Studies on the Fibrous Acetylation of Cotton. (II)

Properties of the Acetylated Cotton Prepared by the Liquid Phase Method*

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Various properties of the acetylated cotton prepared by the liquid phase method using sulfuric acid as catalyst, were examined in detail. It was shown that the thermoplasticity, heat-setting property, dimensional stability, anti-soiling property, rate of drying, electrical resistance, acid and rot resistance were remarkably improved by the acetylation.

Further, the influence of catalyst on properties of the acetylated cotton was studied, using H_2SO_4, $ZnCl_2$ and $HClO_4$ as catalyst. The acetylated cotton prepared with $ZnCl_2$ catalyst has better acid-resistance and less solubility in chloroform and that prepared with $HClO_4$ catalyst has higher moisture absorbency than those prepared with the other catalysts.

Part I. Properties of Cotton Acetylated by Use of Sulfuric Acid Catalyst

INTRODUCTION

In a previous paper[1] we reported the method of the liquid phase acetylation of cotton. In this work various properties of the acetylated cotton prepared by the liquid phase method using sulfuric acid as catalyst were examined. It has been reported in U.S.A.[2~4] that acetylated cotton has shown excellent heat-, rot- and acid-resistance, but many other properties have not been made clear in detail. It is the object of this work to examine the various properties of acetylated cotton, especially to find out the advantage as textile for apparel or domestic uses.

EXPERIMENTAL AND DISCUSSION

In this part of the work the acetylation was carried out using the acetylation bath composed of acetic anhydride, sulfuric acid and trichlene. Sulfuric acid was added to the bath after previous heating with acetic anhydride as described in the previous paper[1]. Scoured and bleached cotton cloth, which had been used in the previous work[1], was used as the raw material.

1. Tensile Property

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It was described in the previous report[1] that cotton fabric could be acetylated to high degrees of acetylation under suitable conditions without the decreases of tensile strength. As an example, Table 1 shows the result obtained with the acetylated cotton fabric prepared under a mild condition. It is shown that the tensile strength of fabric does not decrease until high degree of acetylation is reached. Ultimate elongation increases as the degree of acetylation increases.

Table 1. Tensile property of the acetylated cotton fabric.

Sample No.	The acetylation condition		Degree of acetylation (mole%)	Tensile strength (warp)		Elongation (warp) (%)
	temperature (°C)	time (hrs)		(kg/cm)	(g/yarn)	
Control	—	—	0	9.0	282	8.9
424	15—16	1	29.8	9.0	282	8.6
425	15—16	2	41.1	9.2	287	10.0
642	15—16	4	52.8	9.6	290	12.5
427	15— 9	24	74.3	10.0	316	14.5

Acetylation bath : acetic anhydride 15, trichlene 85, sulfuric acid 0.23/100cc (acetic acid and acetic anhydride was mixed at first and heated to 95°C for 10 min.).
Tensile strength was measured with Schopper Tester using 10 test pieces of 1cm width. In the control test 50 test pieces were used.

When the acetylation was carried out at 20°C using the same acetylation bath as described in the table, it was found that the tensile strength of fabric was not decreased, though it was somewhat decreased in the case of 25°C. When the concentration of sulfuric acid was doubled the reaction rate was increased, but the tensile strength of fabric was not decreased, if the acetylation was carried out at 15°C.

2. Water and Moisture Absorption

Figs. 1 and 2 show the relation between the water and moisture absorption and the degree of acetylation of the cotton acetylated under tension or under no tension. Both the water and moisture absorption were decreased with increasing the degree of acetylation till about 30 mole%, but in the region of higher degrees of acetylation the moisture absorbency was rather increased. It may

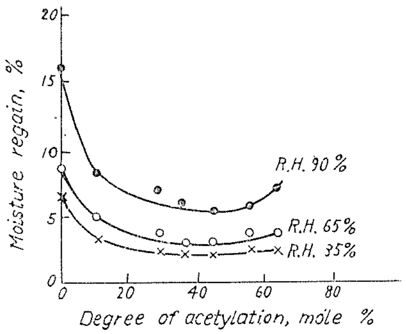


Fig. 1. Moisture regain of acetylated cotton fabrics at different relative humidity.

