—	75.0	75.4	69.2
3	97	Degree of acetylation	1 hr	36.6	56.7	53.5	43.0
		(mole %)	2.5 hr	49.7	73.7	70.6	62.5

^{a)} Acetylation bath is composed of 15 cc of above mixture and 85 cc of trichlene.

^{b)} Temperature of acetylation: 25°C, Liquor ratio: 30.

^{c)} Time of acetylation.

^{d)} Mole % means how many OH groups in 100 OH groups of cellulose molecules are acetylated.

It is shown that in these cases the heating time of about 10 min. gives the highest velocity of acetylation and stability of acetylation bath. It was found qualitatively by using BaCl_2 solution that free sulfuric acid did not exist in the bath at the heating time of about 5 min.

The deterioration of the acetylated fiber can be avoided when sulfuric acid is applied in this way. Moreover, the velocity of acetylation is increased nearly equal to that for perchloric acid. Therefore in our work sulfuric acid was chiefly used after mixed with acetic anhydride and heated at 95°C for about 10 min.

b. Perchloric acid catalyst. It was found that the acetylation power of acetylation bath containing perchloric acid as catalyst was remarkably affected by various factors. Table 3 shows the results of acetylation when perchloric acid and acetic anhydride are mixed and stored at room temperature or heated to 90°C and used as acetylating liquor after adding trichlene.

Table 3. Decreasing of acetylation power of the acetylation bath containing perchloric acid by the storing at room temperature or heating to 90°C.

Storing time (hr)		1/6	2	24	48	144	90°C, 30 min.
		Degree of acetylation (mole %) ^{a)}	10 min. ^{b)}	53.9-57.0	45.5	23.4	22.6-37.3
	30 min.	75.6-77.0	73.4	44.9	37.3-49.1	26.3	—

^{a)} Acetylation bath is composed of 15 cc of acetic anhydride, 85 cc of trichlene, 0.01 N perchloric acid; liquor ratio 30; temperature 25°C.

^{b)} Time of acetylation.

It was found that the acetylation power was remarkably decreased by storing or especially by heating.

It was confirmed that this decrease of acetylation power should be attributed to the decomposition of perchloric acid. The change of the concentration of perchloric acid in various solvents was pursued quantitatively and it was found that the concentration was remarkably decreased in acetic anhydride by storing at room temperature or especially by heating to 90°C, though the variation was little in water, trichlene or acetic acid. It was supposed that this decomposition of perchloric acid in acetic anhydride should be caused by some reducing material contained in acetic anhydride, which was supposed probably to be acetaldehyde.

Table 4 shows the effect of liquor ratio and the kind of materials of the vessel of acetylation bath on the velocity of acetylation. It is shown that these effects are rather large. The effect of liquor ratio is probably due to selective absorption of perchloric acid by the cotton fiber swelled with acetic acid. These effects were found to be little when sulfuric acid was used as catalyst.

Table 4. The effect of the liquor ratio and the kind of material of the vessel of acetylation bath on the velocity of acetylation (HClO_4 catalyst).

Material of vessel	Liquor ratio	Degree of acetylation (mole %)
Glass	30	18.2
	50	18.2
	100	34.1
	1000	38.3
Stainless steel	30	14.0
	100	27.8

c. **Zinc chloride catalyst.** Zinc chloride was dissolved into acetic anhydride and used as the acetylating liquor with or without heating to 95°C for one hour before the adding of trichlene. The velocity of acetylation in 75°C was almost the same in either case, but the cotton cloth was discoloured more markedly when zinc chloride solution was previously heated. So it is favourable to dissolve zinc chloride into acetic anhydride at room temperature or at comparatively low temperature and add diluent to it. But the solubility of zinc chloride in acetic anhydride is limited within some extent. Thus the acetylating liquor contained acetic anhydride 15 cc/100 cc and 0.03 mole/l of zinc chloride showed white turbid, but it became transparent when cotton cloth containing acetic acid was put into it.

The acetylating power of the acetylation bath containing zinc chloride as catalyst was found to be affected by the liquor ratio.

3. Acetylation under Various Conditions

Scoured and bleached cotton cloth was acetylated under various conditions, and some properties were examined. Some examples of the results are shown in following tables. In these cases the pretreatment of cotton cloth with acetic acid was carried out at 25°C for about 1 hr, but this time will be shortened to about 2 min. if the temperature of acetic acid is raised to 90°C.

a. Sulfuric acid as catalyst, trichlene as diluent.

Table 5 shows the result obtained when the acetylation was carried out at 40°C for various time using the acetylation bath composed of acetic anhydride 15, trichlene 85, sulfuric acid 0.23 (volume ratio). In this case sulfuric acid was mixed with acetic anhydride and preheated at 100°C for 2 hr.

Table 5. Degree of acetylation and properties of acetylated cotton cloth using sulfuric acid as catalyst and trichlene as diluent.

