



**TOGETHER**  
*for a sustainable future*

## OCCASION

This publication has been made available to the public on the occasion of the 50<sup>th</sup> anniversary of the United Nations Industrial Development Organisation.



**TOGETHER**  
*for a sustainable future*

## DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as “developed”, “industrialized” and “developing” are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

## FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

## CONTACT

Please contact [publications@unido.org](mailto:publications@unido.org) for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at [www.unido.org](http://www.unido.org)



D02944



United Nations Industrial Development Organization

Distr.  
LIMITED

ID/WG.102/20  
21 July 1971

ORIGINAL: ENGLISH

Expert Group Meeting  
on Pulp and Paper

Vienna, 13 - 17 September 1971

DISSOLVING PULP FROM MANGROVE WOODS

AND PARA RUBBERWOOD 1/

by

T. Kayama, M. Nakamura, A. Nagoshi  
Pulp and Paper  
Laboratory Forest Products  
Chemistry Division Government  
Forest Experiment Station  
Tokyo, Japan

1/ The views and opinions expressed in this paper are those of the authors and do not necessarily reflect the views of the secretariat of UNIDO. This document has been reproduced without formal editing.

id./1-5800

We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.

### Summary

Dissolving pulp should have uniform quality, because severe restriction exists on evaluating the quality, therefore, it is desirable to use one species or species having similar characteristics as raw material for production of dissolving pulp. Since the species in natural tropical hardwood forests are mixed, it is quite restricted to get raw material for the production of dissolving pulp.

Mangrove woods and Para rubberwood, which could be considered suitable raw material for the production of dissolving pulp, had been investigated by several institutes in Japan, and dissolving sulphite pulp from blended domestic hardwoods with mangrove woods or Para rubberwood have been produced commercially since 1965 and 1967 respectively.

#### Mangrove woods

Based on preliminary investigation, it was found that Lunggadai (*Bruguiera* spp.), Bakawan (*Rhizophora* spp.), and Tengar (*Cerops* spp.) were suited as raw materials for production of dissolving pulp by sulphite process.

Basic specific gravity of mangrove woods ranged from 0.7 to 0.8. Fibre length (about 1.5 mm.) and cellwall thickness (about 9 microns) were higher than the average of Japanese hardwoods. Fibre diameter (about 25 microns) was approximately the same as Japanese hardwoods.

Generally, most of the tropical hardwoods were relatively high in lignin and low in pentosan contents, however, those of mangrove woods, were similar to Japanese hardwoods. Ash content was higher than Japanese hardwoods.

Unbleached pulp yield was similar to that of Japanese hardwoods. The pulps from mangrove woods had higher  $\alpha$ -cellulose content, and screened pulp yield, and lower permanganate number than those of the pulps from Japanese hardwoods in same relative viscosity. The pulp from Bakauan was relatively high in ash content, which was decreased by mechanical method or hydrochloric acid treatment. The viscose reactivity and filament quality of the pulps were reasonably satisfactory.

#### Para rubberwood

Rubberwood had a basic specific gravity about 0.54 and possessed fibres similar to most Japanese hardwoods, i.e., diameter (about 22 microns), cell wall thickness (about 3.0 microns). Fibre length (about 1.5 mm) was longer than the average of Japanese hardwoods. Starch was detected in parenchyma and ray cells.

Rubberwood was relatively high in ash and hotwater solubles and low in pentosan content. Otherwise, chemical properties of rubberwood was similar to those of Japanese hardwoods. Rubberwood was very easily stained by fungus, and the basic specific gravity of stained wood was decreased on storage.

unbleached pulp yield ranged from 42 % to 44 %, and it was found that the suitable relative viscosity of unbleached pulp to produce viscose was 8.0 to 8.5. Chemical consumption of the pulps from blue stained wood were higher than that of the pulps from sound wood. The viscose reactivity and filament quality of the pulps from rubberwood were almost same as

those of the pulps from Japanese hardwoods. The latex content of bleached pulp was less than 0.02 %, and had no influence upon the viscose and filament quality.

## I. Introduction

The most widespread dissolving pulp at present used in the artificial fibre industry are that produced from the conifers and the hardwoods of the temperate zone. Little is known, however, about the use of tropical hardwoods for the production of dissolving pulp.

Dissolving pulp should have uniform quality, because severe restriction exists on evaluating the quality, therefore, it is desirable to use one species or species having similar characteristics as raw material for production of dissolving pulp. Since the species in natural tropical hardwood forests are mixed, it is quite restricted to get raw material for the production of dissolving pulp.

Mangrove woods and Para rubberwood, which could be considered suitable raw material for the production of dissolving pulp, had been investigated by several institutes in Japan, and dissolving sulphite pulp from blended domestic hardwood with mangrove woods or Para rubberwood have been produced commercially since 1965 and 1967, respectively.

Putping studies on mangrove woods and rubberwood have been done by several laboratories and institutes but we have seen only two published informations on producing dissolving pulp from mangrove woods<sup>1)</sup> or rubberwood<sup>2)</sup> other than the research works in Japan. The dissolving pulps have been prepared by prehydrolysis sulphate process in both cases.

This paper deals with the production of dissolving pulp from mangrove woods and rubberwood by sulphite process.

## II. Raw materials

### 1. Mangrove woods

Mangrove is found widely distributed in southeast Asia and covers very extensive coastal areas. The dominant species of mangrove belong to Rhizophoraceae in the region. At present the timber is not sufficiently utilized in spite of its large quantities of growing stock, although the timber is used as fuel and for making charcoal and its bark is used for tanning leather and for dyeing purposes.

Preliminary experiments to evaluate the suitability for producing dissolving pulp had been done on about twenty species of mangrove, which were collected from Philippines, Sabah, Saravak, Malaya and Sumatra. The results are shown in Table 1.

Table 1

It has been found that the species of Rhizophoraceae including the genera of *Brugiera*, *Rhizophora* and *Ceriops* were suitable for production of dissolving pulp.

Dissolving pulp has been produced commercially from the species of Rhizophoraceae, in which Bakauan (*Rhizophora* spp.), Tangal (*Ceriops* spp.), Langgadai (*Brugiera parviflora*) and Pototan (*Brugiera sexangula*) are included. Bakauan and Tangal as well as Langgadai and Pototan are very similar in their suitability for producing dissolving pulp. The ash content of Bakauan is higher than that of Langgadai, therefore, it is necessary to decrease ash content from the pulp from Bakauan.

### 2. Rubberwood

There are about 7200,000 acres of land planted with Para rubber trees in south east Asia. These rubber trees are being replanted by replanting programs with 30 to 40 years rotation. A large quantities of wood waste,

Table 1. Mangrove species and their suitability for producing dissolving pulp

Genus	Suitability for producing dissolving pulp	Remark
Rhizophora	good	
Brugiera	good	
Ceriops	good	
Lumnitzera	good	
Sonneratia	not bad	Small specific gravity Not easy to bleach
Avicenia	bad	Poor viscose reactivity
Heritiera	bad	"
Xylocarpus	bad	Not easy to cook Poor viscose reactivity
Camptostemon	bad	Poor viscose reactivity
Excoecaria	bad	Small specific gravity High extractive content remaining in pulp



at 50 tons of oven dry wood per acre, should be produced. For example about 6 million tons of wood waste per year has been produced in Malaya.<sup>3)</sup>

It is botanically uniform. Only a small fraction is used at all, as fuel so that it is considered that rubberwood is promising raw material for production of dissolving pulp and for papermaking.

The wood under the tapping panels usually contains dark discolourations accompanied with latex, the results of wounds made during tapping. It was found that the pulps from this portion showed poor quality as dissolving pulp. This portion, therefore, has not been used as raw material for dissolving pulp.

### III. Properties of the wood

#### 1. Physical (properties)

Specific gravity of the mangrove woods and rubberwood is shown in Table 2.