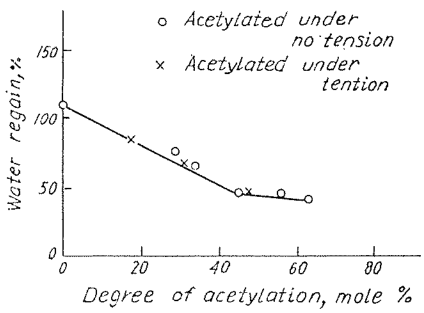


Fig. 2. Water absorption of acetylated cotton fabrics.

be supposed that, until about 30 mole% acetylation, the hydroxyl groups in the amorphous region are acetylated, thus resulting in a decrease of the moisture absorption, while in the region of higher degrees of acetylation the reaction would proceed into the crystalline region and, as the result, a region which may absorb moisture would be widened. Fig. 1 shows the result on the fabric acetylated under no tension, but in the case of the acetylation under tension almost the same result was obtained.

3. Specific Gravity

In Fig. 3 the specific gravity of the acetylated cotton is plotted against the degree of acetylation. The specific gravity has been measured by a submerged-float method using carbon tetrachloride-benzene mixture. The experimental points appear fall on a straight line having an inflection point in the range of 35-40 mole%. In other words, it decreases proportionally with increasing the degree of acetylation, but the rate of the decrease retards when the acetylation exceeds 35-40 mole%.

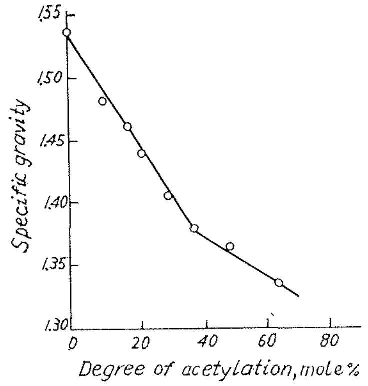


Fig. 3. Specific gravity of acetylated cotton.

4. Thermal Property

a) Mechanical property at high temperature. Several properties were measured at the range from room temperature to 250°C using a single fiber as a test piece. The tensile strength and Young's modulus were decreased and elongation was increased with increasing temperature. The result suggests that the increase of thermoplasticity was caused by the acetylation.

b) Heat setting property. The effect of acetylation on heat setting property was examined by an iron test. The degrees of acetylation of sample used in this test were 8.6, 15.8 and 31.7 mole%, and a commercial acetate fabric was used as a reference. It was found that the heat setting property of cotton was increased with increase of the degree of acetylation. The fabric of about 30 mole% acetylation exhibited an excellent heat setting property comparable to that of the acetate fabric.

5. Flammability

Flammability was measured by an ASTM tester. The state of combustion of the acetylated fabric was nearly equal to that of a sample tested as a control, while the rate of combustion of the acetylated sample was slower than that of the control fabric.

6. Shrinkage by the Boiling in Water

Both cotton fabrics acetylated under tension and under no tension did not show any appreciable shrinkage by boiling them in water or soap solution, and it is considered that they have high dimensional stability.

7. Soiling and Deterging

The cotton and acetylated cotton fabrics were soiled using an artificial soiling medium (a mixture of carbon black, liquid paraffin, beef tallow and carbon tetrachloride) and washed with a 0.5% Marseilles soap solution at 40°C for 4 min. By this test it was generally recognized that the acetylated cotton fabric was more difficult to be soiled but easier to be de-soiled in comparison with the unacetylated samples. The degree of soiling was measured by an optical method.

8. Drying and Wetting Property

The drying property of cotton, acetylated cotton and acetate fabrics were tested by measuring their rate of drying. Fig. 4 shows the results obtained in the drying at RH 43%. Acetylated cotton fabrics showed higher drying rate than cotton fabric. Wetting property was decreased by the acetylation.

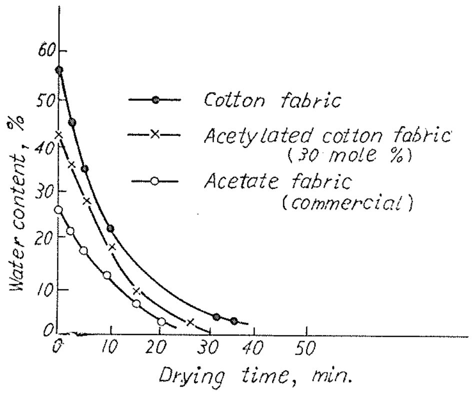


Fig. 4. Drying property of acetylated cotton fabrics.

