Acetylation of Holocellulose in Fibrous State

By Toshikazu FUJIMURA*

(Received December 27, 1954)

When wood pulp is used as raw-material for cellulose acetate, the effect of pentosan comes into question. In a previous paper, it was reported that pentosan hindered acetylation of holocellulose with acetic anhydride—acetic acid—sulfuric acid system[1]. Because the product is gradually dispersed in that case, acetylation process in acetic anhydride—benzene—sulfuric acid system, which keeps its fibrous state and proceeds layer by layer, seems suitable to be used to disclose the hindering effect of pentosan and the structure of holocellulose. In this paper, the change of acetic acid content with the time of acetylation was compared with the equation, the rate-determining step of which is internal diffusion or surface resistance. The process of acetylation of single fiber was also observed by birefringence, based on the small little birefringence of the acetate. Then, the effect of alkaline refining on acetylation was studied and compared with beech sulfite rayon pulp and Bemberg rayon, which have circular section.

Derivation of Theoretical Rate Equation

The equation which was suggested for the combustion of spherical pyrite particle, was modified for a cylinder of infinite length[2]. It was assumed as follows:

(1) The reaction is so fast that the progress of acetylated layer is controlled by the migration rate of the reagent.

(2) The migration velocity at the surface is proportional to the difference of concentration.

(3) Diffusion in the acetylated layer follows Fick's law.

(4) Steady state is attained in a short time.

(5) The concentration of reagent in the surrounding medium is constant.

From the assumption (4), (2) and (3) respectively, the following relations are established per unit length,

$$2\pi R dm'/dt = 2\pi r dm/dt = 2\pi r'' dm''/dt$$
$$= -2\pi r'' a(dr''/dt) \qquad (1)$$
$$dm'/dt = k(C^* - C') \qquad (2)$$
$$dm/dt = D dc/dr \qquad (3)$$

where:

a: mass of reagent to react with unit volume of fiber.

R, r'': outer radius, unreacted radius of fiber.

C^*, C', C'': Concentration of reagent in the surrounding medium, at the surface and at the interface of unreacted layer.

m', m'', m: Migrated mass of reagent at the surface, at the interface of unreacted layer and in acetylated layer of radius r.

Rearranging (3) and combining (1) gives

$$D dc = (dm/dt)dr = -ar''(dr''/dt)dr/r$$

Integrating from r'' to R

$$D(C' - C'') = -\ln(R/r'')ar''(dr''/dt) \qquad (4)$$

Combining (2) and (1) yields

$$C' = C^* + ar''(dr''/dt)/kR \qquad (5)$$

Combining (5) and (4)

$$(C^* - C'')dt = a\{1/kr + \ln(R/r'')/D\}(r''dr'')$$

Integrating between zero and t

$$(C^* - C'')t = a[(1/2k + R/4D)R - r''/2kR$$
$$+ \{r''\ln(R/r'')/2D + r''/4D\}r'']$$

r'' becomes zero when t is T

$$(C^* - C'')T = a(1/2k + R/4D)R$$

i) When surface resistance is rate-determining,

$$k \ll D, \qquad t/T = 1 - (r''/R)^2$$

---

* Present addres: Kokoku Rayon and Pulp Co. Ltd., Yatsushiro Mill, Kumamoto.

[1] T. Fujimura, *J. Chem. Soc. Japan* (*Ind. Chem. Sec.*), 56, 99 (1953).

[2] S. Yagi and D. Kunii, *J. Chem. Soc. Japan* (*Ind. Chem. Sec.*), 56, 131 (1953).

ii) When internal diffusion is rate-determining,

$$k \gg D, \qquad t/T = 1-(r''/R)^2\{1-2\ln(r''/R)\}$$

When it is converted into acetic acid content,

i) $$t/T = 9A/(10-7A)$$

ii) $$t/T = 1-(10-16A)\{1-\ln(10-16A) + \ln(10-7A)\}/(10-7A)$$

Because acetic acid content A is calculated, assuming no volume change by acetylation,

$$A = 180\{1-(r''/R)^2\}/[162(r''/R)^2 + 288\{1-(r''/R)^2\}]$$

Then,

$$(r''/R)^2 = (10-16A)/(10-7A)$$

Materials and Methods

As material, beech wood fiber was selected because of its nearly cylindrical form. Holocellulose was prepared by treating five times with sodium chlorite[3]. Its yield was 81.6% and it contained 33.3% pentosan and 3.45% lignin. The rayon pulp was commercial beech sulfite pulp. Bemberg rayon of 40 denier/30 was used.

