

Bull. Univ. Osaka Pref., Ser. B, Vol. 16.
大阪府立大学紀要, 農学・生物学, Jan., 1965.

Studies on Dissolving Bamboo Pulp

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(Received September 1, 1964)

Introduction

On the manufacturing of dissolving pulp from Grasses, K. ONO and others (1, 2) have succeeded to produce rayon pulp by the application of the processes of "alkali pulping subsequent to dilute acid hydrolysis".

There are some reports on the dissolving bamboo pulp by M. H. JAGLEKAR, C. P. DONAFRIO (3) and others (4, 5). They have made the dissolving bamboo pulp by the theoretically same way as K. ONO, which decreases pentosan contents in bamboo pulp. Few investigators have studied on a viewpoint of the degree of polymerization of pulp and filterability of viscose made from bamboo pulp.

Bamboo has higher pentosan and ash contents in comparison with those of coniferous wood, moreover a great deal of silica is contained in the ash. When the large amount of pentosan is remained in pulp, pentosan reacts oneself with carbon disulfide to produce a soluble xanthate during the viscose making process (6), and becomes lower molecular matters which give a baneful influence on the physical strength of rayon (7,8,9).

C. D. DONAFRIO (4) has reported that if the pentosan contents in the dissolving pulp were less than 5 per cent, there was no trouble in the viscose processing steps, and no effect on the physical properties of the viscose.

Some workers have reported that silica in pulp deteriorated the filterability of the viscose (10) and made a trouble in the spinning process (11).

T. TONO (12) has reported that there were at least 7~9 layers in bamboo fiber in his studies on fine structure of bamboo, and he has also explained that these layers might be the chief cause of undissolved fibers in the viscose making process from dissolving bamboo pulp and then these fibers might give bad effects on filterability of the viscose. In any case, it is essential to remove the pentosan during the prehydrolysis step and to remove the silica from the pulp by a appropriate method in the dissolving bamboo pulp manufacturing processes.

From the reports by T. TONO (13), it is clear that the distribution curve of degree of polymerization shows the maximum at 2,000 in bamboo cellulose, and this value is close to 2,200 in red pine by T. E. TIMELL (14), 2,400 in aspen by L. JØRGENSEN (15) and 2,100 in western hemlock by R. E. MITCHELL (16). From the standpoint of degree of polymerization, bamboo compares favorably with wood as the raw materials for dissolving pulp.

The present investigation was undertaken to study on the progress of removal of pentosan at prehydrolysis and the changes of the average degree of polymerization of cellulose in pulping by the application of the processes of "sulphate pulping subsequent to water cooking", using *Phyllostachys reticulata* (Madake) from Japan and *Bambusa bambos* from Indonesia as the raw materials, and further on the analytical properties of the dissolving pulp and the filterability of viscose.

Experimental

Part 1. Investigation of the prehydrolysis condition

Experiment and results

§ 1. Prehydrolysis

This experiment was undertaken to investigate the effects of cooking temperature and time of prehydrolysis by water on yield and pentosan removal of chip. As the material, *Phyllostachys reticulata* (Madake) chips prepared by hand to approximately 3cm in length and 5mm in thickness, were used. In this experiment, the nodes of bamboo were removed.

Analytical data of bamboo are shown in Table 1.

Unless otherwise stated, routine methods were used for analysis.

Table 1. Chemical analysis of Bamboo

Cold water extract	6.6 %
Hot water extract	8.0
1% NaOH extract	22.7
Alcohol-benzen extract	8.2
Holocellulose	61.9
α -cellulose	42.2
Pure α -cellulose (diminished pentosan from α -cellulose)	*38.4
Pentosan	22.7
Lignin	23.7
Ash	1.19
Silica in ash	19.05

* 9 per cent of Pentosan contained in α -cellulose.

Cookings of prehydrolysis were taken as followings: 350 g. of bamboo chips (as dry matter) were charged in 3-liter stainless steel autoclave, and a stainless steel plate was put on the chips to prevent rising to the surface, then 1,750 ml. of distilled water (chip: water = 1 : 5) was added, and were cooked for 3 and 4 hrs. at 160°C, 165°C and 170°C, respectively. Each cooking was reached to maximum temperature in 30 min.. The prehydrolyzed chips were washed with hot water for several times, then with tap water until washed water was no longer coloured, and were dried in air.

Analytical data of prehydrolyzed chips are shown in Table 2.

Table 2. Analysis of Prehydrolyzed bamboo chip

Cooking Temp.	°C	160	165	170	160	165	170
		3	3	3	4	4	4
Cooking Time	hr.						
Yield	%	79.4	76.9	69.1	71.8	69.6	68.3
Pentosan	%	18.2	15.7	13.6	13.7	10.6	7.9
Ratio of pentosan removal	%	36.2	46.7	58.6	56.8	67.4	76.2
Ratio of removed pentosan to dissolved matters	%	40.1	45.9	44.2	45.7	50.3	54.6
Alcohol-benzen extract	%	7.9	10.4	12.7	11.2	12.9	13.3
Lignin	%	23.2	22.9	22.3	23.3	22.6	22.2
Ratio of lignin removal	%	22.7	26.1	35.3	29.8	34.0	36.1
Ratio of removed lignin to dissolved matters	%	26.1	26.8	27.2	25.2	26.6	27.1

Ratio of pentosan removal and ratio of removed pentosan to dissolved matters were calculated from the following formulas:

$$\text{Ratio of pentosan removal} = \frac{A - B \times \text{yield}}{A} \times 100$$

$$\text{Ratio of removed pentosan to dissolved matters} = \frac{A - B \times \text{yield}}{100 - \text{yield}} \times 100$$

where A: pentosan contents in original bamboo

B: pentosan contents in treated chip

The former shows percentage of pentosan dissolved into liquor to pentosan in the raw bamboo, and the latter shows percentage of dissolved pentosan to total matters dissolved into liquor.

In similar formulas, those of lignin were calculated.