9. Abrasional Resistance

The flex, surface and edge abrasional resistances of cotton and acetylated cotton fabrics (degree of acetylation 31.1 mole%) were tested by a Custom Universal Wear Tester. It was found that the surface and edge abrasional resistances were considerably increased, while the flex abrasional resistance was somewhat decreased by the acetylation.

10. Light and Weathering Resistances

The light resistance test was carried out by exposing the acetylated fabric to the sunlight for about 143 days in a period of summer. Tensile strength and elongation of yarn were measured before and after the exposure. No effect of the acetylation was observed. The weathering test was made using an Atlas Weather Ometer. The influence of acetylation was not observed also in this test. The cotton fabric colored to light yellow, but the acetylated cotton did not discolor.

11. Electrical Property

The frictional electricity and the electrical resistance were measured using the acetylated cotton (the degree of acetylation, about 30 mole%). Cotton, acetate, nylon and vinylon were used as a reference.

As shown in Table 2, the frictional electricity of the acetylated cotton was very remarkable. The electrical resistance of acetylated cotton was much higher than that of cotton. The acid and rot resistances were found to be very excellent in agreement with reports in U.S.A.[2~4].

Table 2. Frictional electricity. (unit : Volt)

Relative [a] humidity (%)	B \ A [b]	Cotton	Cotton (water dip and dry)	Acetylated [c] cotton	Acetate	Nylon	Vinylon
60	Cotton	−190	−410	−3900	−3450	+4050	+3600
	Vinylon	−400	−720	−3750	—	—	− 150
80	Vinylon	− 86	−135	−3600	—	—	—

[a] Temperatur : 21°C.
[b] A was rubbed against fabric B.
[c] Acetylated cotton : Degree of acetylation 32.6 mole%.

Table 3. Electriccal resistance.

	Sample	R.H. 64%	R.H. 76%	R.H. 86%	R.H. 91%
Volume specific resistance (Ωcm)	Acetylated cotton	2.6×10^{14}	2.8×10^{13}	4.5×10^{12}	7.2×10^{10}
	Cotton	2.8×10^{9}	—	—	—
	Acetate	2.8×10^{15}	—	—	—
Surface specific resistance (Ω)	Acetylated cotton	5.8×10^{15}	3.7×10^{15}	5.8×10^{14}	1.0×10^{14}
	Cotton	6.8×10^{9}	—	—	—

Part II. Influences of Catalysts for Liquid Phase Acetylation on Properties of the Acetylated Cotton Fabric

INTRODUCTION

In Part I of this study, we reported some general properties of acetylated cotton fabric. However, the reaction might be not always homogeneous throughout the inner structure of cotton, because it is carried out in the fibrous state. Therefore, the properties might be affected by the condition under which the acetylation was conducted. In this part we report some influences of catalysts used for a liquid phase acetylation on properties of the resultant acetylated cotton fabric.

EXPERIMENTAI AND DISCUSSION

The experimental method for the liquid phase acetylation was already reported in detail by the present authors[1]. In this work, except specially described, cotton fabrics were immersed in acetic acid over 1 hour at room temperature and squeezed to around 100% pick up, then the samples were acetylated under a chosen condition in an acetylation bath which was composed of acetic anhydride, trichlene (as diluent) and catalyst. Sulfuric acid, perchloric acid and zinc chloride were used as the catalyst.

1. Acetylation with Various Catalysts

The reaction rate of acetylation depends on the sort of catalyst used. To minimize the influence caused by the difference of reaction rate, the condition of acetylation was so chosen that the reaction rate was almost of the same re-

Table 4. *The acetylation condition with three catalysts.*

No.	Catalyst	Acetylation [a)b)] bath	Reaction temp. (°C)	Reaction time (min)	Degree of acetylation (mole%)
184				2.5	7.4
185		$CHCl{=}CCl_2$ 85	25—26	5	10.6
186	H_2SO_4	$(CH_3CO)_2O$ 15		10	15.3
187		H_2SO_4 0.23		25	31.4
188				60	49.0
189				120	62.5
202				5	9.2
203		$CHCl{=}CCl_2$ 85	25.0	10	16.0
204	$HClO_4$	$(CH_3CO)_2$ 15		15	23.3
205		$HClO_4$ 0.001 N		25	29.7
206				45	46.4
207				60	56.6
196				10	12.5
197		$CHCl{=}CCl_2$ 85	75.0	20	21.4
198	$ZnCl_2$	$(CH_3CO)_2O$ 15		40	37.2
199		$ZnCl_2$ 0.03 mol/1		60	53.1
200				90	65.7
201				120	69.9
213[a)]		$CHCl{=}CCl_2$ 85, $(CH_3CO)_2O$ 15	25	90	4.6
214[a)]		$HClO_4$ 0.001 N		120	5.2
215[a)]		$CHCl{=}CCl_2$ 75	25	30	4.3
216[a)]		$(CH_3CO)_2O$ 25		60	8.6
217[a)]		$HClO_4$ 0.003 N		180	16.7

