Cellulose and Fiber Science Developments: A World View

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A symposium sponsored by

the Cellulose, Paper and

Textile Division at the

171st Meeting of the

American Chemical Society

New York, N.Y.,

April 5–9, 1976

ACS   SYMPOSIUM   SERIES   **50**

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FOREWORD

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PREFACE

The centennial meeting of the American Chemical Society gave the Cellulose, Paper and Textile Division the opportunity to present a timely symposium on International Developments in Cellulose, Paper, and Textiles. Research scientists from academia, industry, and government, representing more than sixteen countries, presented significant research accomplishments in paper, wood, and cellulose chemistry and in cotton, wool, and textile fiber chemistry.

In this volume, world views of cellulose and fiber science developments are contributed in three areas—cellulose, paper science, and fiber science—by investigators from Australia, Canada, Finland, France, Japan, Mexico, Rumania, Sweden, and Switzerland. Two companion volumes, "Cellulose Chemistry and Technology" and "Textile and Paper Chemistry and Technology" include other contributed manuscripts.

I would like to thank the participants and the presiding chairmen of the world views sessions, particularly R. R. Benerito, C. Schuerch, K. Ward, Jr., R. L. Whistler, and J. J. Willard. Herman Mark kindly made significant remarks to open the Symposium.

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New Orleans, LA
May 11, 1977

Recent Research and Technological Development of Cellulose in Japan

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Production of chemical industries related to cellulose in Japan changed as shown in Figure 1. The production of viscose rayon reached to a maximum in 1937-38 and decreased to one twentieth during and after the second world war due to converting of the factories to munitions manufacturing and destruction. From around 1950, the production rapidly increased and the total production of cellulosic fibers is ca. 500,000 tons/year for these ten years. In the field of cellulosic fibers, several companies stopped production of viscose rayon filament yarn and high tenacity yarn for tire cord and the output of those fibers decreased, while the output of cellulose acetate fibers and viscose rayon staples increased. The manufacturers of cellulosic fibers and cellulose derivatives in Japan are listed in Tables I and II.

Investigations on cellulose were active in 1930's and also after the second world war, especially on rayon fibers of new type such as polynosics and high tenacity rayon for tire cord, pulps for cellulose acetate, and crystalline and supermolecular structure of cellulose. Most of companies, however, now stopped basic and application researches on cellulose, although a large number of researchers in universities continue to work on cellulose, especially, in Hokkaido University, Gumma University, University of Tokyo, Tokyo Institute of Technology, Shizuoka University, Tokyo Metropolitan University, and Osaka City University.

The number of articles related to cellulose and published in Japanese journals is ca. 200 for these ten years. Most of them were published in Sen-i Gakkaishi(J. of Soc. of Fiber Science and Technology, Japan, originally published in 1925 as J. Cellulose Institute). Kogyo Kagaku Zasshi(J. Chemical Society, Japan, Industrial Chemistry Section) which was united to Nippon Kagaku Kaishi now , also published a large number of papers together with Kobunshi Ronbunshu(J. High Polymer Society, Japan), Japan TAPPI and Mokuzai Gakkaishi(J. Wood Research Society, Japan). In addition, a considerable number of papers are published in foreign journals. Japan Tappi was established in 1947 just after the war.

3

Table I. Manufacturers of Rayons and Cellulose Acetate Fibers

Viscose rayon filaments;
      Asahi Chemical Ind., Kuraray, Unitica.
      Toray,   Toyo Spinning,   Teijin

Viscose rayon filaments for tire cord;
      Unitica.   Toray, Teijin, Toyo Spinning.

Viscose rayon staples;
      Mitsubishi Rayon, Kanebo, Toho Rayon,   Nitto Spinning,
      Toyo Spinning, Kuraray, Daiwa Spinning, Kojin,
      Fuji Spinning, Nisshin Spinning, Omi Kenshi Spinning.
      Toray

Cuprammonium rayon;
      Asahi Chemical Ind.

Acetate fibers;
      Mitsubishi Acetate,   Daicel,   Asahi Chemical Ind.,
      Teijin.

  The underlined manufacturers indicate those which stopped the production.

   Table II.   Manufacturers of Cellulose Derivatives

  Cellulose nitrate;
      Asahi Chemical Ind., Daicel, Taihei Chemicals.

  Cellulose acetate;
      Daicel, Teijin, Asahi Chisso.

  Carboxymethyl cellulose;
      Daiichi Kogyo Seiyaku, Daicel, Sanyo Kokusaku Pulp,
      Nichirin Kagaku, Adachi Koryo, Shikoku Kasei,
      Kyoto Gosei Kagaku.

  Methyl cellulose;
      Shin-etsu Kagaku, Matsumoto Yushi.

  Hydroxyethyl cellulose;
      Fuji Chemical.

  Hydroxypropyl cellulose;
      Nippon Soda, Shin-etsu Kagaku.

  Hydroxypropyl methyl cellulose;
      Shin-etsu Kagaku.

  Hydroxypropyl methyl cellulose phthalate;
      Shin-etsu Kagaku.

  Cellulose acetate phthalate;
      Wako Junyaku.
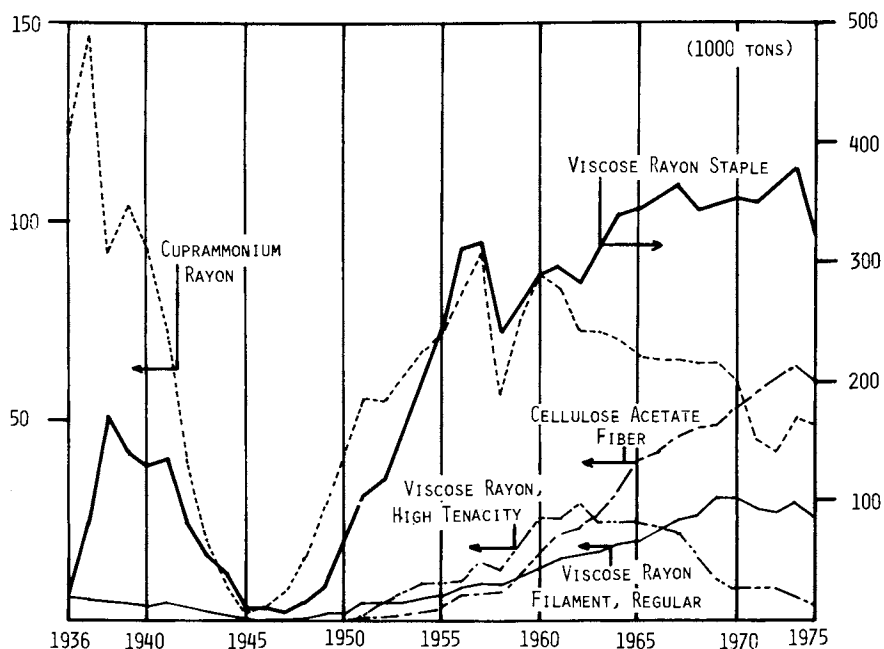
Figure 1.   Change of production of rayons and cellulose acetate fibers

Table III.   Number of Articles Published in Japanese Journals

Year	65	66	67	68	69	70	71	72	73	74	75	Total
Kogyo Kagaku Zasshi	3	5	7	3	4	5	10	–	–	–	–	37
Nippon Kagaku Kaishi	–	–	–	–	–	–	–	2	5	4	5	16
Sen-i Gakkaishi	23	22	26	8	11	11	5	6	3	25	1	119
Kobunshi Kagaku	3	3	0	1	2	2	4	4	5	3	1	28
Japan TAPPI	0	1	0	0	2	0	5	1	3	0	1	13

Main thema of the investigations are the followings:
1. Crystalline structure of cellulose and cellulose derivatives.
2. Folding molecular structure of cellulose.
3. New solvents for cellulose.
4. Synthesis of new cellulose derivatives.
5. Fire-retarding effect of cellulose phosphate and its derivatives.
6. Effect of gamma-ray irradiation or UV light on cellulose, such as change of molecular weight, esr spectra and properties of irradiated products.
7. Grafting of vinyl monomers onto cellulose and its derivatives by gamma-rays, UV light or with chemical catalysts or in the absence of catalyst.