Acetylating reagent was prepared by heating acetic anhydride—benzene—sulfuric acid mixture on water bath for two hours to convert into sulfoacetic acid[4]. After the separate samples of material were treated with acetylating reagent in separate flasks dipped in thermostat for various times respectively, they were filtered, washed successively with ethanol, water and again ethanol, and finally air dried.

The alkaline-refining time was five hours and the liquid ratio was 1:40. The refined product was filtered and washed first by aq. alkali of the same concentration and temperature as the treating alkali, then water, 10% acetic acid and again water, and finally air dried.

Acetic acid content was determined by alkaline saponification method. Retardation was measured by quartz-wedge.

Results

1. Holocellulose.—Acetylating conditions and the results are given in Tables I, II, III, IV and V. In the initial stage readily reacting portion is observed. Pretreatment, boiling with acetic acid as well as replacing successively with water and acetic acid, accelerates the reaction. Lowering liquid ratio to 1:50 has no remarkable effect, but in the final stage the acetic acid content is a little decreased. By reducing acetic anhydride or sulfuric acid content, as well as by lowering the temperature, the reaction is retarded. The yield first decreases abruptly

TABLE I

CONDITIONS OF ACETYLATION

Expt. No.	Pre-treating	Temp. °C	Ac_2O	C_6H_6	H_2SO_4	Liquid ratio
F-11	Air drying	30	100	300	1.8	100
F-12	Replacing	30	100	300	1.8	100
F-13	Boiling	30	100	300	1.8	100
F-21	Air drying	30	100	300	1.8	50
F-22	Air drying	30	50	300	0.9	100
F-23	Air drying	30	100	300	0.9	100
F-31	Air drying	45	100	300	1.8	100
F-32	Air drying	15	100	300	1.8	100

TABLE II

CHANGE OF ACETIC ACID CONTENT WITH TIME

Expt. No.	Acetic acid content (%) at time (hr.)								
	½	1	2	4	6	8	15	20	25
F-11	14.4	16.6	20.1	25.4	30.6	34.7	47.7	57.4	62.6
F-12	42.9	44.9	46.8	50.7	55.1	56.5	61.5	—	65.6
F-13	44.5	45.5	47.6	50.6	53.5	57.4	61.6	—	65.2
F-21	13.5	18.3	21.1	—	31.9	36.7	49.0	—	59.1
F-22	14.4	15.5	16.1	20.2	23.1	26.1	33.2	—	43.8
F-23	15.7	17.4	19.7	22.6	27.0	30.2	42.7	47.3	48.9
F-31	21.7	26.2	38.7	43.2	54.2	58.6	64.0	67.2	68.2
F-32	13.4	14.9	15.9	16.6	18.7	19.1	22.5	26.0	29.1

TABLE III

CHANGE OF BIREFRINGENCE WITH TIME

Expt. No.	Birefringence (×1000) at time (hr.)								
	½	1	2	4	6	8	15	20	25
F-11	13.4	14.9	17.9	17.9	—	12.8	8.5	5.4	4.1
F-12	9.5	8.3	5.5	5.4	6.0	5.0	7.3	—	4.7
F-13	4.3	9.0	6.1	6.3	5.5	4.7	3.8	—	3.2
F-21	12.6	14.2	8.2	10.2	7.9	6.3	4.4	—	3.4
F-22	9.6	7.2	7.7	10.2	12.1	8.4	8.8	—	6.0
F-23	13.4	9.1	9.5	9.7	13.7	10.1	7.0	5.7	11.3
F-31	9.7	5.3	7.7	9.4	5.6	4.7	—	—	4.2
F-32	14.1	13.4	10.8	8.2	15.2	13.2	11.3	9.5	9.6