Note [a)] No. 213—217 The pretreatment with acetic acid was omitted. The others were pretreated with acetic acid for 1 hour at 25°C in advance to the acetylation.
[b)] Trichrene, acetic anhydride and sulfuric acid are expressed in volume ratio. For the others the units used for concentration are designated respectively in the table.

gardless of kinds of catalysts. The conditions of reaction, such as the composition of the acetylation bath or its temperature, and the degree of acetylation of the obtained fabrics are listed in Table 4.

Although the acetylation usually was carried out after pretreatment by acetic acid, some acetylation processes (No. 213–217 in the table) were conducted without the pretreatment. In those cases the reaction rate of acetylation could not be equalized to that of the normal method due to their very slow reaction rates.

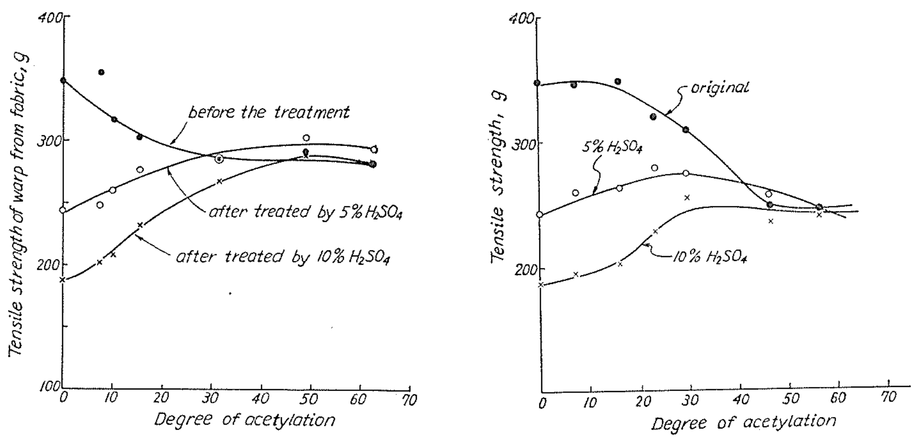
The acid resistance, thermal-stability, rot resistance, solubility in chloroform, and moisiure absorbency of the acetylated fabrics listed in the table were examined. The results will be shown in a following part of this paper.

2. The Resistance to Sulfuric Acid

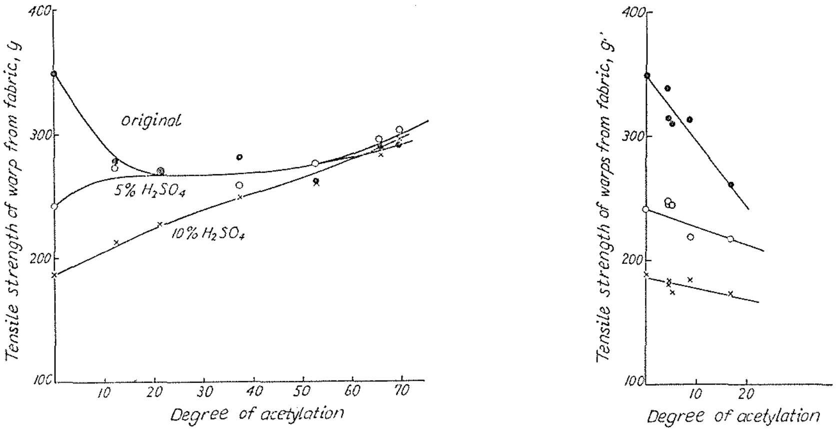
Fig. 5 shows the tensile strength of the acetylated cotton fabrics before and after treated with an aqueous sulfuric acid. The change of the strength by the acid treatment provides the evaluation as to the acid resistance of the acetylated cotton fabrics.

It is generally recognized that the highly acetylated cotton fabrics having higher degrees of acetylation than 40 mole% exhibit so excellent acid resistance that no decrease in the tensile strength by the treatment with 10% H_2SO_4 can be observed regardless of the catalyst sort.