Table 2

Basic specific gravity of mangrove woods ranged from 0.7 to 0.8, and that of rubberwood was about 0.54. The basic specific gravity of mangrove woods was higher than Japanese beechwood and the average of Japanese hardwoods. On the other hand that of rubberwood was almost the same as that of Japanese hardwoods.

Structural elements of the woods are given in Table 3.

Table 3

Mangrove woods had lower vessel and higher fibre contents compared with Japanese hardwoods. The contents of parenchyma and ray cells were similar to those of Japanese hardwoods. Rubberwood had lower vessel contents and higher parenchyma and ray contents than those of Japanese

Table 2. Specific gravity of mangrove woods and rubberwood

Species	Specific gravity g/ml.
<i>Brugiera</i> spp.	0.90 * 4)
<i>Ceriops</i> spp.	0.90 * 4)
<i>Rhizophora</i> spp.	0.90 * 4)
<i>Brugiera parviflora</i>	0.88 * 5)
"	0.65 ** 6)
<i>Brugiera gymmorrhiza</i>	0.74 ** 7)
<i>Rhizophora apiculata</i>	0.81 ** 7)
<i>Brugiera</i> sp.	0.68 ** 8)
<i>Rhizophora</i> sp.	0.81 ** 8)
<i>Hevea brasiliensis</i> (Rubber wood)	0.55 ** 9)
"	0.56 * 5)
"	0.54 **
<i>Fagus crenata</i> (Beech)	0.49 ** 10)

\* Specific gravity                      Air dry weight and volume  
 \*\* Basic specific gravity              Oven dry weight/Green volume

Table 3. Structural elements of the woods

Species	Vernacular name	Wood fibre %	Vessel %	Parenchyma %	Ray %
<i>Rhizophora</i> spp.	Bakauan	65~70	5~10	20~25*	
<i>Hevea brasiliensis</i>	Rubberwood	61.5	9.5	29.0*	
"	" 11)	58.5	10.7	6.3	24.5
<i>Fagus crenata</i>	Beech 10)	32.1	41.2	9.2	17.5
Japanese major hardwoods		58.0	19.0	23.0*	

\* Ray is included in this term.

hardwoods, but wood fibre contents were very similar.

Morphological properties of wood fibre are shown in Table 4.

Table 4

Fibre length (about 1.5 mm) and cell wall thickness (about  $9 \mu$ ) of mangrove woods were higher than the average of Japanese hardwoods. Fibre diameter (about  $25 \mu$ ) was similar to Japanese hardwoods. Rubber wood possessed fibres similar to most Japanese hardwoods except fibre length, i.e. diameter (about  $22 \mu$ ), cell wall thickness (about  $3.0 \mu$ ). Fibre length (about 1.5 mm) was longer than the average of Japanese hardwoods.

The crystals of calcium oxalate were found in the rays of mangrove woods. Starch was detected in the parenchyma and ray cells of rubberwood. Rubber, as latex, occurred only in the bark, and latex tube was not found in wood rays of rubberwood.

## 2. Chemical (properties)

The results of the chemical analysis of mangrove woods and rubberwood are shown in Table 5.

Table 5

Generally, tropical hardwoods were relatively high in lignin and low in pentosan contents. Lignin and pentosan contents of mangrove woods, however, was similar to Japanese hardwoods. Ash content was higher than Japanese hardwoods. Ash was roughly estimated to be composed of 80 % of CaO, 6 % of MgO, 2 % of SiO<sub>2</sub>, 3 % of Fe<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub>, and 9 % of others. Calcium salts were predominant, while the contents of magnesium salts were lower than expected quantity.

Excepting relatively high in ash and hotwater solubles and low in pentosan contents, rubberwood was chemically similar to Japanese hardwoods.

Table 4. Morphological properties of wood fibre

Species	Vernacular name	Wood fibre		
		Length (mm)	Diameter ( $\mu$ )	Cell wall thickness ( $\mu$ )
<i>Rhizophora</i> spp.	Backauan	1.57	24.8	10.0
<i>Bruguiera</i> spp.	Langgadal	1.34	22.9	9.2
<i>Hevea brasiliensis</i>	Rubberwood	1.49	21.8	3.0
"	" 11)	1.20	25.0	1.5~3.0
"	" 9)	1.50	22.0	2.8
<i>Fagus crenata</i>	Beech 10)	1.13	20.0	3.5

Table 5. Chemical components of the above woods and rubberwood

Genus	Rhizophora "Brugiara 5)		Brugiara 6)		Revea 5)		Revea 9)		Pag-sio)		Mixed hard-woods from Kyushu**
	Dakuan	Lengada	Lengada	Lengada	Rubberwood	Rubberwood	Rubberwood	Rubberwood	Beech	Beech	
Ash	1.14	2.01	1.6	—	0.9	1.35	1.08	—	0.64	0.39	0.61
CaC - MgO	0.53	—	—	—	—	—	—	—	—	0.21	0.22
5	2.7	—	—	—	—	—	—	—	—	—	—
6	3.5	2.9	4.4	—	5.9	6.0	5.9	—	—	2.8	4.9
7	1.2	2.8	1.0	—	2.1	3.9	3.5	—	1.8	3.0	6.2
8	1.9	—	—	—	—	—	—	—	1.0	1.0	3.0
9	0.2	—	—	—	—	—	—	—	—	—	—
10	—	23.9	—	—	18.8	22.2	19.2	—	—	—	—
Cellulose	73.9	—	82.5	—	82.1	—	—	—	51.4	76.3	75.2
hemicellulose	—	49.8	—	—	—	46.7	46.7	—	—	—	—
2-cellulose	—	—	47.1	—	—	—	41.4	—	50.9	—	—
Pectone	18.5	22.3	18.5	—	16.3	20.3	19.7	—	18.4	20.7	19.0
Lignin	22.0	19.6	16.2	—	20.2	26.2	25.4	—	23.6	19.0	24.3

\*) Results are based on oven-dry wood and shown in percentages.  
 \*\*) Ash at 425°C

Cellulose Kurschner's method.

The value of % NaOH soluble, Cellulose, Pectone, and Lignin are expressed percentages oven-dry wood free from extraneous substances.

\*\* Kyushu is located in southern part of Japan.

### 3. Storage characteristics of rubberwood

Rubberwood was readily attacked by blue staining fungus and also by insects on storage in the open and was quickly discoloured. Storage under water as logs or as chips, under Malayan conditions, caused evolution of gas, a very unpleasant odour and a slime on the wood surface. These phenomena have been reported by Peal and Peh.<sup>9)</sup> Data on deterioration of rubberwood during storage are given in Table 6.

Table 6

Rubberwood was very easily stained by fungus on storage in the open. On the other hand, under water storage prevented blue staining fungus from growing. Basic specific gravity and holocellulose content were decreased on storage in the open and under water. This is almost certainly due to the biological breakdown of wood components.

## IV. Pulping, refining and bleaching

### 1. Mangrove woods

#### 1.1 Wood samples

Bakawan (*Rhizophora* spp.) woods were used for the investigation. Since the pulps from Bakawan gave relatively high ash content, which was rather difficult to remove.

#### 1.2 Pulping

Pulping conditions and properties of unbleached pulps are given in Fig. 1.