Table 3. Analysis of Unbleached pulp

Prehydrolysis			160	165	170	160	165	170
Cooking Temp.	°C							
Cooking Time	hr		3	3	3	4	4	4
Yield*	%		29.0	28.1	27.7	26.5	26.6	26.3
Pentosan	%		7.9	5.8	4.4	5.4	3.8	3.3
Ratio of pentosan removal	%		89.9	92.8	94.6	93.7	95.6	96.2
Ratio of removed pentosan to dissolved matters	%		28.8	29.3	29.7	28.9	29.6	29.6
Lignin	%		1.5	1.1	1.3	1.4	1.1	1.4
Ratio of lignin removal	%		98.3	98.7	98.3	98.3	98.7	98.3
Ratio of removed lignin to dissolved matters	%		29.7	32.6	32.4	31.8	32.0	31.8
Ash	%		0.17	0.25	0.16	0.18	0.24	0.17
Permanganate number			7.8	6.9	6.4	5.7	6.2	6.8

* Based on original raw material.

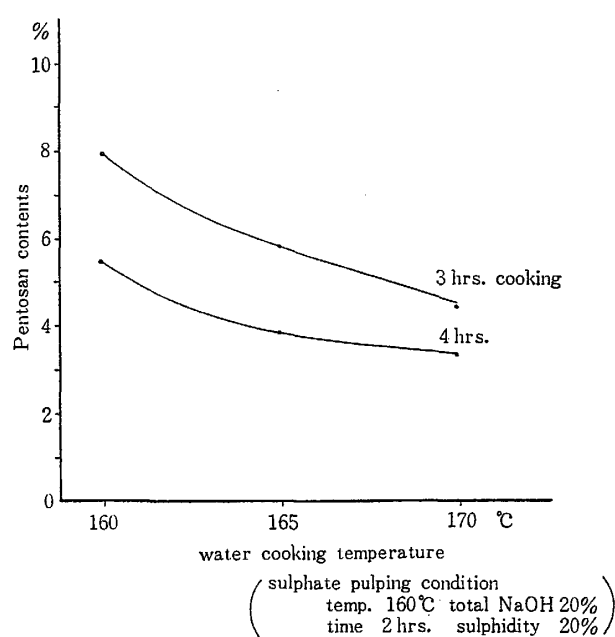


Fig. 1. Effect of temperature at prehydrolysis on pentosan contents of unbleached pulp

§ 2. *Pulping of prehydrolyzed chips*

Sulphate pulpings were taken as followings: 300 g. of prehydrolyzed chips calculated in terms of the original bamboo were charged in the same autoclave, and then were cooked for 2 hrs. at 160°C under the condition of total NaOH 20%, sulphidity 20% and chip: liquor=1:3.3 (based on the original bamboo). Time to reach maximum temperature, however, was controlled in 1 hr..

The obtained pulp (unbleached one) was washed with tap water, then was taken in the flat type screening machine (having cut No. 0.008), and was dried in air.

Analytical data of the pulp are given in Table 3. Also, this is shown in Figure 1 where pentosan contents of unbleached pulp are plotted against the cooking temperature at prehydrolysis by water.

Discussion

The discussion below may be referred from the results of these experiments.

(1) 9 per cent of pentosan which is unaccessibility to alkali is contained in α -cellulose of the original bamboo, while this value is corresponded to 3.8 per cent on the original bamboo. (Table 1).

(2) Pentosan takes 40~55 per cent portion of the dissolved matters during water cooking. (Table 2).

(3) As shown in Figure 1, unbleached pulp contains less than 5 per cent of pentosan at water cooking conditions described below, that is, 170°C 3 hrs., 165°C 4 hrs. and 170°C 4 hrs.. Therefore, from Table 2 it is apparent that, if more than 59 per cent of pentosan is removed during pretreatment, the unbleached pulp produced is suitable for the dissolving pulp in a viewpoint of pentosan contents.

(4) In order to produce the pulp which contains less than 5 per cent of pentosan, more than 94 per cent of pentosan in the raw chip has to be hydrolyzed and dissolve out during the processes of "prehydrolysis—sulphate pulping". (Table 3)

(5) From the consideration of lignin contents and permanganate number, it seems to mention that the unbleached pulps produced in these experiments have a good bleachability.

Part 2. *Manufacturing of the dissolving bamboo pulp and its properties.*

Experiment and results

§ 1. *Production of dissolving bamboo pulp*

In this experiment, the dissolving bamboo pulp was produced by a application of "water cooking—sulphate pulping—multistage bleaching".

As the materials, *Phyllostachys reticulata* (Madake) from Japan and *Bambusa bambos* from Indonesia prepared in the same methods as in part 1, were used.

Cookings of prehydrolysis were taken as followings: 3 kg. of chips (as dry matter) were charged in 30-liter iron autoclave, and 15 liters of distilled water was added, and then were cooked for 4 hrs. at 160°C, 165°C and 170°C, respectively. Each cooking was reached to maximum temperature in about 1 hr.. Prehydrolyzed chips were washed in the same manner as the method described previously.

Analytical data of the original bamboo are shown in Table 4, and those of the prehydrolyzed chips in Table 5.

Sulphate pulpings were taken as followings: 400 g. of prehydrolyzed chips calculated in terms of the original bamboo were charged in 3-liter stainless steel autoclave, and then were cooked. Cooking conditions were the following; at first, prehydrolyzed chips were cooked for 2 hrs. at 130°C, 140°C, 150°C and 160°C, respectively under the condition of

Table 4. Chemical analysis of Bamboo

	<i>Phyllostachys reticulata</i>	<i>Bambusa bambos</i>
Cold water extract	6.3 %	4.6 %
Hot water extract	9.4	6.8
1% NaOH extract	24.6	25.4
Alcohol-benzen extract	4.3	1.7
Holocellulose	69.8	68.0
α -cellulose	48.3	49.2
Pentosan	21.2	20.6
Lignin	22.2	25.1
Ash	1.24	1.79
Silica in Ash	—	5.02