The use of $HClO_4$ as a catalyst seems to give a sample less resistant to acid in comparison with those obtained by the other two catalysts if they are compared at the same degree of acetylation. While the decrease of tensile strength with the degree of acetylation is of the least in the case of the acetylation with $HClO_4$ among those three catalysts. On the other hand, the use of $ZnCl_2$ as a catalyst seems to give a sample better resistant to acid in the lower range of the degree of acetylation, although the decrease of tensile strength by the acetylation is a little more remarkable in the lower range of degree of acetylation than in the cases of the acetylation with $HClO_4$ and H_2SO_4 catalysts. For example, the acetylated fabric obtained by $ZnCl_2$ catalyst shows enough re-



(a) H_2SO_4 catalyst. (b) $HClO_4$ Catalyst.



(c) $ZnCl_2$ catalyst.

(d) $HClO_4$ catalyst. (no pretreatment with acetic acid)

Fig. 5. The acid resistance of acetylated cotton fabrics. (The change of tensile strength by H_2SO_4 *treatment)*

● before H_2SO_4 treatment ; ○ after treated by 5% H_2SO_4 for 7 hrs. at 50°C ; × after treated by 10% H_2SO_4 for 7 hrs. at 50°C. For the tensile strength measurement, 30 pieces of the warp were took out at random from the each fabrics and tested at RH 55~60% at room tempetrature. The experimental points are their averages.

sistance to 5% H_2SO_4 aq. solution by the least degree of acetylation such as 12.5 mole% (Fig. 5-c).

The difference between $HClO_4$ and $ZnCl_2$ as catalyst may be attributed to the difference in uniformity of the reaction through the structure of the fiber. Owing to good affinity of $HClO_4$ to acetic acid which had been contained in the fiber structure of the cotton fabrics by the pretreatment in advance to the acetylation, the acetylation with $HClO_4$ would take place in the amorphous region more uniformly throughout the fiber structure of cotton, whereas, owing to the lower affinity of $ZnCl_2$ to acetic acid, the acetylation with it would not take place uniformly through the fiber structure but start rather preferentially in the amorphous region near to the fiber surface.

It also appears from the Fig. 5(d) that acetylation without the pretreatment by acetic acid does not give any improvement of acid resistance to the cotton fabric over the degree of acetylation examined here. This probably should be attributed to the extreme inhomogeneity of the reaction through the fiber structure.

3. Thermal Stability

It is well-known that the thermal stability of acetylated cotton is excellent, but it also might be affected by the catalyst sort on the same reason as decribed in the previous section. To examine this effect the acetylated cotton fabrics listed in Table 4 was heated at 150°C for 10 hours and the tensile strength was tested before and after heating. The results obtained are shown in Fig. 6.

The acetylated cotton fabrics generally show higher heat resistance with increasing of the degree of acetylation, but it is also recognized that the fabric