Time of acetylation (hr)	Degree of acetylation (mole %)	Shrinkage in acetylation (%)		Tensile strength ^{a)} (Warp)		Elongation (Warp) (%)	Stiffness ^{b)}	Crease ^{c)} recovery (%)
		Warp	Filling	(kg/cm)	(g/Yarn)			
0	0	—	—	8.3	277	16.8	1.57	39.2
1/4	28	4.0	1.1	7.1	237	16.4	1.52	45.7
1/2	35	6.0	4.0	6.9	226	17.0	1.58	47.0
1	44	7.5	6.0	7.9	246	19.0	1.62	46.6
2	55	9.7	7.3	8.2	265	23.0	2.04	44.0
4	63	13.2	7.7	8.1	245	25.0	3.09	43.7

^{a)} Tensile strength was measured with Schopper Tester using test piece of cloth of 1 cm width. As cloth shrank to various extent during acetylation, the number of warp yarn in 1 cm width of each acetylated cloth was counted and tensile strength per warp yarn was calculated.

^{b)} Measured with Clark Softness Tester.

^{c)} Monsanto method; 500 g weight was applied for 5 min. and the crease angle was measured at 2 min. after unloading.

The thickness of cloth was increased by acetylation and full hand was given. Stiffness and elongation were increased when acetylated to high degree. Crease recovery was improved to some extent by acetylation. Tensile strength and tearing strength showed some decrease. When acetylation was carried out under more mild condition, e. g. at 26°C, the tensile strength did not decrease and the lowering of tearing strength was reduced even if the degree of acetylation reached to 60 mole %.

b. Perchloric acid as catalyst, trichlene as diluent.

Table 6 shows the result obtained when the acetylation was carried out at 25°C using the acetylation bath of acetic anhydride 15, trichlene 85 (vol. ratio), perchloric acid 0.003N. In this case tensile and tearing strength were considerably decreased, but if acetylation was carried out under more mild

Table 6. Degree of acetylation and properties of acetylated cotton cloth using perchloric acid as catalyst and trichlene as diluent.
(Acetylation bath—acetic anhydride 15, trichlene 85, perchloric acid 0.003 N ; 25°C)

Time of acetylation (min.)	Degree of acetylation (mole %)	Shrinkage in acetylation (%)		Tensile strength ^{a)} (Warp)		Elongation (Warp) (%)	Tearing strength ^{b)} (g)	Stiffness ^{a)}	Crease recovery (%)
		Warp	Filling	(kg/cm)	(g/Yarn)				
0	0	—	—	8.3	277	16.8	860	1.57	39.2
5	30	2.0	2.7	7.0	236	15.2	764	1.33	46.0
10	39	4.0	3.3	6.0	200	13.2	752	1.76	48.5
15	52	6.0	4.7	6.4	200	15.8	604	2.08	44.9
30	63	9.0	5.3	5.8	181	16.4	532	2.40	49.6
60	71	13.0	8.0	5.4	168	20.4	416	3.29	47.5
90	75	14.0	8.0	3.4	103	16.2	296	2.94	48.8

^{a)} Test method is the same as described in Table 4.

^{b)} Tongue method.

Table 7. Degree of acetylation and properties of cotton cloth acetylated under more mild condition using perchloric acid as catalyst and trichlene as diluent.
(Acetylation bath—acetic anhydride 15, trichlene 85, perchloric acid 0.001 N ; 10–12°C)

Time of acetylation (hr)	Degree of acetylation (mole %)	Shrinkage in acetylation (%)		Tensile strength (Warp)		Elongation (Warp) (%)	Tearing strength (g)	Stiffness	Crease recovery (%)
		Warp	Filling	(kg/cm)	(g/Yarn)				
0	0	—	—	8.9	297	16.4	1040	1.59	36.8
1/2	9.2	1.0	0.7	9.5	306	16.2	872	1.45	40.8
1	17.3	1.5	1.3	8.4	272	16.0	708	1.56	43.7
2	26.0	2.0	2.7	9.1	272	16.2	960	1.44	40.7
4	32.8	2.0	4.0	8.5	266	17.4	688	1.78	41.1
6	49.5	8.5	6.0	9.2	288	20.0	724	3.22	45.2
18	64.0	12.0	8.0	8.5	258	23.8	652	3.05	39.3

condition, e. g. 0.001N HClO₃, 10–12°C, the decrease of strength was remarkably reduced as shown in Table 7. But generally perchloric acid seems to have a tendency to give more damage to fiber and more unstable acetylation bath than sulfuric acid as described above, so it is supposed more favorable to use sulfuric acid in the state of sulfo acetic acid.

c. Perchloric acid as catalyst, acetic acid as diluent.

Table 8 shows some results obtained using perchloric acid as catalyst and acetic acid as diluent. It is shown generally that, when acetic acid is used as diluent, the acetylating velocity is slower and the lowering of strength and shrinkage of cloth are larger than in the case of trichlene diluent.