Some of the topics will be discussed in the followings.

1. Crystalline Structure of Cellulose and Cellulose Derivatives

Watanabe and Hayashi of Hokkaido Univ. proposed that the conformation of cellulose I is different from that of cellulose II and that the differences in the conformation and the stability is the cause of preservation and irreversibleness of crystalline structure of cellulose I and cellulose II.

At first, the crystalline structure of cellulose trinitrate (TNC) was investigated[1,2]. They proposed approximately 5_2 helical structure with a fiber period of 25.75Å for TNC, although cellulose dinitrate obtained in a homogeneous reaction has a crystalline structure with a twofold screw axis and a fiber period of 10.32Å, same as other cellulose derivatives. Transformation of the twofold screw axis structure into 5_2 helical structure by trisubstitution may be caused by twisting of pyranose ring in chair form to semi-boat form. The twisting may be resulted by the bulkiness and repulsion between two nitro groups at C_2 and C_3 positions. The nitro groups which are originally in gauche conformation change into trans conformation. It was noted that natural cellulose always gives TNC with high crystallinity irrespective of sources, while cellulose II such as rayons even with high crystallinity(Fortisan) gives TNC with low crystallinity[3]. They proposed a bent-twisted structure which has no twofold screw axis for cellulose II, as shown in Figures 3 and 4. Therefore, the structure of TNC obtained from cellulose II is fundamentally 5_2 helical, although it is incomplete[4].

They analyzed crystalline structure of cellulose II with the use of the bent-twisted conformation of molecule and obtained reliability factor R = 0.265 for ϕ_1 =30° and ϕ_2 =45° [5]. This structure could explain ir spectra of cellulose II well; that is, two intramolecular hydrogen bond absorptions due to $O_3 \rightarrow O_{5'}$, -CH_2 symmetrical stretching vibration(parallel) and antisymmetrical stretching vibration(antiparallel).

It is well known that cellulose has cellulose III and IV modifications besides I and II. Mann et al.[6] found that OH vi-
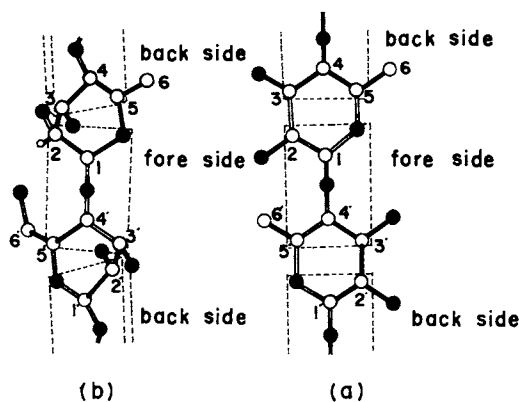
Figure 2. Chain structure of cellulose trinitrate (b) formed by conversion of ring conformation from chair form to semi-boat form. (a) Chair form, 2_1 helical structure; (b) semi-boat form, 5_2 helical structure.

$\phi_1 = 30°$ $\phi_2 = 45°$ $\theta_1 = 50°$ $\theta_2 = 20°$
$r = 0.1850$

Figure 3. Crystalline structure of cellulose II. Projection to A-C plane. Hydrogen bonds between $O_2 \rightarrow O_6$ and $O_6 \rightarrow O_3$ are formed in $(10\bar{1})$ and (002) planes, alternatively.

rations of cellulose III(or IV) change with the crystalline struc-
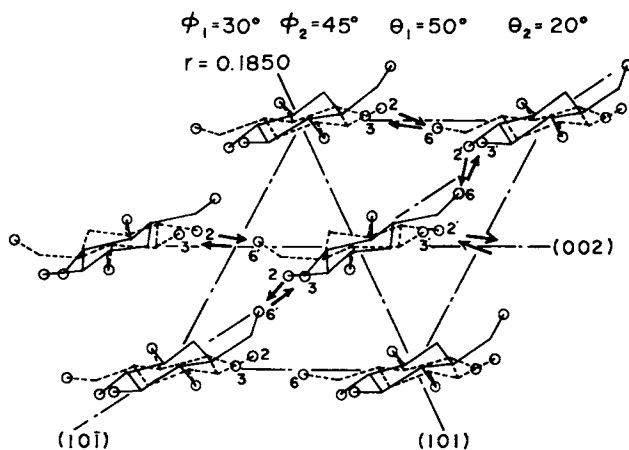ture of cellulose(cellulose I or II) from which cellulose III(or
IV) is derived. However, since X-ray diffractions are not clear-
ly different between cellulose III derived from cellulose I(des-
ignated as cellulose III_I) and that from cellulose II(cellulose
III_{II}), it has not certainly been established that cellulose III_I
has a crystalline structure different from that of cellulose
III_{II}.

     Hayashi and Watanabe determined the ratio of meridional dif-
fractions (040)/(020) on cellulose III and cellulose IV as shown
in Figure 5([7]). The ratio changed with the crystalline structure
of source cellulose but not with the crystallinity or orientation
of crystallites. Therefore, cellulose III_I(or cellulose IV_I) is
a crystalline modification of cellulose different from cellulose
III_{II}(or cellulose IV_{II}), although they show similar equatorial
diffractions.

     Various chemical reactions on cellulose I usually produce
cellulose III_I or cellulose IV_I, and we obtain cellulose III_{II}
and cellulose IV_{II} from cellulose II.   Interconversion between
cellulose I, III_I and IV_I or that between cellulose II, III_{II}
and IV_{II} is possible, but conversion of cellulose I family to cel-
lulose II family is only possible by dissolution and regeneration
or mercerization([8]), and it is irreversible(Figure 6). In the es-
terification such as acetylation and nitration or in the formation
of addition compounds of cellulose I, molecular conformation of
cellulose I is preserved and the regeneration results in cellulose
I([8-13]).

     The facts that the difference in molecular conformation is
not reflected in equatorial diffractions as illustrated in Figure
8 for cellulose trinitrate, but reflected in meridional diffrac-
tions as already mentioned were ascertained by calculating dif-
fraction intensities.

     Thus, irreversibleness of cellulose I family to cellulose II
family and preservation(or keeping memory) of each family struc-
ture during chemical reactions are caused by the molecular con-
formation of each family; that is, the bent structure for cellu-
lose I family and the bent-twisted structure for cellulose II fam-
ily. They are not due to difference in the intermolecular hydro-
gen bonding system. In cellulose I, the distance between H_1 and
H_4' is only 1.85 Å($\phi_1=\phi_2=34°$) by the intramolecular hydrogen bond
between $C_3 \rightarrow O_5$'. This form is very unstable. Formation of cellu-
lose II by twisting results in longer distance between H_1 and H_4',
thus giving a stabilization energy of 2-3 kcal per glucose unit,
which sums up to a large value for a molecule.