#### Fig. 1

Bakawan woods were cooked very easily without any cooking troubles in spite of their high basic specific gravity. The pulps from Bakawan, therefore, gave lower permanganate number and relative viscosity

Table 6. Effect of storage on deterioration of wood qualities

Storage condition and duration	Yard 1 month	Yard 6 months	Yard 10 months	Under water 6 months
Basic specific gravity	0.57	0.53	0.49	0.45
Holocellulose %	87.6	82.2	81.2	81.9



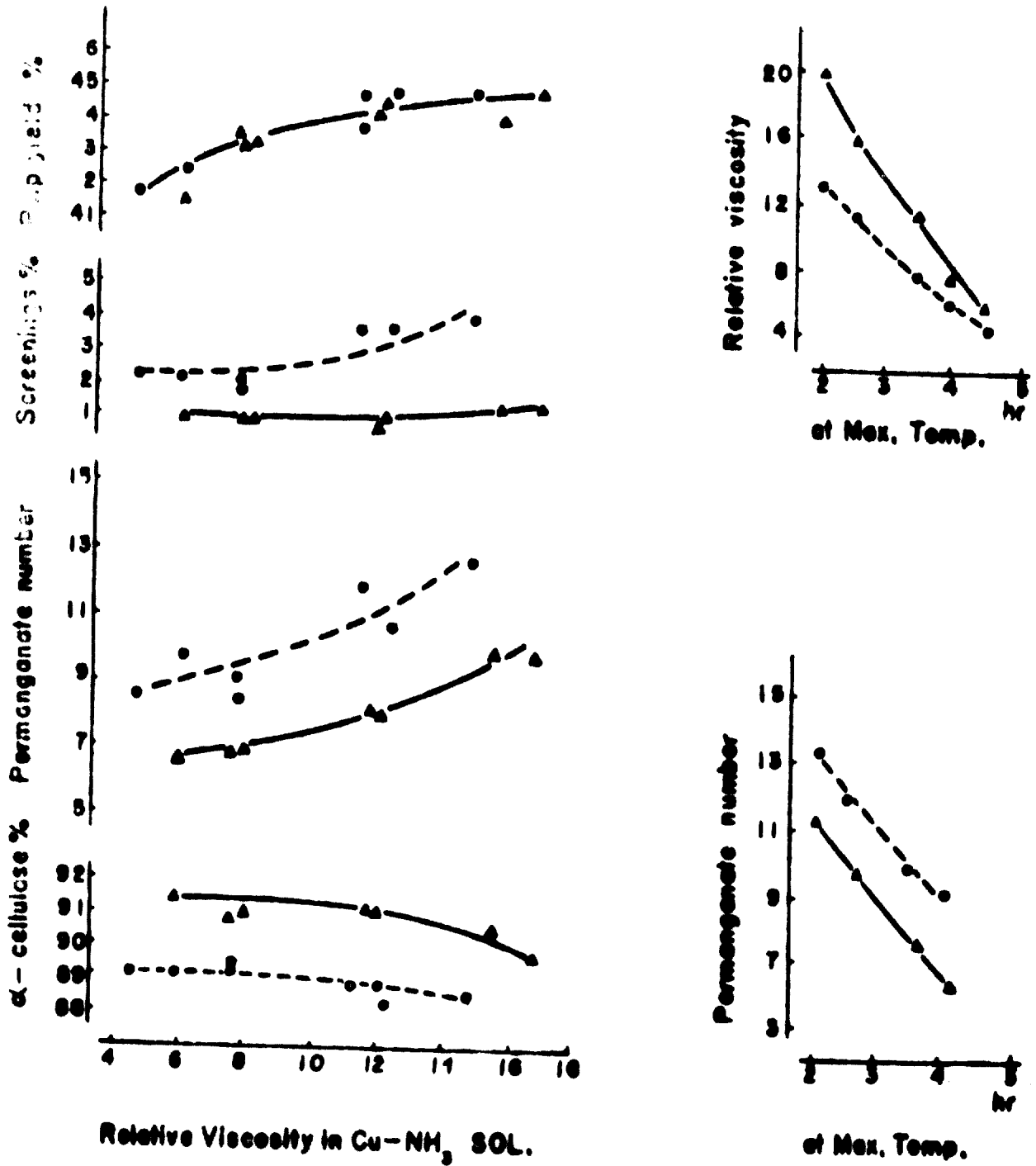


Fig. 1. Properties of Unbleached Pulp

—▲— Bakauan

---●--- Mixed hardwoods (Japanese)

Cs-base sulphite pulping

Total  $\text{SO}_2$  8%. Combined  $\text{SO}_2$  1.5%

than those of the pulps from mixed Japanese hardwoods in case holding time at maximum temperature. These pulps also gave higher  $\alpha$ -cellulose content, similar pulp yield, and lower permanganate number and screenings than the pulps from mixed Japanese hardwoods in the same relative viscosity. It was thought that it might be possible to produce a dissolving pulp having high  $\alpha$ -cellulose content in high average degree of polymerisation from Bakauan.

### 1.3 Screening

It is necessary to develop a residual EDTA ash removing method for producing dissolving pulp from Bakauan woods, because these pulps contain large amount of residual EDTA ash which would be a cause of spinning trouble. Trials were carried out to remove EDTA ash from the pulps from Bakauan.

The results of fibre classifications are given in Fig. 2.

Fig. 2 and Fig. 3

The pulps from Bakauan woods showed higher percentage of long fibre fraction, in comparison with that of the pulps from the Japanese hardwoods. On the other hand, the fractions of 40/60 and 60/150 of the latter showed higher than those of the former. The "fines" fraction passing through the 150 mesh wire, which was mainly consisted from ray cells, showed similar quantity in both cases.

A large quantity of EDTA ash content was found in the "fines" fraction of the pulps from Bakauan woods as shown in Fig. 3. As mentioned above, it was observed that the 80 to 90 % of EDTA ash of unbleached pulps was found in the "fines" fraction after mechanical agitation. Therefore, it might be possible to remove the EDTA ash from the unbleached pulps by mechanical treatment.

The EDTA ash was decreased remarkably by screening of "fines"

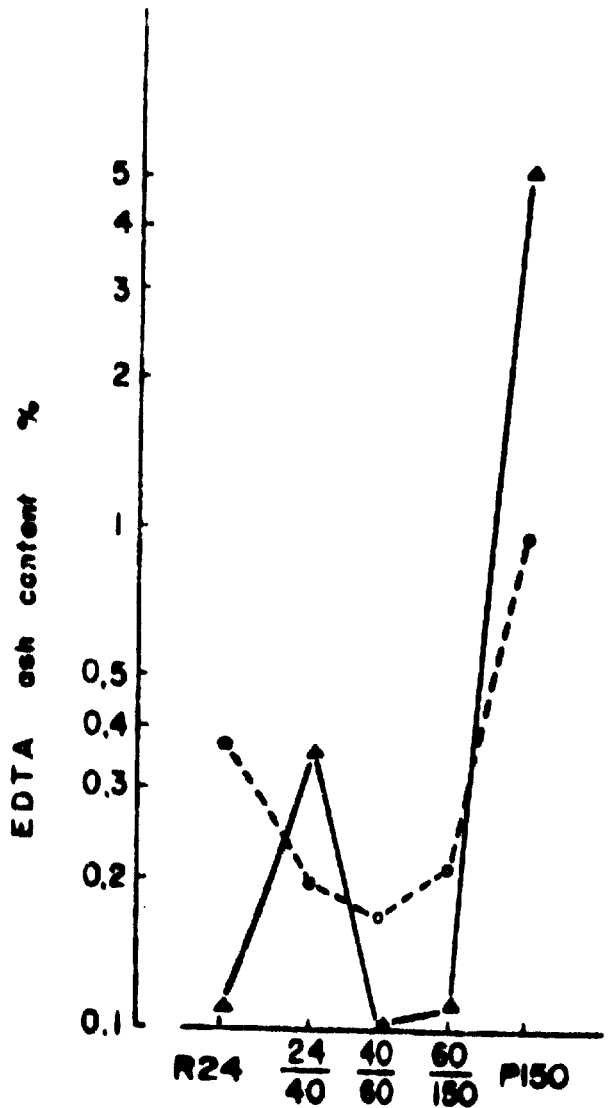
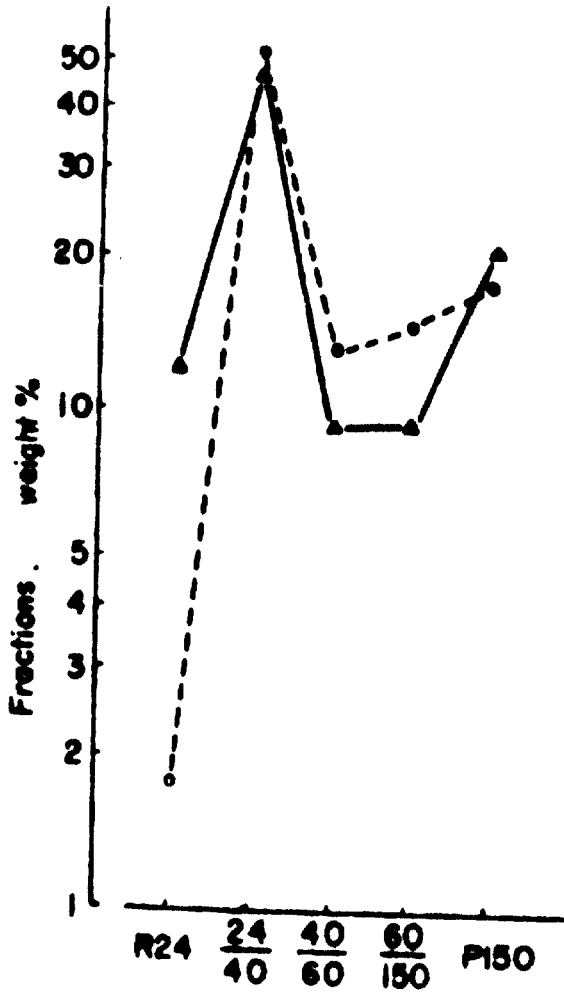