TABLE IV

CHANGE OF YIELD WITH TIME

Expt. No.	Yield (%) at time (hr.)								
	½	1	2	4	6	8	15	20	25
F-11	91.7	90.1	90.4	85.7	90.0	87.7	85.2	80.2	79.9
F-12	97.9	92.8	92.3	87.2	78.1	77.2	89.9	—	69.4
F-13	90.9	96.6	94.9	81.4	78.2	76.3	90.8	—	90.7
F-21	91.2	94.4	89.2	—	87.7	90.6	84.8	—	79.4
F-22	89.4	90.8	87.8	88.6	88.0	82.4	86.3	—	83.5
F-23	88.4	88.7	89.3	91.3	88.7	87.4	88.6	82.6	85.1
F-31	90.7	89.8	87.6	84.3	84.5	86.9	71.9	67.6	59.7
F-32	90.4	89.3	90.9	87.8	85.9	—	90.1	87.1	82.1

TABLE V

CHANGE OF PENTOSAN CONTENT WITH TIME

Expt. No.	Content (%) at time (hr.)				
	½	2	6	15	25
F-11	37.7	39.4	41.1	40.0	43.5
F-12	40.6	41.2	44.2	39.3	—
F-13	40.3	40.0	41.3	34.4	34.5
F-21	34.1	39.7	37.7	26.3	24.0
F-22	36.7	37.7	37.9	26.1	41.1
F-23	37.1	37.8	39.7	41.2	55.4
F-31	47.9	37.0	—	35.2	42.3
F-32	45.6	37.2	47.3	47.8	35.8

---

3) L. E. Wise, M. Murphy and A. A. D'Addieco, *Paper Trade J.*, **122**, No. 2, 35 (1946).

4) I. Sakurada et al., *J. Chem. Soc. Japan* (*Ind. Chem. Sec.*), **37**, 127, 1339 (1934).

and then stays constant. Pentosan is not entirely lost. Birefringence decreases at first abruptly, then increases and finally gradually again decreases, but its value is scattered.

2. Alkali Refined Holocellulose.—The refined products shown in Table VI were acetylated at 30°C. The acetylating mixture was composed of 100 parts acetic anhydride, 300 parts benzene and 1.8 parts sulfuric acid, and the liquid ratio used was 1 : 100. The results are shown in Tables VII, VIII, IX and X.

TABLE VI

REFINING CONDITIONS AND RESULTS

Expt. No.	Refining		Total Yield %	α-Cellulose		Pentosan	
	Temp. °C	NaOH %		Cont. %	Yield %	Cont. %	Yield %
C-41	15	1	63.0	80.9	90.7	27.6	52.1
C-43	15	4	55.9	92.0	91.5	14.8	24.8
C-44	15	8	52.2	94.8	88.0	12.3	19.3
C-42	15	17.5	49.9	96.6	85.9	10.6	16.0
W-62	60	1	66.5	76.8	90.9	29.7	59.4
W-61	60	4	55.9	88.5	88.0	17.3	29.0
H-52	95	1	64.7	77.3	89.0	31.2	60.5
H-51	95	0.2	67.7	75.2	93.4	31.3	65.2
Raw material			100	56.2	100	33.3	100
RP			100	90.9	100	5.1	100

TABTE VII

CHANGE OF ACETIC ACID CONTENT WITH TIME

Expt. No.	Acetic acid content (%) at time (hr)								
	½	1	2	4	6	8	15	20	25
C-41	5.6	6.1	7.3	9.4	11.5	13.5	21.2	25.5	29.2
C-43	4.3	6.4	8.1	8.5	11.9	13.5	18.4	22.3	—
C-44	3.7	4.9	5.1	7.9	8.6	10.4	10.3	13.0	—
C-42	2.0	2.1	2.2	2.3	3.0	3.8	3.7	4.4	6.2
W-62	6.8	8.2	9.4	13.5	15.5	17.6	22.7	26.7	31.6
W-61	3.2	4.9	6.3	8.7	9.9	12.8	19.9	24.1	29.8
H-52	5.5	6.8	7.6	8.9	11.2	13.9	22.6	26.0	30.6
H-51	5.4	5.8	6.8	8.9	12.5	14.4	20.3	25.5	30.2
P-72	1.5	2.8	2.8	3.9	5.3	5.8	10.6	11.9	13.7