     It is known that mercerization is a typical reaction of con-
version of cellulose I to cellulose II in fiber form. Merceriza-
tion of cellulose I under restriction of contraction or at high
temperature to prevent swelling gives Na-cellulose I with ratio
of meridional diffractions, (040)/(080) = 0.5, whereas that of
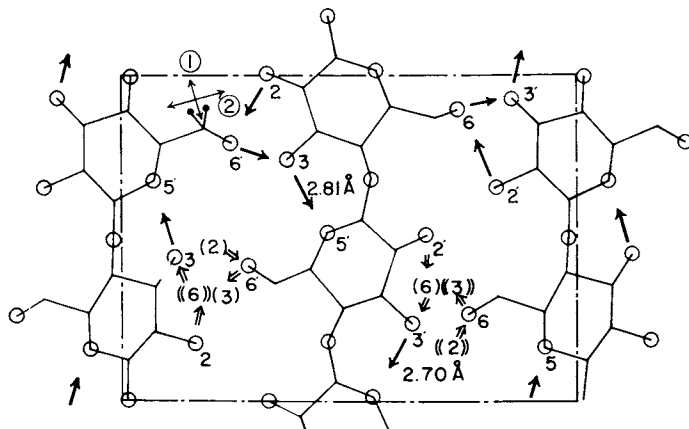Na-cellulose I obtained from cellulose II is 0.02-0.05, irrespec-

Figure 4.   Crystalline structure of cellulose II.   Projection to (10$\bar{1}$)
plane.   ($\rightarrow$) Hydrogen bonds in (10$\bar{1}$) plane; ($\Rightarrow$) hydrogen bonds in
(002) plane.
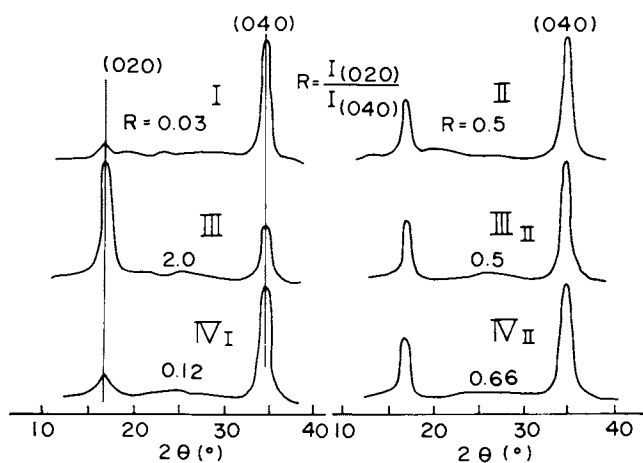
Figure 5.   Crystalline modification of cellulose and meridional
diffractions.   R indicates the ratios of (020) to (040).

Figure 6. Transformation between cellulose modifications and classification of crystalline structures of cellulose based on the conversion

Figure 7. Change of crystalline structure of cellulose in esterification in fiber form. (——) Transformation of crystalline structure; (- — - —) heat-treatment or swelling.

Figure 8. Equatorial diffractions of cellulose trinitrates obtained from various modifications of cellulose

tive of the mercerization conditions($\underline{14}$). Therefore, there are
two types of Na-cellulose I, that is, Na-cellulose⁻I_I and Na-cel-
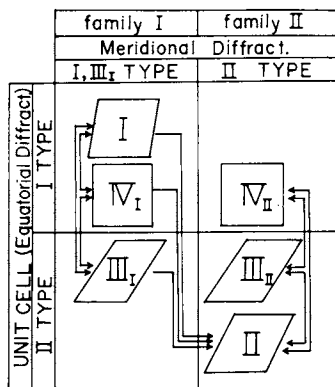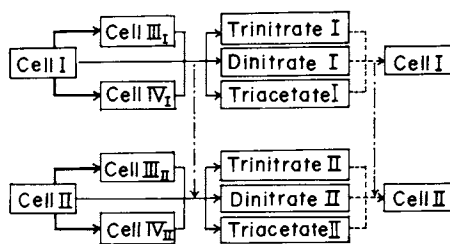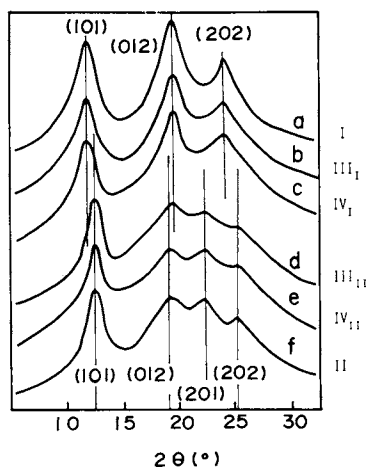lulose I_{II}. Although usual procedure for regeneration of Na-cel-
lulose I_I gives cellulose II, regeneration under little swelling
such as with hot water or with acetic acid gives cellulose I as
illustrated in Figure 9 for ramie. Na-cellulose I_T is formed in
the condition that cellulose is not strongly hydrated. Therefore,
it is deduced that for conversion of cellulose I conformation to
cellulose II conformation, strong hydration of cellulose chains
is necessary to give relaxation to intramolecular hydrogen bond-
ings. Therefore, mercerization or regeneration of Na-cellulose
under strong swelling gives always cellulose II type structure.

2. New Solvents for Cellulose

Recently, various kinds of solvents for cellulose were found;
liquid N_2O_4 added with a little amount of organic compounds by
Fowler et al.($\underline{15}$), dimethyl sulfoxide(DMSO) added with a small
amount of N_2O_4 by Williams($\underline{16}$), pyridine-anhydrous chloral by
Meyer($\underline{17}$), liquid SO_2 added with a secondary or tertiary amine by
Hata et al.($\underline{18}$), and dimethyl formamide(DMF) or dimethyl acet-
amide(DMAc) added with N_2O_4 or NOCl by Schweiger($\underline{19}$-$\underline{20}$).
Nakao et al.($\underline{21},\underline{22}$) developed previous investigations in de-
tail as shown in Table IV and found several new solvents. They
classified cellulose solvents into the following groups:
(i) DMSO, DMF,DMAc and ethyl acetate added with a little amount
     of N_2O_4.
(ii) DMSO,DMF, formamide, acetonitrile, methylene chloride, etc.,
     added with 3-30 moles of liquid SO_2-amine(e.g., diethyl-
     amine) complex.
(iii) DMSO, DMF, DMAc and N-methyl-2-pyrrolidone added with an-
     hydrous chloral.
(iv) DMSO, DMF, DMAc and pyridine added with NOCl, or liquid
     NOCl added with a little amount of polar organic solvents.
Solvents such as DMSO and formamide added with SO_2-amine com-
plex, or DMSO, DMF and pyridine added with N_2O_4 not only dissolve
cellulose in a few minutes, but the solution is stable and degra-
dationof cellulose is low especially at low temperatures lower
than 50°C. The dissolution proceeds by cleavage of fibers and
peeling-off from the fracture surface without appreciable swell-
ing usually observed in dissolution by aqueous solutions such as
cuprammonium solution. It is also noted that at least 3 moles of
reagents per glucose unit are necessary for dissolution of cellu-
lose.
Solvents added with SO_2-amine complex were investigated in
detail($\underline{22}$). Thirty four solvents were found to dissolve natural
cellulose but did not dissolve regenerated cellulose. The spec-
ific conductivities of complex solutions and cellulose solutions
were determined, and the mechanism of dissolution was investiga-
ted. The complex formed between an amine and SO_2 reacts with cel-
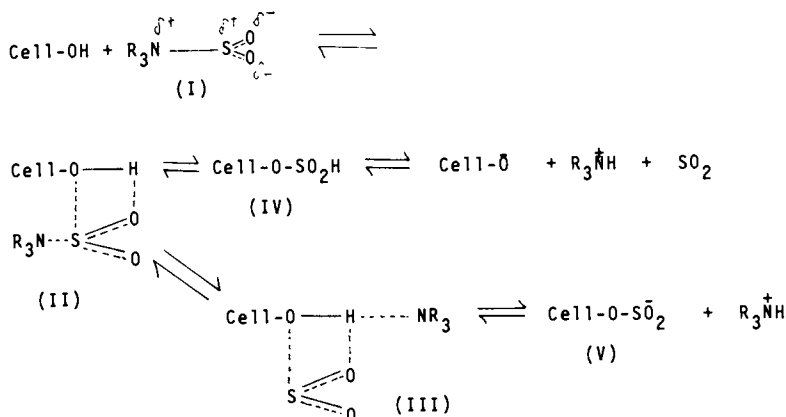
Table IV. Solvents for Dissolving Cellulose.