Fig. 2. Screen classifications of unbleached sulphite pulps

Fig. 3 EDTA ash content in fractions separated by screen classifications

R24 Retained on wire 24 mesh/inch  
 24/40 40/60 60/150 Between wires  
 P150 Pass through wire 150 mesh/inch  
 —△— Bakauen  
 ---○--- Mixed hardwoods (Japanese)

fraction following by mechanical agitation using an usual disintegrator. In the treatment of disintegration, it is unavoidable that a part of wood fibres are simultaneously cut off. However, the most part of wood fibres are retained on 40 meshes screen, as the degree of cutting of wood fibres are not drastic in the range of the treating conditions necessary for isolation of ray cells. Of course, unnecessary cutting of wood fibres should be avoided as it will lower the density of EDTA ash content in "fines" fraction and make it more difficult to selectively remove them.

#### 1.4 Refining and Bleaching

Unbleached pulps from mangrove woods showed high in  $\alpha$ -cellulose content, low in both lignin and extractives contents, and have no troubles to produce dissolving pulp. Refining and bleaching have been carried out by usual method using in pulping of Japanese hardwoods.

The properties of bleached pulps are given in Table 7.

##### Table 7

The pulps from mangrove woods showed higher alkali absorption velocity than that of the pulps from Japanese hardwoods. Moreover, they have had further superiorities in  $\alpha$ -cellulose content,  $\beta$ -cellulose content, extractives content and pentosan content, and have no other inferior properties compared with the pulps from Japanese hardwoods.

## 2. Rubberwood

### 2.1 Wood samples

Sound chips and blue stained chips, which had been stored for 21 days after chipping in the open, were used for the investigation. The latter was prepared to investigate the effect of blue stain on pulping and on the quality of pulp.

The wood qualities of the samples are shown in Table 8.

Table 7. Properties of dissolving pulps

	LDP DP* from Japanese hardwood	LMDP DP* from mixture of Japanese hard- wood and mangrove	MDP DP* from mangrove
$\alpha$ -cellulose %	88.8	89.4	89.4
$\beta$ -cellulose %	5.7	5.0	5.0
Copper number	1.1	1.1	1.1
Extractives %	0.36	0.25	0.25
Ash %	0.06	0.07	0.08
CaO + MgO %	0.03	0.04	0.05
Dust $\text{mm}^2/\text{m}^2$	40	40	40
Relative viscosity	4.6	4.6	4.6
Brightness %	92	92	92
Alkali absorption velocity mm	41	52	63
Swelling volume cc/g	5.9	5.9	6.2
Pentosan %	3.3	2.8	2.4

\* DP : dissolving pulp

Table 8

Six samples having different basic specific gravity, which ranged from 0.44 to 0.57, were also used for the investigation. These samples were considerably penetrated by blue stain.

## 2. 2 Pulping

Pulping conditions are as follows:

Cooking liquor:	total $\text{SO}_2$ 8.0 %, combined $\text{SO}_2$ 1.12 %
Liquor to wood ratio:	4 l/kg
Maximum temperature:	143°C
Maximum pressure:	8 kg/cm <sup>2</sup>
Schedule:	1 hr to 100°C 4.5 hr to 143°C

The holding time at maximum temperature is changed in given ranges in order to get the pulps having different viscosities.

The properties of unbleached pulps are given in Table 9.

Table 9

Screened pulp yield ranged from 40.6 % to 43.9 %, and screenings ranged from 0.3 % to 5.3 % respectively. Screenings increased with increasing relative viscosity of unbleached pulps. The pulps from blue stained chips showed higher pulp yield than that of the pulps from sound chips in the case of same relative viscosity. However, the blue stained chips gave lower pulp yield per one cubic meter of wood than the sound chips, since it has lower basic specific gravity than the sound one. The pulps from blue stained chips showed relatively high permanganate number.

## 2. 3 Refining and bleaching

Refining and bleaching were carried out by 5 stages process (C-E-E-H-D). The conditions and the results are given in Table 10 and Table 11.

Table 10, Table 11

Table 8. Properties of rubberwood samples

		Sound chips	Blue stained chips
Weight loss	%		7.4
Basic specific gravity	g/ml	0.54	0.50
Ash	%	0.74	0.83
Hotwater solubles	%	6.5	4.7
Alcohol-benzene extracts	%	1.9	1.5
Holocellulose	%	82.3	82.2
Pentosan	%	13.8	15.4
Lignin	%	19.6	22.0

Table 9. Properties of unbleached pulps

Sample	Basic specific gravity (wood)	Relative* viscosity	Pulp yield (screened) %	Screenings %	Pulp yield kg/m <sup>3</sup>	KMnO <sub>4</sub> number
Sound chips	0.54	10	40.6	5.6	219	10.2
Blue stained chips		8	41.9	2.8	226	7.5
Blue stained chips		6	41.9	0.3	226	5.4
Sound chips	0.52	10	41.7	5.3	217	11.5
Blue stained chips		8	42.9	2.6	223	9.5
Blue stained chips		6	42.5	0.6	221	8.5
Blue stained chips	0.50	10	43.1	4.0	215	12.5
Blue stained chips		8	43.9	1.0	220	10.8
Blue stained chips		6	43.7	0.5	219	9.3

\* Relative viscosity is measured by JIS method.

JIS relative viscosity      10    8    6  
 Tappi standard viscosity    CP   80   53   32

Table 9



Table 10. Refining and bleaching conditions

	Pulp consistency %	Temperature °C	Reaction time hr	Chemicals %
Chlorination	3.0	25	0.5	30% of $KMnO_4$ number
NaOH extraction	6.0	30	1.0	1.5*
NaOH refining	10.0	100	1.0	1.5*
Na-hypo. bleaching	6.0	50	5.0-6.0	1.3-1.5*
$ClO_2$ bleaching	10.0	75	3.0	0.3*

\* Pulp basis.