Table 5. Analysis of Prehydrolyzed Bamboo chip

		<i>Phyllostachys reticulata</i>			<i>Bambusa bambos</i>		
Cooking Temp.	(°C)	160	165	170	160	165	170
Cooking Time	(hr)	4	4	4	4	4	4
Yield	%	72.5	69.8	67.7	85.0	79.1	75.9
Pentosan	%	11.2	8.4	8.3	14.3	7.5	4.8
Ratio of pentosan removal	%	61.7	72.4	77.0	41.7	71.1	82.4
Ratio of removed pentosan to dissolved matters	%	47.9	50.8	50.5	57.2	69.2	70.5
Alcohol-benzen extract	%	9.3	11.5	12.2	5.0	9.2	11.3
Lignin	%	25.7	23.5	24.4	24.2	25.5	27.4
Ratio of lignin removal	%	16.2	26.1	25.6	18.0	19.7	17.1
Ratio of removed lignin to dissolved matters	%	13.1	19.2	17.6	30.1	23.6	17.9

Table 6. Analysis of Unbleached pulps

(A) Effect. of sulphate cooking temperature

Raw Bamboo: *Phyllostachys reticulata*

Prehydrolysis Cooking Temp. (°C)	160				165				170			
Sulphate cooking Temp. (°C)	130	140	150	160	130	140	150	160	130	140	150	160
Yield (based on original) %	31.0	29.3	28.8	26.6	28.5	28.7	27.7	27.6	—	24.8	—	23.9
Pentosan %	6.1	6.1	5.7	5.8	5.3	5.1	3.8	—	—	3.7	—	3.6
Ratio of pentosan removal %	91.1	91.6	92.3	92.9	92.9	93.1	94.8	—	—	94.8	—	95.9
Ratio of removed pentosan to dissolved matters. %	28.2	27.5	27.5	26.9	27.5	27.7	27.9	—	—	27.0	—	26.9
Lignin %	5.7	3.6	1.5	—	6.2	3.8	—	0.7	—	2.9	—	1.8
Ratio of lignin removal. %	92.0	95.7	98.1	—	92.0	95.1	—	99.1	—	96.8	—	98.1
Ratio of removed lignin to dissolved matters. %	29.6	30.0	30.4	—	28.6	29.6	—	30.4	—	28.6	—	28.6
Ash %	0.32	0.31	0.16	0.22	0.30	0.30	0.31	0.25	—	0.36	—	0.30
KMnO ₄ no.	22.4	16.8	10.2	7.7	23.0	16.2	10.5	7.3	—	15.9	—	7.1

Raw bamboo: *Bamusa bambos*

Prehydrolysis Cooking Temp. (°C)	160				165				170			
	130	140	150	160	130	140	150	160	130	140	150	160
Sulphate cooking Temp. (°C)												
Yield (based on original) %	40.0	41.1	38.3	37.5	—	32.7	32.2	31.3	—	29.1	—	28.2
Pentosan %	8.3	7.4	7.2	6.0	—	3.6	3.5	3.2	—	2.9	—	2.7
Ratio of pentosan removal %	83.9	85.3	86.6	89.1	—	94.3	94.5	95.2	—	95.9	—	96.3
Ratio of removed pentosan to dissolved matters %	28.9	29.9	29.0	29.4	—	28.9	28.8	28.6	—	27.9	—	27.7
Lignin %	5.4	4.7	2.6	2.3	—	4.5	3.0	2.1	—	5.0	—	2.4
Ratio of lignin removal %	91.4	92.3	96.0	96.6	—	94.1	96.1	97.4	—	94.2	—	97.3
Ratio of removed lignin to dissolved matters %	38.2	39.3	39.0	38.8	—	35.1	35.6	35.5	—	33.3	—	34.0
Ash %	0.34	0.28	0.25	0.23	—	0.34	0.35	0.34	—	0.40	—	0.16
KMnO ₄ no.	21.5	15.7	9.9	7.6	—	17.7	13.6	9.0	—	15.0	—	7.3

(B) Effect of total NaOH at sulphate cooking

Raw bamboo: *Bambusa bambos*

Prehydrolysis Cooking Temp. (°C)	160				165				170			
	14	17	20	23	14	17	20	23	14	17	20	23
Total NaOH %												
Yield (based on original) %	41.5	39.4	37.5	37.2	33.8	32.5	31.3	31.1	29.3	28.5	28.2	28.0
Pentosan %	6.5	6.0	6.0	5.9	3.3	3.2	3.2	3.2	2.9	2.8	2.7	2.8
Ratio of pentosan removal %	86.9	88.5	89.1	89.4	94.6	95.0	95.2	95.3	95.9	96.1	96.3	96.2
Ratio of removed pentosan to dissolving matters. %	30.6	30.1	29.4	29.4	29.5	29.0	28.6	28.5	28.1	27.7	27.7	27.6
Lignin %	3.8	2.5	2.3	1.8	4.5	3.0	2.1	2.1	6.3	3.8	2.4	2.1
Ratio of lignin removal %	93.7	96.1	96.6	97.3	93.9	96.1	97.4	97.4	92.6	95.7	97.3	97.6
Ratio of removed lignin to dissolving matters %	40.2	39.8	38.8	38.9	35.6	35.7	35.5	35.5	32.9	33.6	34.0	34.0
Ash %	0.43	0.37	0.23	0.28	0.28	0.27	0.34	0.21	0.36	0.25	0.16	0.16
KMnO ₄ no.	16.8	9.3	7.6	6.1	14.2	11.0	9.0	7.7	14.5	9.1	7.3	6.4

total NaOH 20%, sulphidity 20%, liquor : chip=3.3 : 1, to investigate the effects of cooking temperature. To investigate the effects of total NaOH, they were cooked for 2 hrs. at 160°C under the conditions of sulphidity 20%, liquor : chip=3.3 : 1 and total NaOH 11%, 14%, 17% and 20%, respectively. The pulp prepared on these conditions were washed in the same manner as previous, and analytical data of them are shown in Table 6.

In bleaching process, seven stage were used as followings:

- | | |
|------------|----------------------------|
| 1st. stage | chlorination |
| 2nd. stage | sodium hydroxide treatment |
| 3rd. stage | chlorination |

4th. stage	sodium hydroxide treatment
5th. stage	sodium hypochlorite treatment
6th. stage	sodium hypochlorite treatment
7th. stage	0.5% SO ₂ -water treatment in order to remove the remained silica from pulp

The chlorine consumption of unbleached pulp was calculated from the following formula discribed by A. KAMINIWA (20).