Cellulose solvent	SO₂-amine	temp	mole	N₂O₄	temp	mole	NOCl	temp	mole	Chloral	temp	mole
Sulfoxide	DMSO	20	3	DMSO	20	3	DMSO	20	3	DMSO	20	5
Amide	DMF	50	14	DMF	20	3	DMF	20	10	DMF	20	10
	DMAc	50	14	DMAc	20	5	DMAc	20	10	DMAc	20	10
	formamide	20	3	diethyl ethylamide	20	5						
Lactam	δ-butyro-lactam	50	20	NMP	20	15	[NMP]			NMP #	20	5
	ϵ-capro-lactam	50	30									
Amine				pyridine	20	35	pyridine	20	4	pyridine #	20	5
							α-picoline	20	5			
							β-picoline	20	7			
Nitrile	acetonit-rile	20	15	acetonit-rile	20	35	[aceto-nitrile]					
	propio-nitrile	50	15	propio-nitrile	50	5	[propio-nitrile]					
	benzonit-rile	50	25				[benzyl-nitrile]					
Ester				ethyl acetate	20	5	[ethyl acetate]					
				methyl propionate	20	5						
				methyl formate	20	8						
Lactone	γ-valero-lactone	50	20	γ-valero-lactone	50	8						
	γ-butyro-lactone	50	40	γ-butyro-lactone	50	8						
Cyclic carbonate	ethylene carbonate	50	30	propylene carbonate	50	10						
	propylene carbonate	50	30									

[ ] indicates liquid NOCl.
mole indicates moles of reagents per glucosidic unit.
# indicates cellophane is sol., but wood pulp is insol.

lulose resulting three component complex of type II or III. The
ir spectra of the cellulose solution is only overlapping of amine-
SO_2 complex and cellulose, and the absorption of OH groups of cel-
lulose remains intact. Therefore, the formation of -O-S- bonds
as is shown in IV or V is not considered.

$$Cell\text{-}OH + R_3N \overset{\delta^+}{\longrightarrow} \overset{\delta^+}{S} \overset{\delta^-}{\underset{O}{\overset{O}{\lessgtr}}} \quad \rightleftarrows$$

(I)

$$Cell\text{-}O\text{---}H \rightleftarrows Cell\text{-}O\text{-}SO_2H \rightleftarrows Cell\text{-}\bar{O} + R_3\overset{+}{N}H + SO_2$$

(IV)

$$R_3N\text{---}S\underset{O}{\overset{O}{\lessgtr}}$$

(II)

$$Cell\text{-}O\text{---}H\text{-----}NR_3 \rightleftarrows Cell\text{-}O\text{-}S\bar{O}_2 + R_3\overset{+}{N}H$$

(V)

$$S\underset{O}{\overset{O}{\lessgtr}}$$ (III)

Possible applications of new solvents of cellulose are inves-
tigated to some extent and suggested.
(i)   New solvents can dissolve blends of cellulose and synthetic
      polymers such as poly(vinyl chloride), polystyrene, polyacry-
      lonitrile, etc. Blends of cellulose with cellulose acetate
      or cellulose nitrate are also dissolved. Films formed from
      blends of cellulose and poly(alkyl acrylate) are transparent
      and soft without addition of plasticizer.
(ii) Grafted cellulose with vinyl polymers can be dissolved in the
      new solvents.   Starch grafted with vinyl polymers also dis-
      solves.
(iii) Synthesis of cellulose derivatives with high degree of sub-
      stitution or homogeneous distribution of substituents will
      be possible in the reaction in a homogeneous phase(e.g.,
      synthesis of secondary cellulose acetate in one step).
(iv) Production of films, fibers, etc. from organic solutions of
      cellulose, or blends, or grafted cellulose was suggested.
      It is expected that those products may have special proper-
      ties.

3. Synthesis of Cellulose Derivatives

Synthesis of Unsaturated Acid Esters of Cellulose. General
methods to synthesize cellulose esters are:
(i) to treat cellulose with acid anhydride or acid chloride in
the presence of a catalyst such as sulfuric acid, perchloric acid,
zinc chloride, or sodium acetate, or
(ii) to treat cellulose with a mixture of the acid and trifluoro-
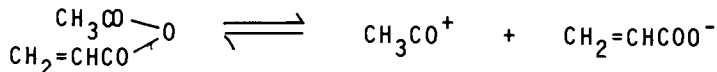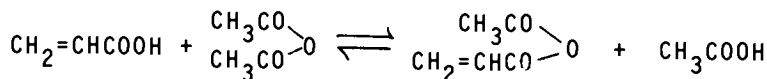acetic acid anhydride or chloroacetic acid anhydride in the pres-

ence of a catalyst.

In our investigations(23,24) on the reaction of mixtures of α,β-unsaturated acid and acetic acid anhydride with cellulose, it was found that the substitution of unsaturated acid and acetic acid depends on the catalyst and the dissociation constants of the unsaturated acids.

When sulfuric acid is the catalyst, strong acid such as a-crylic acid is not introduced, whereas weak acids such as β,β-dimethylacrylic acid are introduced more than acetic acid. In Table V, the results of esterification of linter pulp(cellulose acetate grade) are shown. It shows that the ratios of unsaturated acid to acetic acid depend mainly on the pK_a of the unsaturated acids and do not depend on the composition of the mixed acids for esterification.

Rayon staple fibers treated with 40% potassium acetate as the catalyst were esterified with mixtures of acetic acid anhydride, an unsaturated acid and potassium acetate in toluene at 120°C for 1-30 minutes. The results are shown in Figure 10. When the composition of cellulose mixed esters treated with the mixed acids of the same composition, e.g., unsaturated acid/acetic acid anhydride = 1/1(by weight) is compared, it is seen that acrylic acid is introduced more than β,β-dimethylacrylic acid. This is quite opposite to the esterification with sulfuric acid as the catalyst. The relationship is shown in Figure 11.

When sulfuric acid is the catalyst and the unsaturated acid is a stronger acid than acetic acid, the unsymmetrical anhydride formed by the reaction of the unsaturated acid with acetic acid anhydride, dissociates into an acetoxyl cation and an unsaturated acid anion. The acetoxyl cation produced mainly reacts with cellulose resulting in almost pure cellulose acetate. When the unsaturated acid is a weaker acid than acetic acid, such as β,β-dimethylacrylic acid, dimethylacrylic acid cation is mainly produced and attacks cellulose.