Table 11

Table 11. Properties of bleached pulps from rubberwood

Sample	Viscosity (un-bleached)	$\alpha$ -cellulose %	$\beta$ -cellulose %	Ash %	Copper number	Extractives %	Viscosity (bleached)	Pentosan %	Brightness	Dr
Sound chips	10	87.7	4.8	0.10	1.0	0.16	4.6	4.7	95	315
		89.3	4.7	0.08	1.0	0.12	4.6	3.8	95	328
		92.1	3.6	0.07	0.7	0.08	4.5	3.9	97	221
Sound chips 50% Blue stained Chips	10	87.7	4.1	0.09	1.2	0.26	5.0	5.9	94	324
		89.2	4.6	0.07	1.1	0.25	4.7	4.6	94	274
		91.4	3.7	0.05	0.5	0.18	4.7	4.0	93	230
Blue stained Chips	10	88.8	4.2	0.03	1.2	0.33	5.1	5.8	92	208
		89.7	3.8	0.06	1.1	0.22	4.7	4.6	93	154
		92.1	3.6	0.05	0.8	0.29	4.8	3.9	93	154
Sound chips	7.4	91.4	4.3	0.04	1.2	0.11	4.9	3.6	95	216
Sound chips	6	89.5	5.1	0.03	1.5	0.15	4.6	3.9	93	193
		90.7	5.3	0.03	1.5	0.10	4.5	2.8	95	199
		92.3	4.7	0.04	1.0	0.07	4.4	2.4	96	231
Sound chips 50% Blue stained Chips	5	89.0	4.8	0.03	1.9	0.23	5.2	4.2	91	199
		90.0	5.0	0.03	1.5	0.21	4.8	3.4	93	191
		92.2	4.5	0.02	1.2	0.16	4.6	2.8	91	161
Blue stained Chips	6	88.3	5.4	0.04	1.8	0.33	5.0	4.5	90	260
		90.0	5.1	0.05	1.6	0.29	5.0	3.4	87	269
		91.9	4.7	0.03	1.2	0.26	5.0	2.6	88	226

The pulps from blue stained chips gave relatively low brightness and high extractives content. In the case of the relative viscosity of unbleached pulp was 6, the pulps from blue stained chips showed higher relative viscosity and lower brightness than others after bleaching. It was considered that the effect of oxidizing bleaching by given conditions was not sufficient in this case.

On the other hand, in the case of the relative viscosity of unbleached pulp was 10, the both pulps from sound chips and blue stained chips gave a lot of screenings and high permanganate numbers (Table 9). Therefore, judging from the pulp yield, the consumption of chemicals and the quality of bleached pulp, it could be emphasized that the most suitable relative viscosity of unbleached pulp from rubberwood is approximately 8.

#### V. Viscose reactivity and filament qualities

##### 1. Mangrove wood pulp

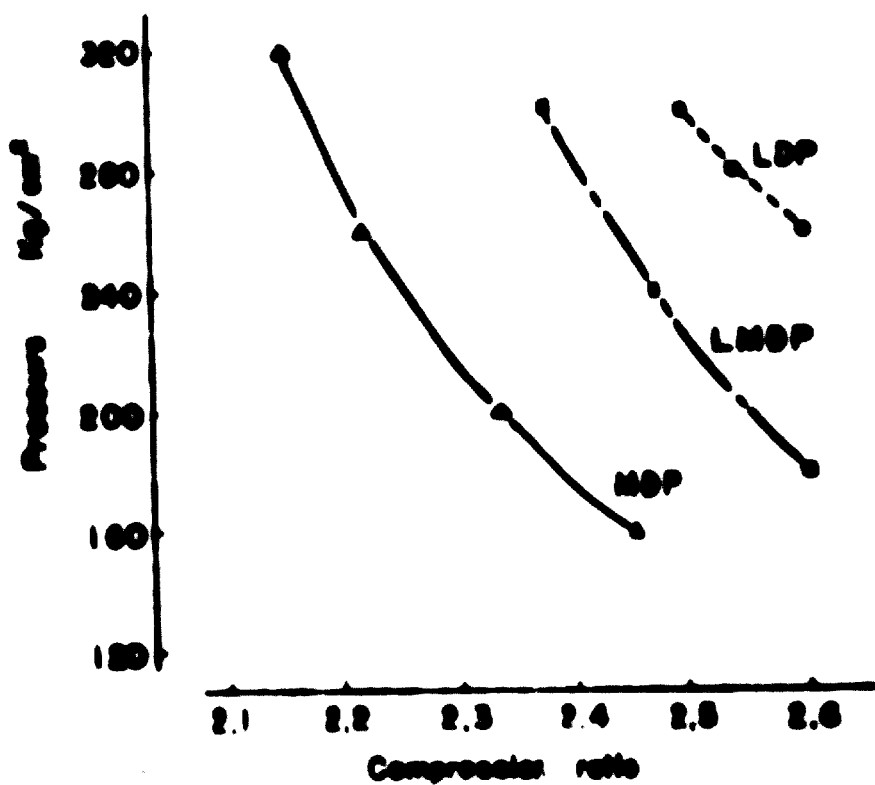
The compressibility of alkali cellulose of the pulps from different kind of woods including mangrove woods and Japanese hardwoods are shown in Fig. 4.

Fig. 4

The alkali cellulose of dissolving pulps from mangrove woods was compressed easily. This is one of the most typical characteristics of mangrove wood dissolving pulp. The compressibility of alkali cellulose is improved by mixing of mangrove wood dissolving pulp with Japanese hardwoods dissolving pulp.

Mercuric chloride resistance and anthracene resistance of mangrove wood dissolving pulp, softwood dissolving pulp and hardwood dissolving pulp are given in Fig. 5 and Fig. 6.