Table 7. Condition of Bleaching

Stage	1	2	3	4	5	6	7
Chemicals	Cl	NaOH	Cl	NaOH	NaClO	NaClO	0.5%SO ₂
Pulp consistency (%)	3	4	3	4	4	4	3
Temperature (°C)	20	60	20	60	40	40	20
Time (hr)	1	1	1	1	2	2	0.5

Table 8. Analysis of Bleached pulps

(A) Effect of sulphate cooking temperature

Raw bamboo: *Phyllostachys reticulata*

Prehydrolysis Cooking Temp. (°C)	160				165				170			
	Sulphate cooking Temp. (°C)				Sulphate cooking Temp. (°C)				Sulphate cooking Temp. (°C)			
	130	140	150	160	130	140	150	160	130	140	150	160
Total Added Chlorine %	12.5	9.3	5.7	4.3	12.8	9.0	5.8	4.0	—	8.8	—	3.9
Consumption %	88.9	83.5	79.5	74.6	84.7	84.0	70.7	76.1	—	70.4	—	88.0
Consumed %	11.1	7.8	4.5	3.2	10.8	7.6	4.1	3.0	—	6.2	—	3.4
Yield (based on unbleached pulp) %	92.4	95.2	96.2	98.1	95.6	95.5	96.6	96.7	—	94.4	—	94.4
Yield (based on original bamboo) %	28.6	27.8	27.8	26.1	27.2	26.5	26.8	26.7	—	23.4	—	22.6
α -cellulose %	97.6	97.2	97.5	97.4	97.6	97.5	97.2	97.4	—	96.5	—	96.5
β -cellulose %	1.4	1.5	1.1	1.8	1.3	1.4	1.4	1.2	—	1.4	—	1.9
Pentosan %	6.1	5.8	—	5.9	5.0	4.9	4.1	4.3	—	3.5	—	3.8
Ash %	—	0.05	—	0.06	—	0.05	—	0.06	—	0.06	—	0.05

Raw bamboo: *Bambusa bambos*

Prehydrolysis Cooking Temp. (°C)	160				165				170			
	Sulphate cooking Temp. (°C)				Sulphate cooking Temp. (°C)				Sulphate cooking Temp. (°C)			
	130	140	150	160	130	140	150	160	130	140	150	160
Total Added Chlorine %	10.6	7.4	4.6	3.5	—	8.3	6.3	4.2	—	9.5	—	4.0
Consumption %	81.1	72.6	76.8	71.4	—	79.0	75.9	78.6	—	75.6	—	75.3
Consumed %	8.6	5.4	3.5	2.5	—	6.6	4.8	3.3	—	7.2	—	3.0
Yield (based on unbleached pulp) %	—	—	—	95.7	—	91.6	93.6	94.8	—	91.0	—	—
Yield (based on original bamboo) %	—	—	—	35.9	—	30.0	30.1	29.7	—	26.5	—	—
α -cellulose %	97.9	97.3	96.7	97.1	—	96.6	96.8	96.6	—	93.6	—	89.9
β -cellulose %	1.9	1.7	2.7	2.4	—	2.4	2.2	2.2	—	5.1	—	9.6
Pentosan %	7.3	6.8	6.2	5.9	—	3.4	3.3	3.0	—	3.0	—	2.6
Ash %	—	0.06	—	0.05	—	0.05	—	0.04	—	—	—	0.05

(B) Effect of total NaOH at sulphate cooking

Raw Bamboo: *Bambusa bambos*

Prehydrolysis Cooking Temp. (°C)	160				165				170				
	Total NaOH	%			Total NaOH	%			Total NaOH	%			
Total NaOH	%	14	17	20	23	14	17	20	23	14	17	20	23
Total Added Chlorine	%	8.1	5.0	3.5	3.2	6.6	5.1	4.2	3.8	8.1	5.0	4.0	3.2
Consumption	%	68.3	67.9	71.4	65.9	78.6	70.1	78.6	66.1	87.8	82.4	75.3	74.2
Consumed	%	5.5	3.4	2.5	2.1	5.2	3.6	3.3	2.5	7.1	4.1	3.0	2.4
Yield (based on unbleached pulp)	%	94.4	93.9	95.7	94.7	93.2	92.8	94.8	93.4	—	—	—	—
Yield (based on original bamboo)	%	39.4	37.0	35.9	35.2	31.5	30.2	29.7	29.0	—	—	—	—
α -cellulose	%	97.5	97.4	97.1	96.0	97.2	97.1	96.6	95.5	90.1	90.5	89.9	90.9
β -cellulose	%	2.2	2.4	2.4	3.1	1.2	1.4	2.2	2.9	9.7	9.1	9.6	7.2
Pentosan	%	6.4	6.0	5.9	5.8	3.2	3.1	3.0	3.0	2.5	2.6	2.6	2.4
Ash	%	—	—	0.05	0.06	—	0.05	0.04	—	—	0.06	0.05	—

$$Y = 0.28 X - 0.03$$

where Y : TAPPI chlorine consumption
X : permanganate number of pulp

In this bleaching, the amount of total chlorine added per pulp (21) was 200 per cent of TAPPI chlorine consumption. The ratio of chlorinated chlorine and available chlorine in sodium hypochlorite was 6 : 4. Also, the ratio of 1st. and 3rd., 5th. and 6th. were 2 : 1, and 3 : 2, respectively. At each sodium hydroxide treatment, 2 per cent of NaOH per pulp was added.

Conditions of the multistage bleaching are shown in Table 7, and analytical data of bleached pulp in Table 8.

The effects of cooking temperature at prehydrolysis on pentosan contents in the unbleached pulp are shown in Figure 2.