TABLE IX

CHANGE OF BIREFRINGENCE WITH TIME

Expt. No.	Birefringence (×1000) at time (hr)								
	½	1	2	4	6	8	15	20	25
C-41	21.8	17.7	18.3	17.0	13.4	17.8	14.6	16.1	13.2
C-43	18.1	21.6	14.9	18.4	12.9	17.2	15.6	15.3	4.5
C-44	19.2	21.1	24.1	15.0	20.7	18.5	13.6	24.3	16.3
C-42	25.1	29.6	28.5	28.9	28.2	30.1	29.6	27.1	20.7
W-62	16.7	24.3	20.5	25.1	17.7	18.2	17.6	17.6	16.9
W-61	17.9	18.4	15.1	19.9	16.7	15.9	17.3	11.9	14.9
H-52	15.4	16.2	16.1	20.4	18.1	18.3	16.6	15.6	14.3
H-51	15.4	12.3	15.5	15.7	18.4	14.5	17.6	17.1	14.1
P-72	11.8	11.5	12.0	9.7	13.0	12.5	11.8	11.7	11.3

TABLE X

CHANGE OF PENTOSAN WITH TIME

Expt. No.	Content (%)		
	½	6	25
C-41	33.2	37.8	33.2
C-43	13.5	14.2	14.8
C-44	14.7	15.2	15.1
C-42	16.1	11.4	11.4
W-62	33.6	32.4	28.8
W-61	16.8	16.5	19.4
H-52	31.5	32.9	26.0
H-51	34.0	32.0	32.9
P-72	7.1	7.7	6.4

The product refined with concentrated cold alkaline education reacted with difficulty. Refining temperature affects little on the reaction rate, but product refined at 60°C seems to be a little superior. The further refined products exhibit less initial decrease of yield, less abrupt change of acetic acid content and more diffused loss of birefringence. Pentosan is apparently little changed.

3. Bemberg Rayon and Pulp.—As shown in Table XI, the reaction is slow. Soaping has no effect. Birefringence decreases naturally.

TABLE VIII

CHANGE OF YIELD WITH TIME

Expt. No.	Yield (%) at time (hr.)								
	½	1	2	4	6	8	15	20	25
C-41	92.8	94.4	95.9	—	95.7	95.9	94.4	93.6	92.0
C-43	96.4	95.2	88.2	93.7	95.8	94.6	96.4	96.0	—
C-44	97.4	97.6	98.4	95.7	95.8	93.5	94.7	92.3	—
C-42	94.8	95.0	95.8	98.2	98.6	95.5	96.4	96.2	97.7
W-62	93.6	90.4	91.4	91.8	89.9	92.4	91.8	92.4	103.2
W-61	96.3	95.0	95.9	95.6	95.2	95.8	93.6	93.5	92.1
H-52	102.0	101.4	100.7	101.8	101.4	100.7	99.0	99.3	94.6
H-51	92.8	95.1	94.1	93.3	93.5	92.2	93.2	93.2	86.2
P-72	105.0	106.1	100.3	106.9	100.1	101.3	95.2	100.0	100.4

TABLE XI
ACETYLATION OF BEMBERG RAYON

Expt. No.	Change with time (hr.)											
	½	1	2	4	6	8	15	20	25	50	100	200
	Acetic acid content (%)											
B-81	2.2	3.1	3.2	3.1	3.4	4.2	4.6	4.6	4.5			
B-82	1.4	1.7	3.1	2.8	3.5	3.7	4.8	5.0	5.3	7.6	11.7	13.1
B-83	14.2	22.7	24.1	24.7	27.6	27.6	32.9	34.5		48.7	51.1	54.5
	Yield (%)											
B-81	94.6	97.0	97.6	98.1	97.3	97.0	95.3	96.4	96.0			
B-82	98.8	99.8	98.1	98.5	98.4	97.7	97.7	96.4	97.6	94.8	94.2	96.7
B-83	97.1	96.9	92.9	93.6	94.2	93.5	93.4	98.5	86.4	82.2	85.9	89.4
	Birefringence (×1000)											
B-81	22.9	21.7	24.8	21.7	20.5	21.3	22.3	21.5	21.1			
B-82	26.8	26.4	25.0	22.2	24.1	22.1	21.6	22.9	20.3	21.3	20.2	19.5
B-83	25.6	21.3	22.1	20.8	20.0	20.1	18.0	18.7	19.1	19.0	16.1	9.1