Fig. 5. Fig. 6



**Fig. 4 Compressibility**

**LDP : Dissolving pulp from mixed hardwoods**

**LMOP: Dissolving pulp from mixed hardwoods and mangrove woods**

**MOP : Dissolving pulp from mangrove woods**

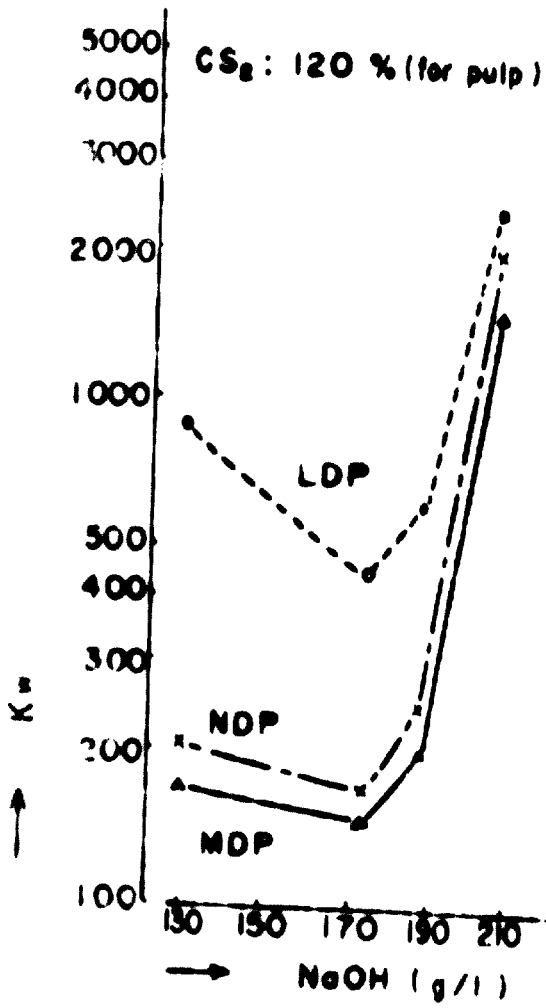


Fig. 5 Mercerization Resistance

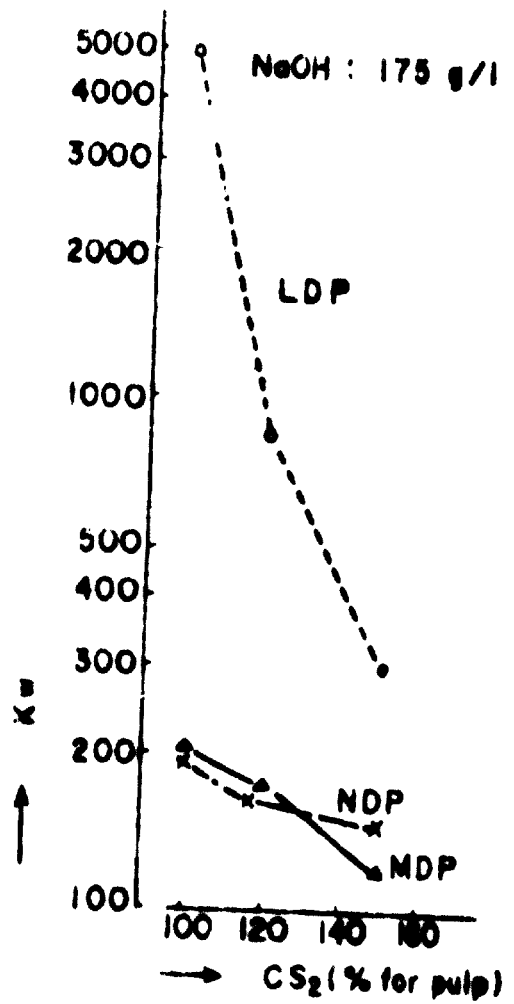


Fig. 6 Xanthation Resistance

LDP } Same as Fig. 4  
 MDP }  
 NDP : Dissolving pulp for mixed softwoods.

Mercerization resistance and xanthation resistance of mangrove wood dissolving pulp was lower than that of Japanese hardwoods dissolving pulp, and it showed rather similar viscose reactivity to that of softwood dissolving pulp.

In comparison of the viscose reactivity of the pulps from wood fibres, ray cells of mangrove wood dissolving pulp with that of Japanese hardwood, mercerization resistance and xanthation resistance become higher in the order of: mangrove wood fibre  $\ll$  mangrove wood ray cells  $\frac{1}{2}$ , Japanese hardwood fibre  $<$  Japanese wood ray cells. Fig. 7

However, there are some differences in the relationships between compression ratio and Kw (resistance of filtability of viscose) of mangrove wood pulp and Japanese wood pulp, i.e. the minimum Kw of mangrove wood pulp viscose is in the strongly compressed reagon. In the weakly compressed reagon, Kw numbers are rapidly increased owing to insufficient dissolving of wood fibres. Fig. 7

In other words, the proper compression ratios for mangrove wood dissolving pulp is much smaller than that of Japanese hardwood dissolving pulp, it should strongly affect the properties of viscose.

## 2. Rubberwood pulp

The conditions of preparation of viscose and spinning of filament are as follows:

### Preparation of viscose

Dissolving pulp	400 g (oven dry)
Concentration of NaOH	17.5 %
Consistency of slurry	4 %
Temperature	50°C
Duration	30 min.

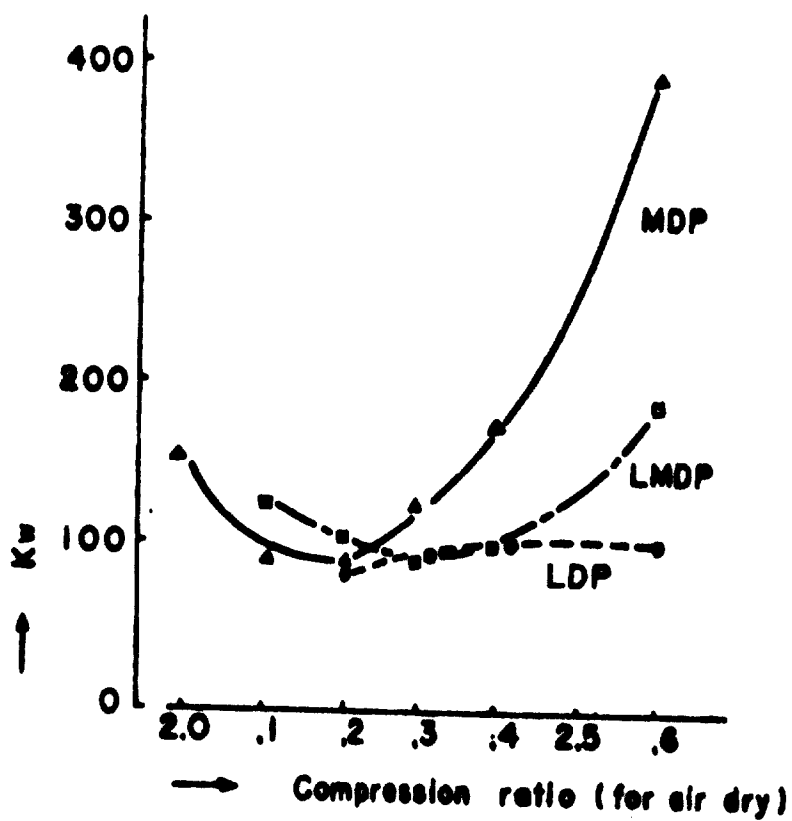


Fig. 7. Relation between compression ratio and Kw

LDP } Same as Fig. 4  
LMDP }  
MDP }

Revolution	600 r.p.m.
Compression ratio	2.95 (oven dry)
Shredding	20°, 1 hr.
Xanthation	CS <sub>2</sub> 35 %, 26°C, 3 hr.
Dissolution	Cellulose content 8 % Total alkali 6 % 20°C, 3 hr.

Spinning test

Nozzle	0.06 mm $\phi$ , 1,000 holes
Composition of spinning bath	H <sub>2</sub> SO <sub>4</sub> 8.35 $\pm$ 0.05 w %
	ZnSO <sub>4</sub> 1.30 $\pm$ 0.05 w %
	Na <sub>2</sub> SO <sub>4</sub> 25.5 $\pm$ 0.05 w %
	Temperature 52°C
Secondary bath	Hot water 92°C
Secondary stretch	1.30
Filament quality test	JIS L 1013

As an important index on viscose reactivity the Kw numbers (resistance of filtability) are shown in Table 11.

The Kw number decreased with reducing the relative viscosity of unbleached pulp. In case that the relative viscosity of unbleached pulp was 6, the pulps from blue stained chips showed higher Kw numbers than others. This perhaps due to insufficient oxidizing bleaching for these pulps as described in Section IV.

Data on the effect of refining on the viscose reactivity are also given in Table 11.

When the relative viscosity of unbleached pulps was 10, which was relatively high for dissolving pulp as described before, it could be noted that the Kw number was greatly decreased if the pulps were refined up to



the extent of  $\alpha$ -cellulose 92 %, while there was no remarkable differences in the Kw numbers if the pulps were refined to the extent of  $\alpha$ -cellulose 88-90 %. In case the relative viscosity of unbleached pulp was lowered to 6, the effect of refining was not seen remarkably. Therefore, it is presumed that the viscose reactivity is much caused by cooking extent than refining extent.

It was also interesting to note that the pulps from blue stained chips did not always show any poor viscose reactivity except the case which cooking was extremely proceeded, and that Kw numbers from these pulps obtained in this test was rather low. This is perhaps due to the fact that the pulps from blue stained chips required much quantity of chemical for refining.

The qualities of dissolving pulps and their rayon filaments are given in Table 12.

Table 12

These pulps were prepared from six samples of rubberwood having different basic gravity and different degree of penetration by blue stain. Cooking had been carried out with the most suitable conditions, which were previously found satisfactorily for the producing of dissolving pulp from rubberwood.

All pulps from rubberwood samples showed similar properties compared with those of the pulps from mixed Japanese hardwoods, any adverse effect of blue stain on the qualities of pulps and rayon filaments was not found.

As the latex remaining in bleached pulps are adversely affected on viscose reactivity and filament qualities, various removing methods of latex have been carried out in wood preparation and pulping process.