With potassium acetate as the catalyst, the dissociation of anhydride may be supressed by the presence of a large amount of salt and a nonpolar solvent(toluene), and the unsymmetrical anhydride may directly be concerned with the esterification. In this case, the composition of mixed acids affects the composition of cellulose esters, because the esterification by acetic acid anhydride and unsaturated acid anhydride also occurs and the ratio of the two anhydrides changes with the composition of the mixed acids.
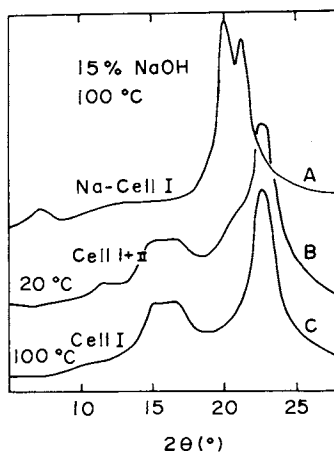
$$CH_2=CHCOOH + \begin{matrix} CH_3CO \\ CH_3CO \end{matrix} {>} O \rightleftharpoons \begin{matrix} CH_3CO \\ CH_2=CHCO \end{matrix} {>} O + CH_3COOH$$

$$\begin{matrix} CH_3CO \\ CH_2=CHCO \end{matrix} {>} O \rightleftharpoons CH_3CO^+ + CH_2=CHCOO^-$$

Table v. Esterification of Cellulose with Mixtures of an Unsaturated Acid and Acetic Anhydride (cat; H_2SO_4)

Time of Reaction	2hr		5hr		unsaturated acid acetic acid	pKa of acid
	unstaturated acid(wt%)	acetic acid(wt%)	unsaturated acid(wt%)	acetic acid(wt%)	(mol/mol)	
Acrylic acid a	0.25	58.6	0.74	59.8	0.0103	4.25(25°C)
b	0.26	58.8	0.64	60.0	0.0089	
Methacrylic acid a	0.9	50.1	6.7	52.7	0.0941	4.43(25°C)
b	0.8	56.0	2.1	59.1	0.028	
Crotonic acid a	11.9	46.7	13.5	48.8	0.193	4.69(25°C)
b	7.9	48.0	10.0	49.9	0.142	
β,β-Dimethyl-acrylic acid a	—	—	52.1	11.1	2.82	5.12(25°C)
b	—	—	47.0	10.25	2.75	

a: cellulose 2g, unsaturated acid 0.4 moles, acetic anhydride 0.16 moles, H_2SO_4 0.2 ml.
b: " 2g, " 0.28, " 0.28, " 0.2 ml

Figure 9. Equatorial diffractions
of Na-cellulose obtained by mer-
cerization at high temperature
and its regenerated cellulose
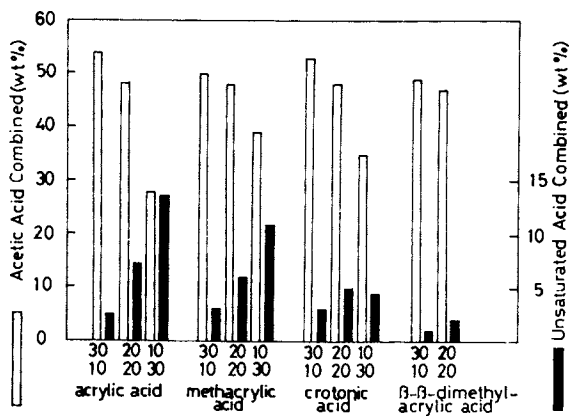
Figure 10. Change of composition of cellulose esters
with the composition of mixed acids. The upper num-
ber indicates wt % of acetic anhydride in the mixed
acids, and the lower one shows that of an unsaturated
acid.

In the next experiments(25), esterification of cellulose
with mixtures of α,β-unsaturated acid, acetic acid and trifluoro-
acetic anhydride was attempted in the presence of sulfuric acid
as catalyst. Linter pulp was treated with mixed acids which were
ripened at 35°C for 3 hr after the mixing, at 35°C for 25 minutes.
Trifluoroacetic acid is not introduced in these procedures. The
change of the composition of cellulose ester expressed by

$$\text{Ester Ratio} = \frac{\text{unsaturated acid content(mole)}}{\text{acetic acid content(mole)}}$$

changed with the composition of esterification bath. The rela-
tionship is expressed by the following equation.

$$\text{Ester ratio} = \left(\frac{\text{unsaturated acid in the mixed acid}}{\text{acetic acid in the mixed acid}}\right)^{a} \cdot K$$

where, a = 0.72 and K is a constant which depends on the kind of
unsaturated acid.
     From the ir spectra of the mixed acids, it is deduced that
unsymmetrical anhydride is formed in the mixed acids. For exam-
ple, in the mixture of acrylic acid, acetic acid and trifluoro-
acetic anhydride, both trifluoroacetic acetic anhydride and tri-
fluoroacetic acrylic anhydride are formed. The anhydrides disso-
ciate into an acetoxyl cation, an acryloyl cation and a trifluoro-
acetate anion. The ratio of unsaturated acid cation to acetoxyl
cation may depend on the composition of the mixed acid, thus re-
sulting in the dependency of the composition of cellulose esters
on the mixed acid composition. K in the equation was found to de-
pend on the dissociation constant of unsaturated acids.

$$CH_2=CH-COOH + CH_3COOH + (CF_3CO)_2O \longrightarrow$$

$$
\begin{array}{ccc}
\begin{array}{l} CH_2=CH-CO \\ \quad\quad\quad\quad\diagdown \\ CF_3CO \longrightarrow O \end{array} & + & \begin{array}{l} CH_3CO \\ \quad\quad\quad\diagdown \\ CF_3CO \diagup O \end{array} \\
\downarrow & & \downarrow \\
\begin{array}{l} CH_2=CH-CO^{+} \quad + \\ CF_3COO^{-} \end{array} & & \begin{array}{l} CH_3CO^{+} \quad + \\ CF_3COO^{-} \end{array}
\end{array}
$$
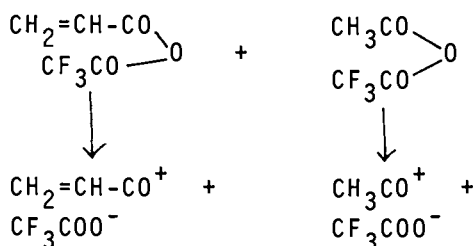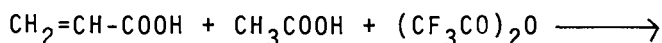
     By those methods described above, it is possible to prepare
mixed acid esters of cellulose with the desired composition.

     Synthesis of Cellulose with Reversible Crosslinkings. It is
known that wool has cystine linkages in the molecule. The treat-
ment of wool fabrics with a reducing agent followed by mild oxida-
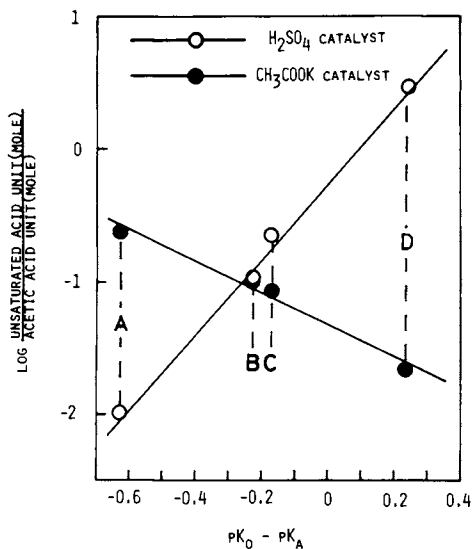tion in a desired shape is the basis of a commercial chemical set-