Discussion

1. Unreacted Radius.—Assuming that pentosan is concentrated at outer layer and preferentially acetylated,

$$A=\frac{180(1-x^2/y)/162+120(x^2-1)/132}{x^2/y+288(1-x^2/y)/162+216(x^2-1)/132}$$

where x: unreacted radius/radius excluding pentosan.
$X=1/(1-P)$: total radius/radius excluding pentosan
P: content of pentosan in product
y: yield of product, fraction of theoretical value.

Then, $x^2=(10-16A)y/(10-7A)(1-P)$
$-2yP/(1-P)$

x is plotted against time fraction, which is arranged so as to lay the last experimental point on the calculated line of reaction controlled by surface-resistance, which is given as a full line in the figure. The broken line shows the case controlled by internal diffusion. As shown in Figs. 1, 2, 3 and 4, air-dried holocellulose tends to follow the reaction controlled by surface resistance regardless of the composition of acetylating mixture, acetylating temperature and degree of refin-

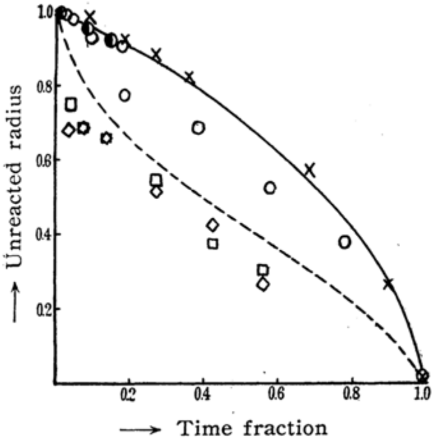

Fig. 1. Effect of pretreatment and temperature on acetylation rate of holocellulose.
(○, at 45°C; ×, at 30°C; ◐, at 15°C (air-dried); □, ◇: replacing or boiling with acetic acid)

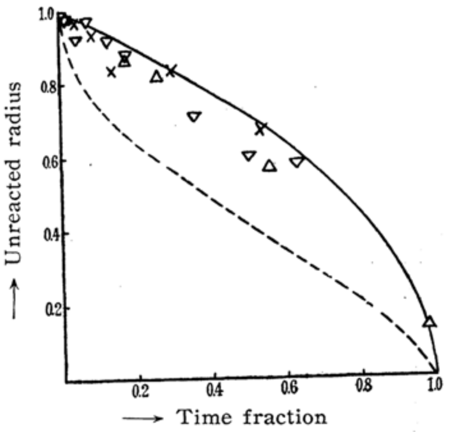

Fig. 2. Effect of composition of reagent on acetylation rate of holocellulose.
(△, +, ▽: low liquid ratio, low acetic anhydride or low sulfuric acid)

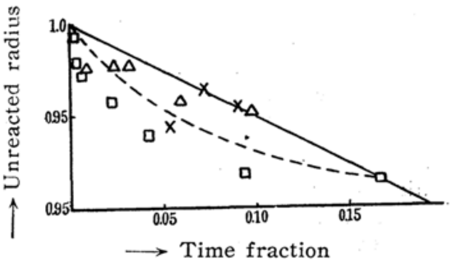

Fig. 3. Effect of cold alkali concentration on acetylation rate of refined holocellulose.
(×, △, □: 1%, 4%, 8% NaOH)

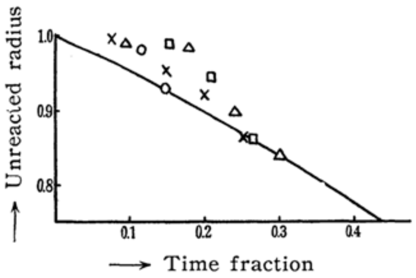

Fig. 4. Effect of warm and hot alkali concentration on acetylation rate of refined holocellulose.
(×, △, ○, □: 1%, 4% at 60°C; 1%, 0.2% at 95°C)

ing. Pretreated sample follows close by the curve controlled by internal diffusion. Hence pentosan layer may hinder the acetylation in air-dried state, but pretreatment would remove the hindrance. Figs. 5 and 6 shows that not only pretreated Bemberg rayon but also air-dried rayon is likely counted as the type controlled by internal diffusion.