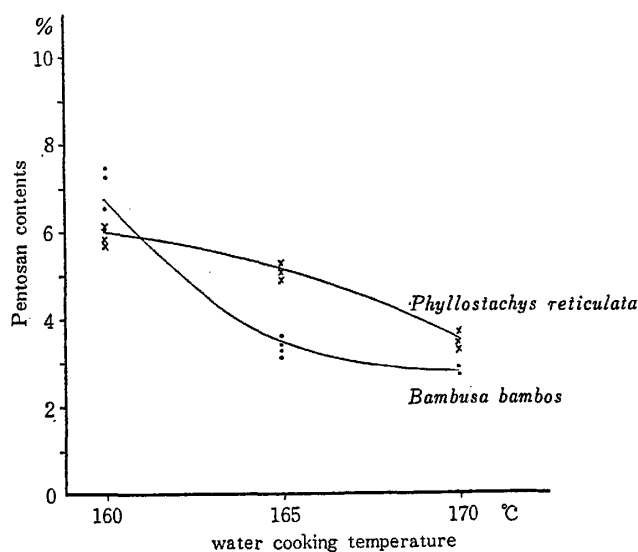


Fig. 2. Effect of temperature at prehydrolysis on pentosan contents of unbleached pulp

§ 2. Changes of average degree of polymerization during dissolving pulp manufacturing processes

This experiment was undertaken to investigate the change of average degree of polymerization at water cooking—sulphate pulping and multistage bleaching.

Average degree of polymerization of unbleached and bleached pulps were obtained by measuring the viscosities of their nitrated celluloses.

(Preparation of delignified pulp) (17)

Five grams of unbleached pulp and 10 g. of distilled water were weighed into a glass bottle, and then sodium hypochloride was added to the extent of 18~40% in proportion to lignin contents in pulp, and acetic acid was added to be 0.5% solution. The delignification was allowed to proceed for approximately 30 min. at 60°C. At the end of the reaction period, the pulp was filtered and then washed with distilled water for several times, and was dried at 50°C.

(Preparation of nitrating mixture) (18, 19)

For a standard batch of nitrating acid, 1,000 g. of 90 per cent nitric acid were weighed into a 2-liter flask and placed in an ice-cold bath. A 404 g. portion of phosphoric anhydride was added slowly. It was kept cool and shaken until solution with P₂O₅ was complete, then it was filtered through glass wool. The acid was stored in a dark cool place and used within 2 or 3 days after make-up.

(Nitration of pulp)

An 80 g. portion of the nitrating acid mixture was weighed into a wide-mouth glass stoppered bottle and cooled in a constant temperature bath to 20.0°C. 1 g. of pulp was added quickly and stirred into the mixture. The nitration was allowed to proceed for 30 min. at 20.0°C.

At the end of the reaction period the nitrated pulp was filtered using 1-G-1 sintered glass to free them from excess acid and were drowned in a large volume of cold water. To stabilize the nitrated pulp, it was steeped in the saturated sodium carbonate solution, then in the 10 per cent acetic acid, and was washed with distilled water. Finally, to remove the nitrated lignin, the nitrated pulp was boiled for 20 min. in 200 ml. of distilled water, and then was washed with methyl alcohol, and dried at 50°C in a dry atmosphere.

(Measurement of viscosity and calculation of degree of polymerization)

A solution was made of the nitrated pulp in absolute acetone. Viscosities were determined at 20 ± 0.1°C in Cannon Fenske type viscometer at concentration of 0.05 g. per 100 ml. of solvent.

The following formula gives values for degree of polymerization which are consistent with the experimental viscosity and concentration data.

$$DP = K[\eta]$$

where

$$[\eta] = \frac{\eta_{sp}/C}{1 + k'\eta_{sp}}$$

$$\eta_{sp} = \eta_{rel} - 1$$

$$\eta_{rel} = \frac{\text{viscosity of solution}}{\text{viscosity of solvent}}$$

$$C = \text{concentration of cellulose nitrate (g/100 ml. solvent)}$$

$$K = 100$$

$$k' = 0.35$$

The results of the average degree of polymerization of unbleached and bleached pulps determined are given in Table 9, and the effects of the temperature and total NaOH at sulphate cooking on the average degree of polymerization of pulps are shown in Figure 3.

Table 9. Average degree of polymerization of Unbleached and Bleached pulp
(A) Effect of sulphate cooking temperature.

Prehydrolysis cooking temp. °C	160				165				170			
Sulphate cooking temp. °C	130	140	150	160	130	140	150	160	130	140	150	160
Raw bamboo: <i>Phyllostachys reticulata</i>												
D.P. of unbleached pulp	1960	1850	1660	1450	1750	1650	1480	1220	—	1085	—	760
D.P. of bleached pulp	1030	1005	1000	950	—	730	—	700	—	610	—	600
Raw bamboo: <i>Bambusa bambos</i>												
D.P. of unbleached pulp	1880	1780	1630	1370	—	1670	1490	1310	—	900	—	600
D.P. of bleached pulp	1570	1520	1370	1120	—	990	900	810	—	630	—	490

(B) Effect of total NaOH at sulphate cooking

Prehydrolysis cooking temp. °C	160				165				170			
Total NaOH %	14	17	20	23	14	17	20	23	14	17	20	23
Raw bamboo: <i>Bambusa bambos</i>												
D.P. of unbleached pulp	1640	1490	1370	1285	1500	1360	1310	1230	810	680	600	540
D.P. of bleached pulp	1270	1160	1120	1100	900	810	800	780	490	500	490	480