Figure 11. Relationship between ester ratio and dissociation constant of unsaturated acids. (A) Acrylic acid; (B) methacrylic acid; (C) crotonic acid; (D) dimethylacrylic acid.
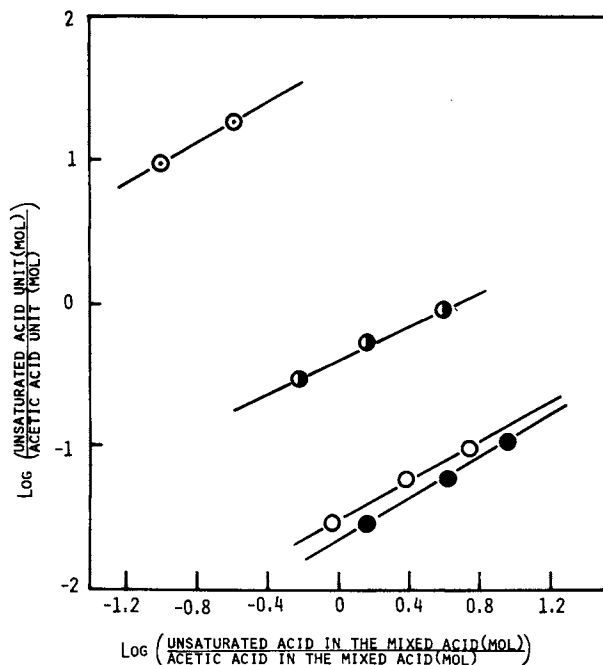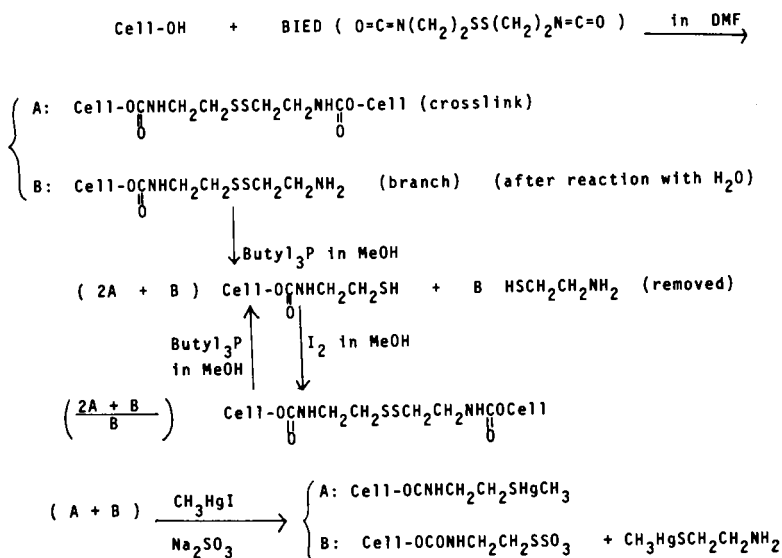

Figure 12. Relationship between ester ratio and composition of mixed acid. (●) Acetic acid–acrylic acid–trifluoroacetic anhydride; (○) acetic acid–methacrylic acid–trifluoroacetic anhydride; (◑) acetic acid–crotonic acid–trifluoroacetic anhydride; (☉) β,β-dimethylacrylic acid–trifluoroacetic anhydride.

ting process. The chemically reversible crosslinking in cotton and other cellulose fibers has been subjects of interest from both theoretical and practical viewpoints. Schwenker et al.([26],[27]) synthesized mercaptocellulose by the reaction of tosylated cotton with potassium thioacetate in acetone followed by alkaline hydrolysis.

Sakamoto and Tonami of Tokyo Institute of Technology synthesized bis-β-isocyanatoethyl disulfide(BIED) and bis-γ-isocyanatopropyl disulfide(BIPD) and investigated their reactions with cotton fabrics in DMF under various conditions([28-30]). The modified cotton contained two types of reaction products, A(crosslink) and B(branch). When the cystine linkages are reduced with tri-n-butyl phosphine, cellulose mercaptoethylaminocarboxylate is formed, but a part of branch is removed as aminoethylmercaptan. Therefore, from the difference in sulfur contents before and after the reduction, the crosslinking efficiency expressed by

crosslinks/total crosslinking agent combined

can be determined.

$$Cell\text{-}OH \quad + \quad BIED \; (\; O=C=N(CH_2)_2SS(CH_2)_2N=C=O \;) \quad \xrightarrow{\;in\; DMF\;}$$

A: Cell-OCNHCH$_2$CH$_2$SSCH$_2$CH$_2$NHCO-Cell (crosslink)
        ‖   ‖
        O   O

B: Cell-OCNHCH$_2$CH$_2$SSCH$_2$CH$_2$NH$_2$ (branch)   (after reaction with H$_2$O)
        ‖
        O
                        ↓ Butyl$_3$P in MeOH

(2A + B) Cell-OCNHCH$_2$CH$_2$SH + B HSCH$_2$CH$_2$NH$_2$ (removed)
                      ↑ O ‖
          Butyl$_3$P | | I$_2$ in MeOH
          in MeOH | ↓

$\left(\dfrac{2A + B}{B}\right)$ Cell-OCNHCH$_2$CH$_2$SSCH$_2$CH$_2$NHCOCell
                              ‖   ‖
                              O   O

(A + B) $\xrightarrow[Na_2SO_3]{CH_3HgI}$ A: Cell-OCNHCH$_2$CH$_2$SHgCH$_3$

                                           B: Cell-OCONHCH$_2$CH$_2$SSO$_3$ + CH$_3$HgSCH$_2$CH$_2$NH$_2$

The crosslinking efficiency is also determined from nitrogen analysis of samples before and after reduction([29]). It can also be estimated by polarography of CH3HgI in the reaction with BIED-treated cotton in the presence and absence of Na$_2$SO$_3$([30]). An example of crosslinking efficiency is shown in Table VI. The reaction of BIED with ramie and viscose rayon were studied([31]). The reaction of ramie proceeded similarly to that of cotton, while that of viscose rayon proceeded more rapidly and the crosslinking

efficiency was higher than those for cotton and ramie.

BIED-treated cotton fabrics showed improved dry and wet wrinkle recovery and significantly decreased breaking strength (30). When -SS- bonds in BIED-treated cotton were reduced, the wrinkle recovery value decreased to that of the control cotton and the loss in breaking strength by the introduction of cross-links was recovered as shown in Table VII. When the SH groups in the reduced cotton were oxidized to -SS- bonds with iodine in methanol, the dry and wet wrinkle recovery was improved and the breaking strength decreased to about 50% of the untreated cotton.

In order to clarify further the effects of crosslinks on the mechanical properties, repeated alternating reduction-oxidation treatments were carried out. Figure 13 illustrates the change of the properties. The content of -SS- crosslinks is shown by (A), which indicates that the reduction and oxidation proceed quite reversibly. The dry and wet wrinkle recovery also changed reversibly along with the chemical change. Tesoro et al.(32) reported that the crease recovery of mercaptoacetamidoethyl cellulose changed during oxidation-reduction treatments, but the crease recovery obtained in each oxidation treatment decreased gradually as the number of treatments were proceeded. About 40% of flex abrasion resistance of cotton fabric was lost by the treatment with BIED. However, about 75% of the lost abrasion resistance was recovered by the subsequent reduction. The levels of abrasion resistance decreased gradually with repeated treatments, probably due to the change in the surface of the fibers.