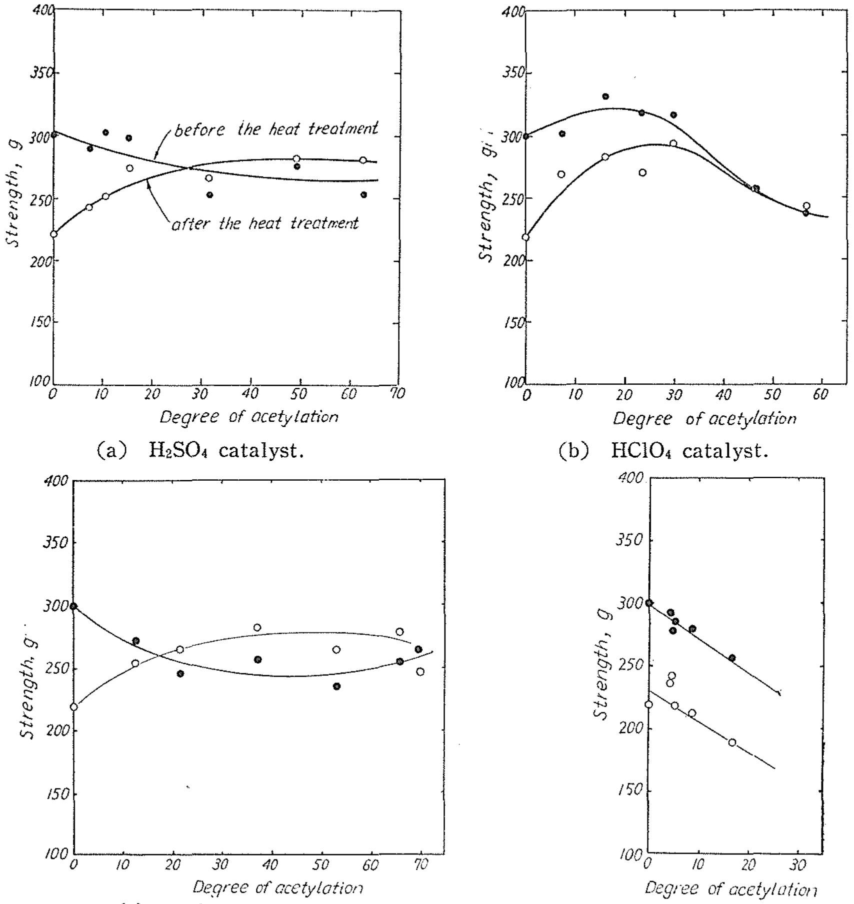
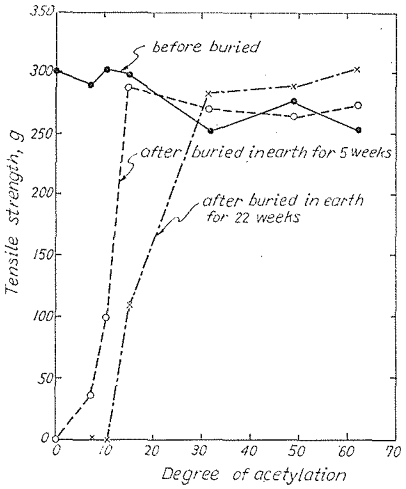


Fig. 6. The thermalstability of acetylated cotton fabrics (The change of tensile strength by heating), ● before heating; ○ after heating of 10 hours at 150°C in air. For the tensile strength measurement, 30 pieces of the warp were took out from the each fabrics and tested at RH 55~60% at room temperature. The experimental points are their averages.

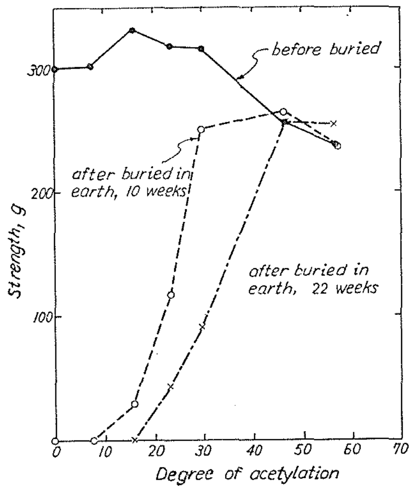
acetylated by $ZnCl_2$ catalyst shows good heat resistance in the lower range of of degree of acetylation than that acetylated by H_2SO_4 catalyst, particularly than that by $HClO_4$ catalyst. It appears also in this case that the acetylation without the pretreatment by acetic acid does not give any improvement in the heat resistance of the treated fabrics.

4. Rot Resistance

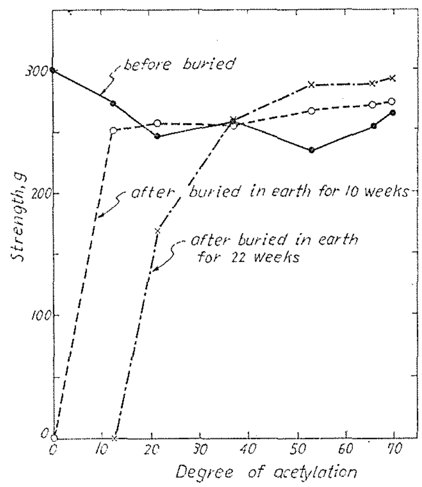
It is also known that the rot resistance of cotton is improved by the acetylation. The present problem is to know how far such a property depends on the degree of acetylation and is influenced by the sort of catalyst used for the acetylation. For this purpose, the acetylated cotton fabrics listed in Table 4 were buried in the earth for 5 and 22 weeks and the tensile strengths of them were examined before and after burying.



(a) H_2SO_4 catalyst.



(b) $HClO_4$ catalyst.



(c) $ZnCl_2$ catalyst.

Fig. 7. The rot resistance of the acetylated cotton fabrics (the change of the strength by burying in the earth.)