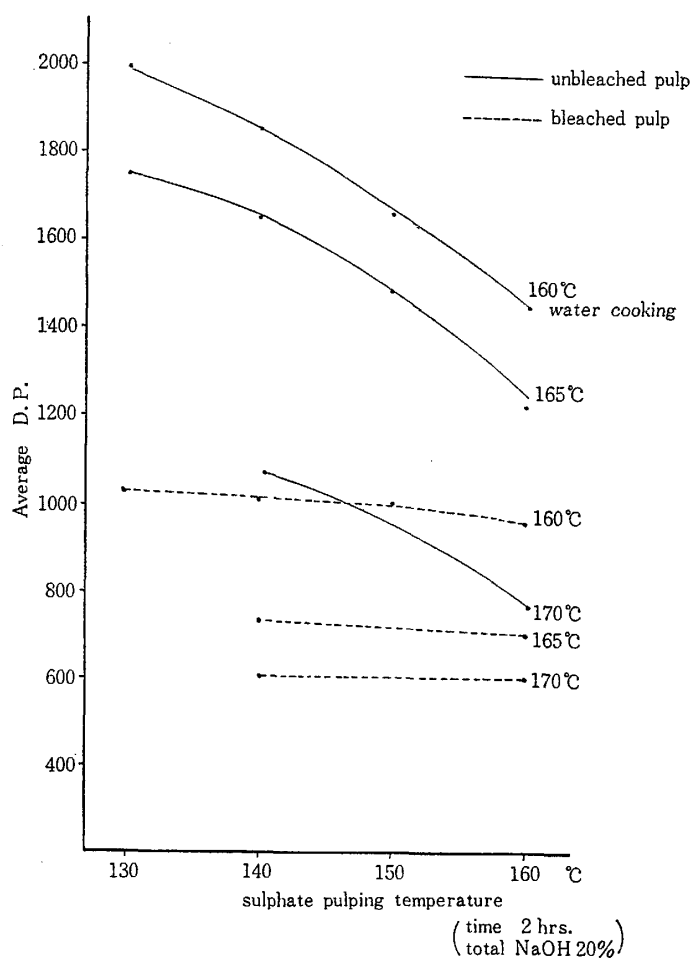


Fig. 3-1. Effect of temperature at sulphate pulping on degree of polymerization of pulp (*Phyllostachys reticulata*)
(time 2 hrs. total NaOH 20%)

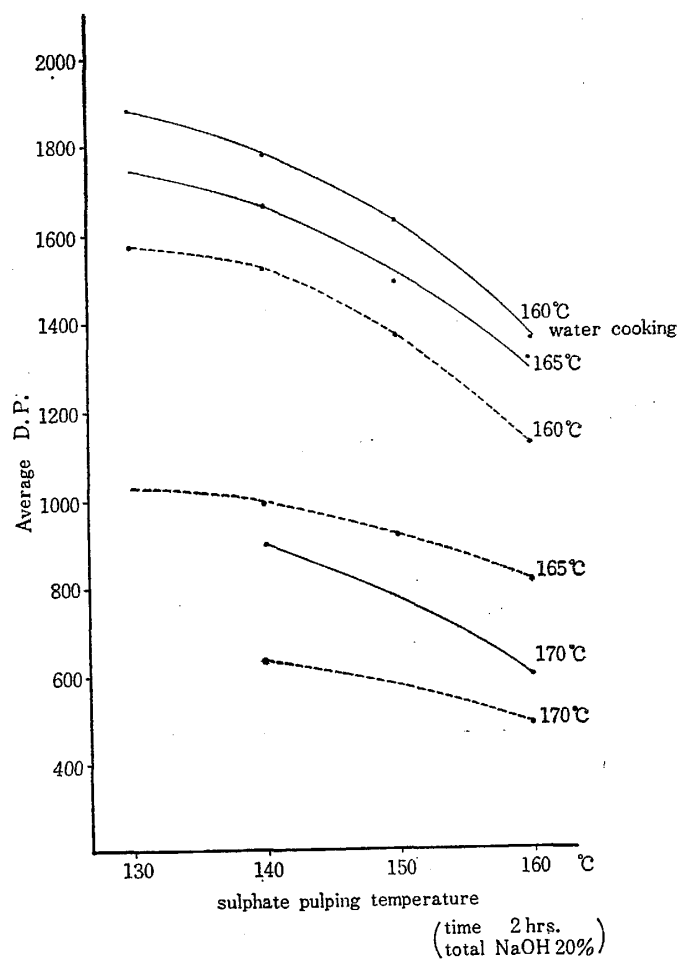


Fig. 3-2. Effect of temperature at sulphate pulping on degree of polymerization of pulp (*Bambusa bambos*)

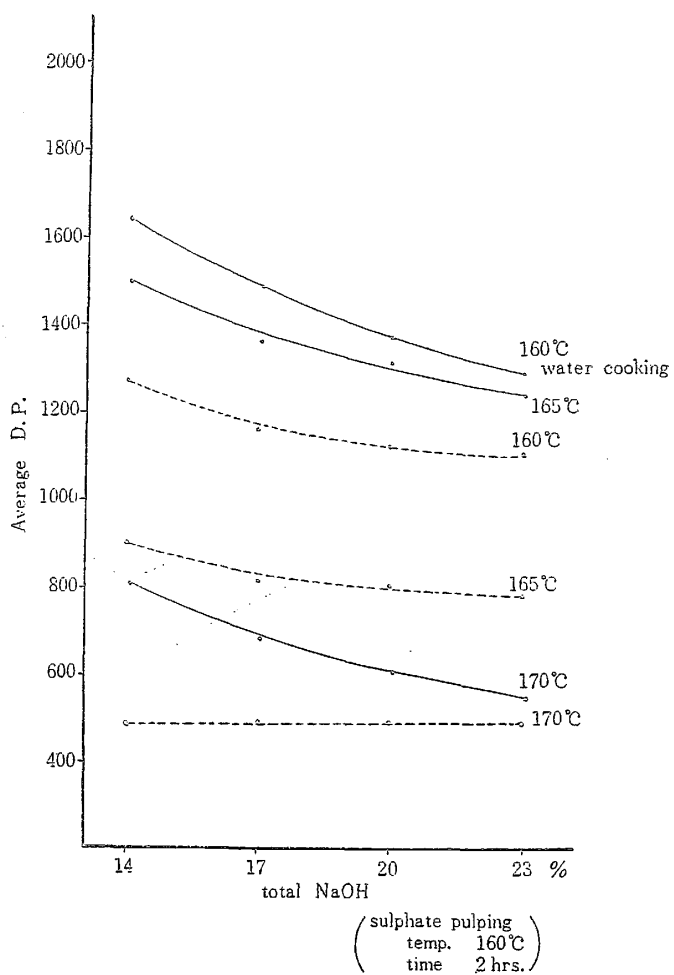


Fig. 3-3. Effect of total NaOH at sulphate pulping on degree of polymerization of pulp (*Bambusa bambos*)

§ 3. *The chemical properties of typical dissolving bamboo pulp*

Characteristics of several dissolving bamboo pulp which had been manufactured in this laboratory were investigated, and were compared with those of the dissolving sulphite pulp from coniferous wood and the dissolving sulphate pulp from deciduous wood which were contributed from the factories. The results are shown in Table 10.