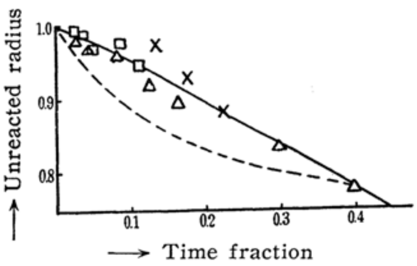

Fig. 5. Acetylation rate of air-dried rayon pulp and bemberg rayon.
(△, □, × : rayon, soaped, rayon, pulp)

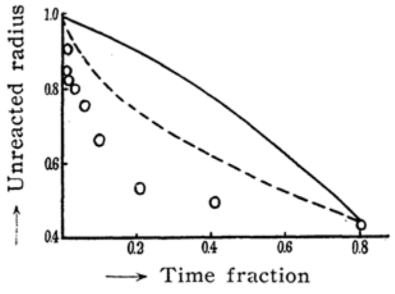

Fig. 6. Acetylation rate of pretreated bemberg rayon.

2. Relation to Structure.—Steep increase of acetic acid content and loss of yield in initial stage may be derived from the readily reacting and dispersing amorphous portion, for its magnitude is almost independent of acetylating conditions. The behavior of birefringence is elucidated by considering that initially it is reduced by acetylation of the accessible part, secondly it is raised by loss of amorphous portion, both bringing about the increase of residual crystallinity, and thirdly it is reduced again gradually by acetylation of crystalline region. Since the final acetic acid content is higher than the value corresponding to the birefringence and the yield is low, so acetolysis might have occurred.

3. Effect of Refining.—Slower reaction resulting from cold concentrated alkali refining is likely due to hornification, the loss of accessible portion or transformation into cellulose hydrate. The low reactivity of the sample refined with more dilute alkali than 4% is explained probably by the incomplete removal of the acetylation hindering layer and its gelatinization. The slow reaction of pulp and Bemberg rayon may be ascribed to more compact structure.

4. Behavior of Pentosan.—The content of pentosan in the product is apparently rather higher. Slight solubility of acetate and the easy production of oxymethylfurfural may be responsible for this. If all pentosan in holocellulose is preferentially acetylated, its acetic acid content should amount to 24.8%, but the value of only 12% observed in its initial stage suggests that pentosan is not exclusively accessible.

Summary

Acetylation in fibrous state of holocellulose, its alkali-refined product, rayon pulp and Bemberg rayon was undertaken to disclose the effect of pentosan and the structure of holocellulose.

1) Acetylation of air-dried holocellulose is roughly controlled by surface resistance, regardless of various ratios depending on conditions of acetylation and degree of refining. The rate of pretreated sample seems to be determined by internal diffusion.

2) The birefringence decreases at first abruptly and then increases and finally decreases again. The final higher birefringence compared to acetic acid content may be ascribed to acetolysis. Definite amorphous portion is acetylated easily at the initial stage and lost, so that residual crystallinity, and also birefringence, increase.

3) By alkali-refining, acetylation is retarded and initial abrupt change, which is caused by the amorphous portion is diffused. There is optimum point in the concentration of refining alkali, probably relating to hornification, loss of amorphous portion, transformation of crystal form and hindrance by residual pentosan layer. The refining temperature affects the acetylation slightly.

4) Pentosan in product is not reduced apparently, probably due to oxymethylfurfural yielding and poor solubility of acetate. Also pentosan may not be entirely accessible at initial stage.

The author wishes to thank Prof. H. Sobue for his guidance and inspiration.

Department of Applied Chemistry,
Faculty of Engineering,
Yamanashi University, Kofu