Fig. 7 shows the result. When buried for 10 and 22 weeks, the fabrics acetylated by H_2SO_4 and $ZnCl_2$ catalysts show no decrease of strength if the degree of acetylation exceeds arround 15 and 30 mole%, respectively. On the other hand in the case of $HClO_4$ catalyst slightly higher degrees of acetylation seems to be required to obtain the equivalent rot resistance as in the case of H_2SO_4 and $ZnCl_2$ catalysts.

In general the rot resistance of cotton fabric may be improved by relatively lower degrees of acetylation than in the case of the acid resistance and thermal stability. The cotton fabric acetylated without the pretreatment by acetic acid did not show any improvement in its rot resistance. Thus its tensile strength was decreased to zero when buried for 10 weeks, even though the degree of acetylation amounted to 16.7 mole%.

5. Solubility in Chloroform

The solubility in chloroform of acetylated absorbent cotton was reported by Sakurada and others[5]. In oder to compare our results on the acetylated cotton fabric with theirs and also to see the influence of the catalysts, the solubilities of all fabrics listed in Table 4 were examined by the same method as they have used. For this purpose around 0.2 gram of the specimens was immersed in chloroform at 30°C for 24 hours, filtered with a filter paper and then the solubility was estimated by weighing its evaporated residual of the filtrate of 25 ccm.

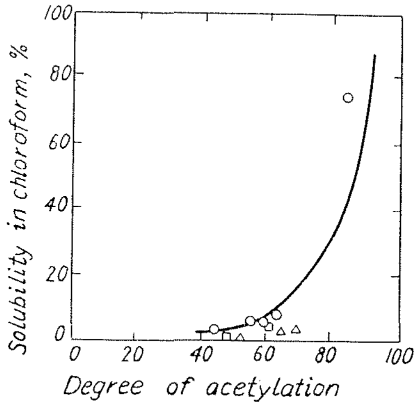


Fig. 8. The solubility in chloroform of the acetylated cotton fabrics.
Catalyst : H_2SO_4 □, $HClO_4$ ○, $ZnCl_2$ △.
Solid curve is the results of acetylated cotton fiber by Sakurada and others[5].

In Fig. 8, the solubility of the acetylated cotton fabrics as well as that of the acetylated absorbent cotton by Sakurada and others is plotted against the degree of acetylation. In general, the solubility of the acetylated cotton fabrics seems to be lower than that of the acetylated absorbent cotton at a corresponding degree of acetylation. It is observed that the cotton acetylated by $HClO_4$ catalyst has slightly higher solubility than that acetylated by other catalysts. It probably should be attributed to the higher uniformity of the reaction as was discussed in the previous section.

6. Moisture Absorbency

It is supposed that the moisture absorbency of cotton fabric may be decreased by acetylation because hydrophilic OH groups are partly converted to hydrophobic-$OCOCH_3$ groups by acetylation. The moisture regains of the acetylated cotton fabrics mainly listed in Table 4 were estimated at room temperature and RH 65%. Fig. 9 shows the plot of these values against the degree of acetylation. As can be seen, the moisture regain of the acetylated cotton fabrics decreases with increase of the degree of acetylation rather quickly in the lower range of the degree of acetylation and reaches an equilibrium value at around 30 mole% acetylation. In addition, it seems to increase slightly again in the

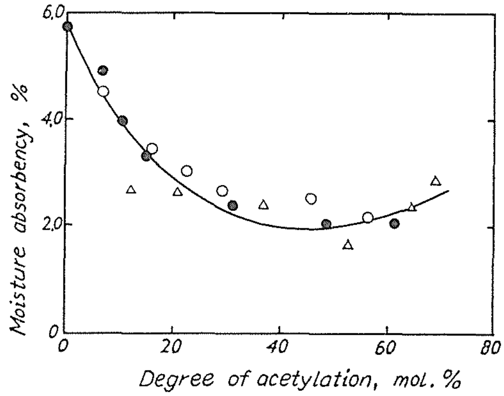


Fig. 9. The moisture absorbency of acetylated cotton fabrics.
Catalyst : H_2SO_4 ●, $HClO_4$ ○, $ZnCl_2$ △.

higher range of degree of acetylation. The influence of the catalysts on the moisture regain of acetylated cotton was not distinct, though the acetylated cotton prepared with $HClO_4$ catalyst seemed to show somewhat higher moisture regain.

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