Table 10. Analysis of Bamboo DKP*, N-DSP** and L-DKP***

	Bamboo DKP				N-DSP	L-DKP
	<i>Phyllostachys reticulata</i>		<i>Bambusa bambos</i>			
Prehydrolysis Cooking Temp. (°C)	160	165	160	165	—	—
Sulphate Cooking Temp. (°C)	160	160	160	160	—	—
Yield (based on original bamboo) %	26.1	26.7	35.9	29.7	—	—
Brightness %	91	92	90	91	—	—
α -cellulose %	97.4	97.4	97.1	96.6	94.1	95.5
Pentosan in α -cellulose %	4.3	2.9	4.0	2.2	0.6	1.8
Pure α -cellulose %	93.2	94.6	93.2	94.5	93.5	93.8
β -cellulose %	1.8	1.2	2.4	2.2	4.4	3.7
Pentosan %	5.9	4.3	5.9	3.0	2.0	4.1
Ash %	0.06	0.06	0.05	0.04	0.03	0.05
Copper number	0.3	0.3	0.3	0.5	0.7	0.6
Average degree of polymerization	950	700	1120	810	930	670
Relative viscosity	—	—	—	—	4.6	3.7

* Bamboo DKP: Dissolving bamboo pulp

** N-DSP : Dissolving sulphite pulp from coniferous wood

*** L-DKP : Dissolving sulphate pulp from deciduous wood

Discussion

The discussion below may be referred from the results of these experiments.

(1) It is recognized that *Bambusa* is hydrolyzed less than *Phyllostachys* as shown in Table 5, moreover, the ratio of removed pentosan to dissolved matters in *Bambusa* is much bigger than in *Phyllostachys*.

(2) As shown in Figure 2, pentosan contents in the unbleached pulp depend upon the prehydrolysis condition.

(3) As the removal of pentosan does not occur during bleaching process, pentosan contents in bleached pulp is decided by the prehydrolysis process.

(4) β -cellulose contents in bamboo pulp produced at 170°C 4 hrs. cooking of prehydrolysis is higher than at the other conditions. From this result, it is illustrated that this treatment is over cooking. (Table 8)

(5) Although α -cellulose contents of dissolving bamboo pulp are more than those of dissolving sulphite pulp from coniferous wood and dissolving sulphate pulp from deciduous wood, its contents are calculated approximately equal when pentosan contained in α -cellulose was reduced. (Table 10)

(6) α -cellulose in dissolving bamboo pulp contains 2~4 per cent of resistant pentosan, while dissolving pulps from coniferous wood and deciduous wood contain 0.6 per cent and 1.8 per cent, respectively. (Table 10)

(7) Chemical properties of dissolving bamboo pulp compare favorably with those of dissolving pulps from woods as shown in Table 10.

(8) As shown in Figure 3, the average degree of polymerization of unbleached and

bleached pulps depend upon the prehydrolysis conditions. When both *Phyllostachys* and *Bambusa* bamboos were prehydrolyzed at 170°C 4 hrs. water cooking, the average degree of polymerization of the unbleached and bleached pulps decrease sharply.

(9) The values of average degree of polymerization of the several dissolving bamboo pulps are in the available range, namely 600 to 1,000, for the material of rayon, as those of coniferous and deciduous wood pulps.

Part 3. Filterability tests of viscose

Experiment and results

This experiment was undertaken to investigate the properties of viscose made from dissolving bamboo pulp, comparing with viscoses of dissolving pulp from coniferous and deciduous woods.

Viscose was prepared as followings: 50 g. of pulp (of uniform air dry moisture contents) were steeped for 2 hrs. in 1,000 ml. of 17.5 per cent caustic soda solution kept within 18~20°C. After the steeping process, the pulp mass was pressed to remove excess caustic soda solution.

Table 11. Filterability of Bamboo DKP, N-DSP and L-DKP.

		N-DSP	L-DKP	<i>Phyllostachys reticulata</i>		<i>Bambusa bambos</i>	
				Exp. 1	Exp. 2	Exp. 1	Exp. 2
α -cellulose contents (%)		94.1	95.5	93.2		93.2	
Average D.P.		930	670	950		1120	
Aging Time (hr.)		35	40	35	30	35	30
Viscosity of Viscose (sec.)		28	29	20	32	18	34
Hottenroth no. (ml.)		9.6	10.8	9.8	10.4	9.0	9.8
Weight of viscose filtered	0~5 min. (g.)	56.08	63.28	67.76	94.94	127.00	60.96
	5~10	51.52	53.66	61.43	74.58	89.77	52.25
	10~15	48.05	46.83	52.07	57.98	65.47	41.95
	15~20	45.71	41.89	45.77	47.34	50.11	35.08
	20~25	42.64	37.20	40.11	37.97	39.72	30.22
	25~30	39.25	33.91	35.42	33.11	36.65	26.63
	30~35	36.37	30.47	31.76	28.05	32.87	23.85
	35~40	32.55	27.60	28.08	24.70	30.60	21.57
	40~45	32.09	25.03	25.59	24.30	27.12	19.74
	45~50	31.86	22.31	24.49	23.74	25.20	18.35
	50~55	30.85	21.56	23.25	23.05	23.72	17.19
	55~60	29.80	20.51	22.58	21.57	22.50	16.35
60~65	28.91	20.06	21.83	21.63	21.40	15.65	
A (g.)		51.52	53.66	61.43	74.58	89.77	52.25
B		36.37	30.47	31.76	28.05	32.87	23.85
C		28.91	20.06	21.83	21.63	21.40	15.65
D		187.91	179.58	199.38	217.88	245.07	159.49
E		261.68	201.44	213.00	200.15	220.06	159.34
30 min. Filterability (%)		70.6	56.8	51.7	37.6	36.6	45.6
60 min. Filterability (%)		56.1	37.4	35.5	29.0	23.8	29.9
Kw		135	231	226	259	237	314

The pressing factor, i.e., ratio of pressed wet alkali cellulose to pulp used was about 3.5. After pressing, the alkali cellulose was mechanically shredded to small uniform crumbs. The alkali cellulose crumbs were placed in glass bottle which have loosely fitting cover, and then were allowed to aging for 30~40 hrs. at 20°C. After aging, 40 per cent carbon disulfide (based on the weight of the α -cellulose) was added, and the xanthating was taken for 4 hrs. at 20°C.