4.   Problems Related to Graft Copolymerization onto Cellulose and Cellulose Derivatives

Graft copolymerization of vinyl monomers onto cellulose and its derivatives has been investigated intensively in the purpose of modifying cellulose and its derivatives. In Japan the production of viscose rayons grafted with styrene or acrylonitrile was attempted in pilot plant scale, but it did not attain to the industrial scale. Although the grafting onto cellulose and its derivatives did not succeed in industries, it gives us interesting targets to solve problems from academic viewpoint. Some of them will be discussed in the followings.

(1) Active Species in Grafting Copolymerization. It is clear that graft copolymerization onto cellulose acetate acrylate(33, 34), cellulose methacrylate(35), and allyl cellulose(36,37), all containing double bonds, with chemical catalysts occurs at the double bonds, since when the double bonds are absent such as in cellulose acetate, graft copolymerization does not occur(34). In the graft copolymerization with cerium salt or irradiation, however, the bonds where the grafting reaction occurs are not clear.

Investigations of cellulose radicals formed in the irradiation was intensively carried out by Arthur et al.(38)   Ogiwara,

Kubota and Matsuzaki(39-42) studied cellulose radicals which are formed by irradiation with UV light and capable of graft copolymerization.

Figure 14 shows the esr spectra of untreated(a) and Fe^{+3} sensitized(b and c) samples of wood cellulose observed after irradiation at 77°K. The untreated sample yielded a three-line spectrum with spacings of 24 gauss(half height width) and 64 gauss with a g-value of 2.003. When the Fe^{+3} sensitized sample(5 mmole/l. Fe^{+3}) was irradiated under the same experimental condition, a five-line spectrum with spacings of 7, 27 and 65 gauss was observed. Figure 14 also shows the change and decay of esr spectra by warming the samples to ambient temperature and recorded at 77°K. Upon warming, the spectrum intensity of the untreated sample decreased and the three-line spectrum changed to a singlet. The Fe^{+3} sensitized sample also showed a decrease in the intensity and the five-line spectrum finally changed to a singlet through a three-line spectrum similar to the spectrum observed for the untreated sample.

Thus, it is clear that both singlet and triplet components are superimposed on the three-line spectrum and five-line spectrum and the singlet component radicals show higher stability toward warming than the triplet component radicals. The singlet component is ascribed to alkoxy radicals produced at either C_1 or C_4 position of the glucose unit by scission of glycosidic bonds, while the triplet component results from the dehydrogenation of cellulose main chains.

Table VIII shows that the relative signal intensities of the irradiated samples increase by irradiation with shorter wave length, with addition of sensitizer and swelling of the samples. It was also observed that the light of shorter wave length increased the number of scissions of cellulose chains. Therefore, it is considered that these factors contribute to increasing both the esr signal intensity and the number of scissions.

Figure 15 shows the effect of solvents on the decay of radicals in the samples irradiated at room temperature. The decay was generally accelerated by solvents, the effect of which was in the order of water = methanol > acetone > dioxane. The kind of vinyl monomers affected the radical decay in the order, methacrylic acid > methyl methacrylate = styrene. The rate of radical decay is related to the affinity of the solvents to cellulose fibers and the rate of penetration of solvents into fibers.

The preirradiated samples are capable of initiating the graft copolymerization, while the unirradiated sample is not at all. Therefore, it is concluded that the ability of the samples preirradiated at room temperature to initiate graft copolymerization is attributable to the cellulose radicals stable at room temperature. These radicals showing a singlet spectrum are believed to be alkoxy radicals at either C_1 or C_4 position of the glucose unit resulted by the scission of glycosidic bonds.

In order to verify the formation of alkoxy radicals by scis-

Figure 13. Changes of mechanical properties of BIED-treated cotton fabrics by reduction and oxidation treatments. (A) Content of SS linkages; (B) flex abrasion resistance (untreated cotton 1380 cycles); (C) breaking strength retention; (D) warp wrinkle recovery, (○) dry, (●) wet. (U) Untreated, (T) BIED-treated; (R) reduction, (O) oxidation.
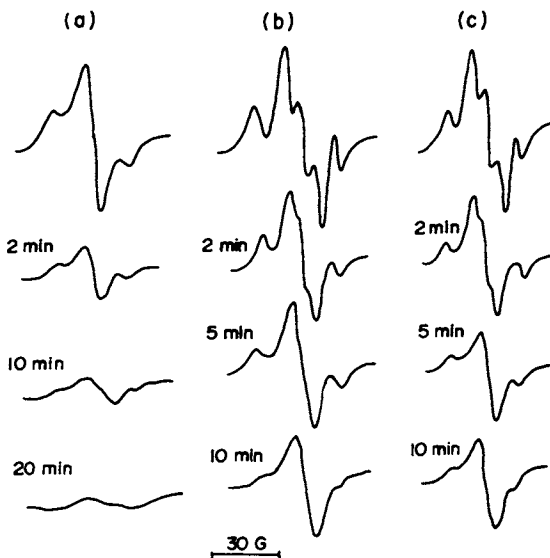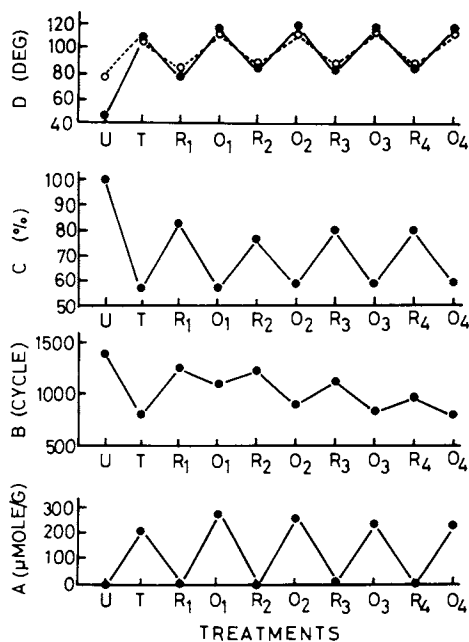

Figure 14. Decay of ESR spectra by warming the samples to room temperature and recorded at $77°K$. (A) Wood cellulose irradiated with high-pressure mercury lamp for 60 min at $77°K$; (B) Fe^{3+}-sensitized wood cellulose irradiated with high-pressure mercury lamp for 60 min at $77°K$; (C) Fe^{3+}-sensitized wood cellulose irradiated with super high-pressure mercury lamp for 90 min at $77°K$.

Table VI   Reaction   of   Cotton   with   BIED

Reaction time(hr)	Total BIED combined (μmoles/g)	Branch	Cross-links (μmoles/g)	Efficiency (%)
1	110	55	55	50
5	207	88	119	57
10	267	110	157	58
24	303	153	250	49
48	404	209	195	48

Table **VII**, Mechanical properties of modified cotton fabrics

Sample	Treatment	SH	SS	Warp wrinkle recovery angle		Breaking strength retention (%)
		(μmoles/g)		dry	wet	
Untreated				76	44	100
DMF-treated				72	46	99
"	reduced			73	47	97
BIED-treated	-	0	484	104	111	57
*	reduced	733	0	70	67	73
"	oxidized	23	328	1o9	115	48

Table **VIII**. Relative signal intensities of cellulose samples irradiated with high-pressure mercury lamp at room temperature.