Table 12. Qualities of rayon filaments

Wood	Rubber wood					Mixed Japanese hardwoods	
	0.44 ++	0.48 ++	0.50 +++	0.53 +	0.56 ++		0.57 +
Basic specific gravity							
Penetration by blue stain							
α-cellulose %	89.4	87.1	88.7	89.5	88.4	89.2	88.4~89.5
β-cellulose %	4.3	5.1	4.3	3.9	4.4	3.7	3.7~5.2
Relative viscosity	4.7	4.5	1.9	4.3	4.6	4.3	3.5~4.9
Pentosan %	4.4	5.5	4.9	4.7	5.5	4.7	3.5~6.3
Compressibility	2.10	3.14	2.06	3.11	2.90	3.14	.06~3.19
Y value	43.5	42.4	41.5	42.6	44.7	43.1	.5~45.1
Viscosity K <sub>2</sub>	2.2	2.12	2.45	2.40	2.76	2.60	80~270
Denier	—	1.70	1.72	1.70	1.69	—	.68~1.69
Dry strength g/d	—	3.08	3.09	2.90	3.07	—	.95~3.01
Wet strength "	—	1.88	1.84	1.78	1.96	—	.84~1.94
Knot strength "	—	1.76	1.82	1.73	1.66	—	1.66~1.75
Loop strength %	—	1.89	1.92	1.97	1.88	—	1.89~2.03
Dry elongation %	—	18.4	17.5	17.8	16.8	—	17.1~17.6
Wet elongation %	—	21.0	19.9	21.0	19.3	—	20.9~21.6

However, there still remains 0.01-0.02 % of latex in pulp, even if the wood under the tapping pannel has not been used as raw material.

Trials were carried out to show the effect of latex on viscose reactivity and filament qualities. The results are shown in Table 13.

Table 13

This experiment was carried out as follows:

#### Preparation of adding latex

Air dried latex film was cooked by sulphite process and bleached in five stages (C-E-E-H-D). Then it was reduced into fine particles and immersed into 17.5 % NaOH solution. This adding latex had been added at the time of shredding alkali cellulose.

The dissolving pulp used in this experiment were prepared from Japanese hardwoods.

The data show that there is no significant effect on the viscose reactivity and filament qualities by adding latex, even though latex content is increased up to 0.2 %.

## VI. Pulp production

### 1. Mangrove woods

#### 1.1 Wood preparation

Generally, it is considered that it would be difficult to obtain pulpwood for producing dissolving pulp having uniform quality from mangrove woods, since various species of mangrove are found intermixed in the forests. However, due to the fact that there is a pretty big difference between the circumstances of growth of suitable species and unsuitable species for producing of dissolving pulp, and that it is easy to distinguish visually the suitable species from the others, constant supply of woods having suitable properties for producing dissolving pulp would be rather easy.

Dissolving pulp has been produced commercially from the species

Table 13. Effect of latex on viscose and filament qualities

Pulp	$\alpha$ -cellulose	%	89.5		
	$\beta$ -cellulose	%	4.9		
	Relative viscosity		4.7		
	Pentosan		6.0		
Latax adding		%	0	0.02	0.2
Viscose	Kw		264	242	260
Filament quality	Denier		1.66	1.68	1.68
	Dry strength	g/d	2.85	2.84	2.89
	Wet strength	g/d	1.73	1.73	1.75
	Knot strength	g/d	1.78	1.80	1.68
	Loop strength	g/d	1.99	2.03	1.92
	Dry elongation	%	18.0	18.2	17.7
	Wet elongation	%	21.5	21.8	21.2

of Rhizophoraceae, as mentioned in Section II. These mangrove woods have been imported as chips mainly from Sarawak. The timber has been transported to the chipping factory, and converted into chips after barking in Sarawak. The production of chips is 12,000 tons per month.

It is desirable to use the chips for production of dissolving pulp within two to three months after logging, because the chips, under tropical conditions, are readily deteriorated by fungus on storage.

## 1.2 Pulp production

### a) Cooking

The mangrove woods are cooked separately, under approximately the same conditions used for the Japanese hardwoods, and the produced pulps are mixed with the pulps from Japanese hardwoods.

Cooking conditions are as follows :

Cooking liquor : total  $\text{SO}_2$  7.5-8.5 %, combined  $\text{SO}_2$  1.5-2.0 %

Maximum temperature : 130-140 °C

Time at maximum temperature : 3-4 hr

Cooking time : 10-14 hr

These conditions are varied a little according to the species of mangrove wood used as raw material and the brand of resultant pulp.

### b) Refining and bleaching

Approximately same conditions, using for the pulps from Japanese hardwoods, are adopted in four or five stages, namely, C-E-E-H-D process.

### c) Removing of the residual ash content

The residual ash in the pulps from mangrove woods is removed mainly by mechanical treatment, as described in Section IV. The mechanical treatment consists of screening process, which is carried out before and after refining and bleaching process. Therefore, the screening process

is very important for decreasing ash content from the pulps. The screen equipped with fine meshed wire, and centrifugal cleaner are used for this purpose. The screening of the pulps from Bakauan should be carefully carried out, because a lot of EDTA ash has been remained in these pulps. As usual chemical removing method for ash, the pulp stock is washed by soft water following by treating with dilute  $\text{SO}_2$  solution at final stage of bleaching in mill operation. If Bakauan wood was used as a raw material, strengthening acid treatment by  $\text{SO}_2$  solution would not show sufficient effect. It has been found that the treatment with hydrochloric acid shows the most sufficient effect, according to the results of investigation for decreasing effect of ash content using various kinds of acids, in that case.

#### d) Properties of rayon filament

Various grades of dissolving pulps from Japanese mixed hardwoods blended with 50 % of the pulps from mangrove woods have been produced in mill operation. The comparison of the properties of rayon filaments of the blended pulps and of Japanese hardwoods pulps is shown in Table 14.

Table 14

The data show that the blended pulps give similar properties to the pulps from Japanese hardwoods.

## 2. Rubberwood

### 2.1 Wood preparation

It has been recognized that blue stain and residual latex are adversely affected on the qualities of dissolving pulp from rubberwood. The effort to reduce those adverse effect has been carried out in wood preparation as much as possible.

The treatments are described in the following :

Table 14. Quality of rayon filaments (2 denier)

	DSP* from Japanese hard wood	DSP* from mixture of Japanese hard wood and mangrove
Dry strength g/d	100	101.1
Dry strength g/d	100	100.6
Knot strength g/d	100	100.6
Dry elongation %	100	101.7
Wet elongation %	100	98.8
Brightness %	100	100.5

\* DSP : dissolving sulphite pulp.

a) Blue stain

Rubberwood has been imported as logs which still keep their pale yellow colour, but are discoloured within 1 to 2 months on storage in the open. Therefore, it is desirable to use rubberwood for producing the pulps as early as possible after arriving in Japan. The storage duration is controlled within 1 to 4 months after felling. It will be expected that the penetration of blue stain will be prevented by use of fungicide.

Some prevent effects are found by the application of OCS system for rubberwood chips. The chips on the surface of the pile are discoloured, but inside of the chip pile no blue stain is visible. However, at present, rubberwood chips have been little used for producing of dissolving pulp, since those chips are contaminated with latex.

b) Latex

It is observed that the deterioration of dissolving pulp from rubberwood are caused by residual latex, although no deterioration is found if the pulps contained up to 0.2 % of residual latex, and that would be increased with increasing residual latex.

Wood preparation process is the most important for reducing the latex from wood, since latex is produced from latex tube in cambium and the wood is contaminated on barking. Furthermore, it was observed that latex still flowed on cutting the bark with an axe 5 weeks after felling the tree.<sup>9)</sup>

By the fact presented above, it is necessary to avoid the barking on freshly felled logs. The logs should be barked and cut after hardening of latex.

If the chipping of the wood was carried out in the countries in which rubberwood was growing, resultant chips were highly contaminated by latex. Therefore, rubberwood is imported as logs to avoid this trouble.



As the wood under the tapping panels contains a large amount of latex, it has not been used as raw material.

Before chipping, the logs are washed with barking drum to reduced the latex stuck on the surface of the logs in mill operation.