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Table 8. Degree of acetylation and properties of cotton cloth acetylated at 25°C using perchloric acid as catalyst and acetic acid as diluent.

Acetylation bath			Time of acetylation (hr)	Degree of acetylation (mole %)	Shrinkage in acetylation (%)		Tensile strength (warp)		Elongation (Warp) (%)	Tearing strength (g)
(CH ₃ CO) ₂ O (Vol. %)	CH ₃ COOH (Vol. %)	HClO ₄ (N)			Warp	Filling	(kg/cm)	(g/Yarn)		
			0	0	—	—	8.5	283	16.0	860-1040
15	85	0.003	1/2	16.8	2.0	2.0	7.8	260	17.4	—
			1	20.4	2.5	2.7	7.6	245	17.4	—
			2	25.8	4.5	3.3	7.3	235	18.6	—
25	75	0.01	1/2	26.1	6.0	3.3	6.5	203	17.2	668
			1	37.8	13	8.7	7.0	219	17.6	732
			2	59.4	22	19	7.6	224	23.2	776
			20	75.6	25	20	6.9	209	22.4	572

4. Acetylation by the Semi-liquid Phase Method (so-called Padding Method)

a. Acetylation in sealed tube. After many preliminary experiments we found that cotton cloth could be acetylated up to 20-30 mole % in short time, if cotton cloth, pre-treated with acetic acid, was heated in air or vapor of acetic anhydride in sealed tube after immersed in acetic anhydride

Table 9. Semi-liquid phase (so-called padding) method of acetylation using stainless steel sealed tube.

(Acetylation bath—sulfuric acid 1.0 cc, acetic anhydride 100 cc. Weight cotton cloth—about 0.4 g. Inner volume of sealed tube—about 130 cc)

Heating in tube		Degree of acetylation (mole %)	Tensile strength (Warp) (g)	Elongation (%)
Temp. (°C)	Time (min)			
—	0	0	326-348	6.0-7.1
	0*	6.1	353	7.7
40	3	20.0	318	7.4
	7	23.0	297	7.3
	15	26.7	308	8.4
	30	32.4	322	7.7
	2	22.4	299	7.3
50	3	25.2	319	8.1
	7	29.0	317	8.5
	15	30.6	278	8.8

* Cloth was immersed in acetylating solution at 20°C for 1 min. but was not heated in sealed tube.

solution of catalyst, e. g. sulfuric acid, and squeezed (so-called padded).

Table 9 shows the result obtained using stainless steel sealed tube. Cotton cloth was pretreated in acetic acid at 25°C for 1 hr (this time might be shortened to about 2-5 min. if acetic acid was used at 100°C), then immersed in the acetic anhydride solution of sulfuric acid (this solution was preheated at 95°C for 5 min.) at 20°C for 1 min. and heated in sealed stainless steel tube after squeezed with stainless rolls to about 70% pick up. It was shown that by this way cotton cloth could be acetylated to 20-25 mole % in 2-3 min. without any loss of tensile strength.

b. Continuous acetylation by semi-liquid phase method. Next, cotton cloth was continuously acetylated in small scale by semi-liquid phase method. Cotton cloth pre-treated with acetic acid was immersed in acetic acid solution of sulfuric acid in small stainless steel jigger and was rolled up through the heating chamber after squeezed with stainless steels. The roll up velocity was 83 cm/min, and the immersing or heating time was changed by altering the way length of cloth in acetylating liquid or in heating chamber. Reaction was stopped by pouring water on cloth immediately after it came out the heating chamber.

Some results thus obtained were shown in Table 10. It was shown by

Table 10. Continuous acetylation by semi-liquid phase method.

H ₂ SO ₄ -(CH ₃ CO) ₂ O*		Heating in reaction chamber		Degree of acetylation (mole %)	Tensile strength (Warp)	
Temp. (°C)	Time (min)	Temp. (°C)	Time (min)		(kg/cm)	(g/Yarn)
				0	6.4—8.4	200—263
24	1	41—42.5	1	19.9	6.5	203
24	"	53—54	"	24.7	6.8	219
26—27	"	59—62.5	"	26.0	7.1	222
25	"	42—43	1.5	21.9	6.3	191
25	"	47—49	"	25.0	8.4	254
22	"	56—58	"	26.8	7.0	206
25	0.5	50	"	22.4	5.4	168

* Sulfuric acid 2 cc, acetic anhydride 100 cc.

this method that cotton cloth could be acetylated up to about 25 mole % in 1-1.5 min. without much decrease of strength.

The semi-liquid phase method of acetylation described above has following advantages compared with the ordinary liquid phase method.

- 1) Time for acetylation is shortened.
- 2) Diluent is not needed.

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3) Most of acetic anhydride contained in cotton cloth is consumed for reaction.

4) Acetic acid produced by the acetylation reaction does not enter in the acetylating solution.

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