The cellulose xanthate was mixed for 5 hrs. with dilute sodium hydroxide to produce 8.0 per cent α -cellulose and 7.0 per cent sodium hydroxide solution.

In regard to α -cellulose value of dissolving bamboo pulp, however, the value corrected for the pentosan contained in α -cellulose, that is, pure α -cellulose value was used.

This viscose solution was allowed to ripen for about 4 days at 20°C.

The filterabilities of viscose were determined as described below.

(Condition)

Filtering area	10.0 cm ²
Filtering filament	Cotton (JIS No. 19) 4 sheets
Filtering pressure	30 cmHg

(Method for calculation)

The filterabilities of 30 min. and 60 min., and clogging constant, K_w , were calculated from the following formulas.

$$30 \text{ min. Filterability (\%)} = B/A \times 100$$

$$60 \text{ min. Filterability (\%)} = C/A \times 100$$

where A = weight of viscose filtered between 5~10 min.

B = weight of viscose filtered between 30~35 min.

C = weight of viscose filtered between 60~65 min.

$$K_w = 100,000 \times \frac{2 - E/D}{E + D}$$

where D = weight of viscose filtered between 5~25 min.

E = weight of viscose filtered between 25~65 min.

The results of filterability determined are shown in Table 11.

Discussion

The discussions below may be referred from the results of this experiment.

(1) It is apparent from Table 11 that the dissolving bamboo pulps have characteristics in aging time of the alkali cellulose, that is, the aging time of bamboo pulp is shorter than those of dissolving pulps of coniferous and deciduous woods.

(2) The filterability of viscose made from the dissolving bamboo pulp is inferior from that of dissolving pulp from coniferous wood, but is as similar as that of dissolving pulp from deciduous wood.

(3) There is not a great variation between viscose made from bamboo pulp and wood pulp on the standpoint of the weight of viscose filtered.

Summary

(1) Dissolving bamboo pulp can be manufactured by application of the processes of "sulphate pulping subsequent to prehydrolysis". When water cooking is applied for prehydrolysis, cooking conditions of 160°C 4 hrs. and 165°C 4 hrs. are favorable to produce the dissolving bamboo pulp. In this case, the sulphate cooking condition is the followings; temperature 160°C, time 2 hrs., total NaOH 20% and sulphidity 20%.

(2) Pentosan contents in the unbleached pulp depend upon the prehydrolysis conditions, and the pulp which is produced during the above treatments, has less than 5 per cent of pentosan contents.

(3) Average degree of polymerization of bleached dissolving bamboo pulp compares favorably with those of dissolving pulp from woods.

(4) Chemical properties of dissolving bamboo pulp have no great difference from those of dissolving pulp from woods.

(5) There is no a wide difference between the filterabilities of viscose made from bamboo and those from woods.

(6) The dissolving bamboo pulp manufactured through these processes, may be possible to be utilized in industrial practice. *Bambusa* from Indonesia is more suitable than *Phyllostachys* from Japan for the raw materials of dissolving pulp, in viewpoints of the yield and the average degree of polymerization of pulp.

References

- 1) Hamaguchi, E., Miyake, Y. and Ono, K., *Industry of Cellulose (Japan)* **16**, 193 (1940)
- 2) Hamaguchi, E., Miyake, Y. and Ono, K., *J. Soci. Trop. Agri.*, **12**, 9 (1940)
- 3) Naffziger, T.R., Matuszewski, R.S. and Wolff, I.A., *TAPPI*, **43**, 591 (1960)
- 4) Jaglekar, M.H. and Donafrio, C.P., *TAPPI*, **34**, 254 (1951)
- 5) Horio, M., *Bull. Inst. Chem. Res., Kyoto Univ.*, **36**, (1957)
- 6) Heuser, E., *TAPPI*, **33**, 118 (1950)
- 7) Davis, W.E., *Ind. Eng. Chem.*, **43**, 516 (1951)
- 8) Bachlott, D.D., Miller, I. K. and White, W. D., *TAPPI*, **38**, 503 (1955)
- 9) Spurlin, H.M., *Cellulose and Cellulose derivative*, 930 (1943)
- 10) Fahmy, V. Y. and Abu-State, A., *Das Papier*, **15**, 44 (1961)
- 11) Hass, H., Battenberg, E. and Teves, D., *TAPPI*, **35**, 116 (1952)
- 12) Tono, T., *Bull. of Univ. Osaka Pref., Ser. B*, **11**, 155 (1961)
- 13) Tono, T., *Bull. of Univ. Osaka Pref., Ser. B*, **14**, 127 (1963)
- 14) Timell, T. E., *TAPPI*, **40**, 25 (1957)
- 15) Heuser, E. and Jørgensen, L., *TAPPI*, **34**, 57 (1951)
- 16) Mitchell, R. L., *Ind. Eng. Chem.*, **38** 843 (1946)
- 17) Fukuda, Y., Kaminiwa, A. and Hatanaka, T., *Japan TAPPI*, **9**, 491 (1955)
- 18) Mitchell, R. E., *Ind. Eng. Chem.*, **45**, 2526 (1953)
- 19) Alexander, W. J. and Mitchell, R. L., *Anal. Chem.*, **21**, 1497 (1949)
- 20) Kaminiwa, A., *Japan TAPPI*, **12**, 102 (1958)
- 21) Hayashi, M. and Ono, K., *Bull. of Univ. Osaka Pref., Ser. B*, **11**, 161 (1961)