## 2.2 Pulp production

### a) Cooking

The rubberwood is cooked with Japanese haruwoods. Cooking conditions are almost the same as those described in Section IV, but holding time at maximum temperature is regulated to get the pulps having suitable relative viscosity, approximately 8, for producing dissolving pulp.

### b) Refining and bleaching

Refining and bleaching are carried out essentially the same conditions which are given in Table 10, namely, C-E-E-H-D process. However, in mill operation, as stock consistency is differed from the experimental conditions, retention time, amount of adding chemicals and others have been a little bit changed.

### c) Removing of the residual latex

The residual latex in the pulps is removed by screening, which is carried out before and after refining and bleaching process. Centrifugal cleaners are used for unbleached pulps and centrifugal screen, flat screen and centrifugal cleaners are used for bleached pulps to remove latex. The residual latex are sufficiently removed by above mentioned screening system.

### d) Properties of rayon filaments

The qualities of rayon filaments of rubberwood pulp and of softwood pulps are shown in Table 15.

Table 15

Table 15. Qualities of rayon filaments

			DSP* from rubber- wood	DSP* from softwood (Japan)	DSP* from softwood (imported)
Pulp	$\alpha$ -cellulose	%	92.5	92.4	93.0
	$\beta$ -cellulose	%	3.7	3.7	4.9
	Pentosan	%	2.3	2.2	1.4
Viscose	Kv		189	168	154
Spinning	Fuzz		none	none	none
	Clogging		none	none	none
	Spinability		good	good	good
Filament quality	Denier		118	116	116
	Dry strength	g/d	1.79	1.74	1.75
	Wet strength	g/d	0.80	0.78	0.75
	Dry elongation	%	19.2	20.3	20.0
	Wet elongation	%	28.6	31.2	27.5
	Secondary swelling		91.1	93.7	95.8
	Degree of polymerization		254	252	276
Copper number		0.34	0.37	0.36	

\* DSP : Dissolving sulphite pulp.

The data show that the rubberwood pulp gives similar properties to the softwood pulps.

### VII. Conclusion

It has been confirmed that mangrove woods and rubberwood are suitable as raw materials for production of dissolving pulp from the viewpoint of growing stock, wood properties, reactivity of resultant pulps etc., and dissolving pulp from these materials have been produced commercially. However, it is difficult to use unsuitable species of mangrove woods as raw materials for producing dissolving pulp.

Rubberwood has been used as a raw material for papermaking, but mangrove woods are unsuitable for that purpose owing to their relatively high cell wall thickness. Mangrove woods are mainly used as raw materials for producing dissolving pulp.

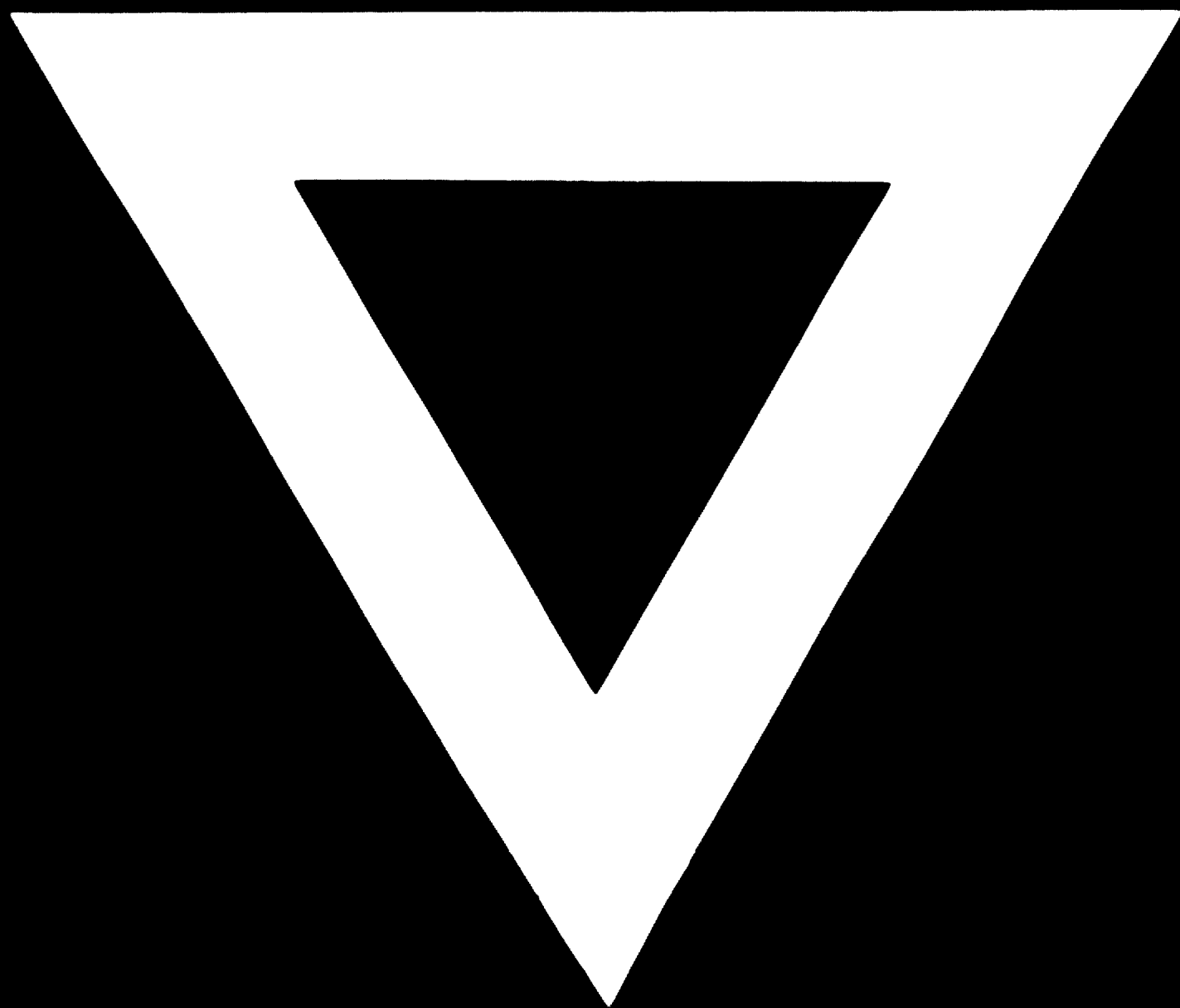
If blending ratio of mangrove woods or rubberwood pulp to dissolving pulp was increased, it was assumed that the troubles, which are caused by EDTA ash of mangrove wood, by blue stain and by residual latex of rubberwood, were arised. However, these troubles could be reduced by further investigations.

### Literature

- 1) Nicolas, P.M., and Sawagan, B. O. : The Philippine Lumberman, January 1970, 40.
- 2) Joedodibroto, Roehjati, and Alaudin : Berita Selulosa II, September 1966, Nr. 2.
- 3) Yonesawa, Y. : Wood Industry (Japan), 23, 111 (1968).

- 4) Sudo, S. : Tropical Woods, 439 pp. (1970).
- 5) Peel, J. D., and Bhaskaran, T. . : Research Pamphlet (Malasia) No. 22, December 1957, 14 pp.
- 6) von Koeppen, A. : Tappi, 41, 460 (1958).
- 7) von Koeppen, A., and Cohen, W. E. : Holzforschung, 10, Heft 1, 18 (1956).
- 8) Yonezawa, Y. : The Tropical Forestry, No. 6, December 1967, 1.
- 9) Peel, J. D., and Peh, Teik Bin : Research Pamphlet (Malasia) No. 34, October 1960, 20 pp.
- 10) Wood Technological Association of Japan : Major Wood Species in Japan, 101 pp. (1960).
- 11) T. Sugawa : Wood Industry (Japan), 23, 432 (1968).





**7 4.09.12**