Sample	Relative signal intensity, arbitrary units		Number of scissions, mmole $\times$ 10^2	
Untreated	1.0 [a]	3.1 [b]	1.0 [a]	14.2 [b]
Oximated	0.8	2.7	0.6	10.4
Swollen	3.0	4.2	11.5	-
Fe^{+3} sensitized	3.1	9.0	15.3	-

a: hard glass, irradiation time 60 min.
b: quartz glass, irradiation time 30 min.

sion of glycosidic bonds, cellobiose as a model compound of cel-
lulose was irradiated with light of wave length longer than 2800
Å at 77°K for 2 hr. The esr spectra of the irradiated cellobiose
and cellulose(soft wood dissolving pulp) are shown in Figure 16.
No radicals were detected on glucose under the same irradiation
conditions. With light of wave length longer than 2200 Å, radi-
cals were formed on glucose, but the intensity was much stronger
for cellobiose as shown in Figure 17. The reason for higher ac-
tivity of cellobiose toward light than glucose is attributed to
the glycosidic bonds in the molecule. Paper chromatographic a-
nalysis of cellobiose irradiated with light of wave length longer
than 2200 Å at room temperature showed the presence of glucose.

    Figure 18 shows the esr spectra of cellulose samples treat-
ed with Ce^{+4}, Fe^{+2}, Fe^{+3}, and Ag^+, and irradiated with a super
high-pressure mercury lamp at 77°K for 90 minutes. Although
there is a small difference in the signal intensity among sensi-
tizers, it is considered that their effects are nearly the same
as those of Fe^{+3}. Namely, these sensitizers contribute to the
formation of radicals showing the singlet and triplet spectra.

    In the irradiation in air, hydroperoxide is generally form-
ed and the grafting reaction occurs by the decomposition of the
hydroperoxides. We found, however, that hydroperoxide is not
produced in the irradiation of cellulose in the air(43). The
hydroperoxide of cellulose may be unstable and decompose rapidly
into stable compounds. Therefore, in the graft copolymerization
by the preirradiation in the air, the grafting occurs at trapped
radicals as in the grafting in vacuum.

    It is noted that cellulose acetate forms hydroperoxide by
the irradiation in the air and the degree of grafting and the
total conversion of vinyl monomer(styrene) are proportional to
1/2 power of the concentration of hydroperoxide. Therefore, the
grafting occurs at hydroperoxide groups formed in cellulose ace-
tate, although the initiation efficiency is low.

(2) Composition of Grafted Polymers(Branch Polymers). Grafting
reaction is very often carried out in heterogeneous phase, espe-
cially in the reaction onto cellulose. In the heterogeneous
grafting, when mixtures of vinyl monomers are grafted onto a
trunk polymer, the monomer reactivity ratios r_1 and r_2 may be
different from those in the ordinary copolymerization in liquid
phase. Sakurada et al.(44) investigated on the grafting of mix-
tures of styrene-acrylonitrile and butadiene-acrylonitrile onto
viscose rayon. Odian et al.(45) investigated on the grafting of
styrene-acrylonitrile onto cellulose acetate.

    In our investigation(43), mixtures of styrene-butyl acrylate
were grafted onto viscose rayon and cellulose triacetate fibers.
The comparison of the monomer reactivity ratios in the grafting
with those in the ordinary copolymerization indicated that sty-
rene is contained in the grafted polymer more than in the ordina-
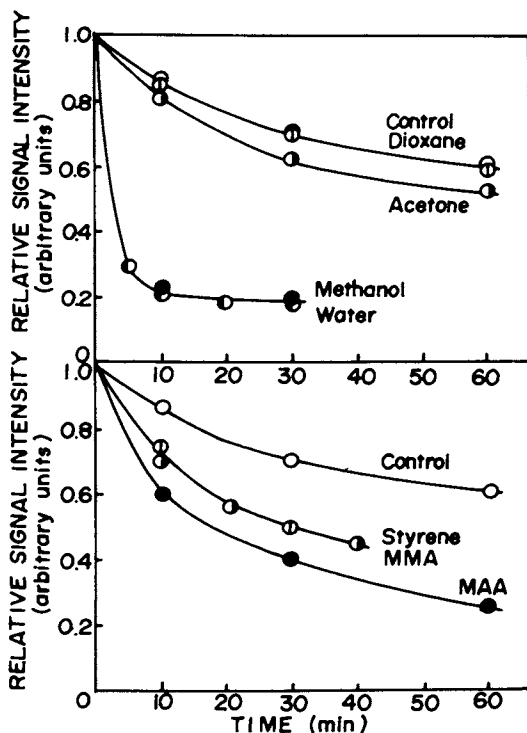ry copolymers, as shown in Table IX. The cause was explained by

Figure 15. Effect of various solvents on the decay of radicals produced by irradiation at room temperature. The Fe³⁺-sensitized sample was irradiated at room temperature for 30 min in quartz system.

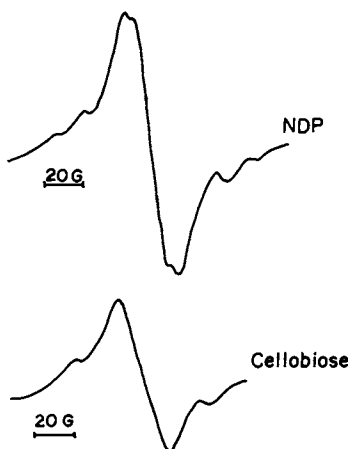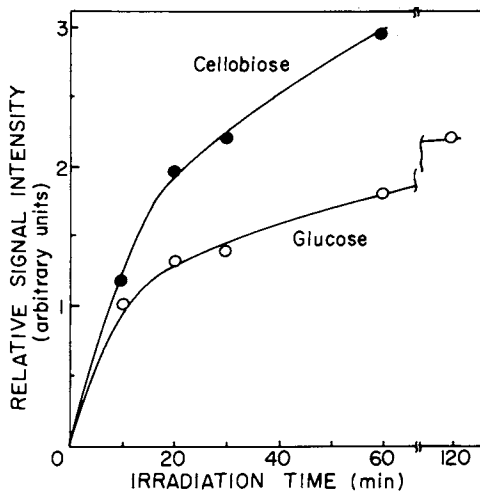*Figure 16. ESR spectra of cellulose and cellobiose irradiated with light of > 2800 Å at 77°K*

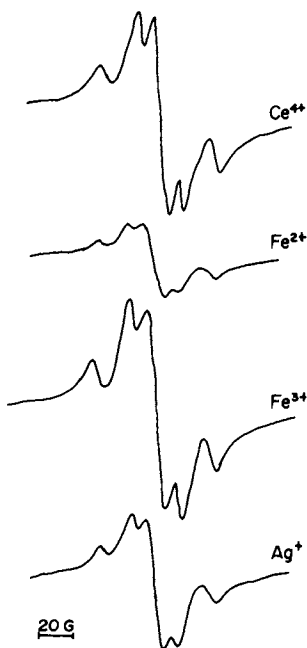Figure 17. Formation of radicals in glucose and cellobiose by irradiating with light of > 2200 Å

Figure 18. ESR spectra of sensitized samples irradiated with a super high-pressure mercury lamp at 77°K for 90 min
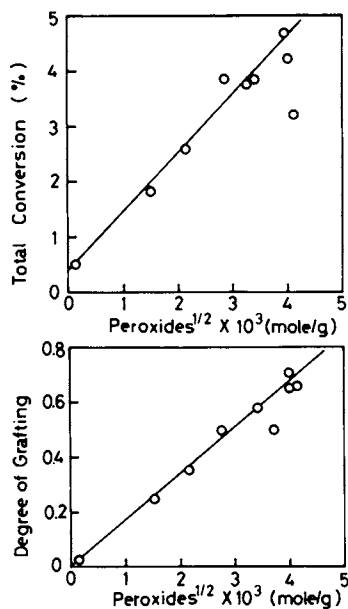
Figure 19. Relationship between total conversion vs. peroxide concentration and the degree of grafting vs. peroxide concentration in graft copolymerization of styrene onto cellulose triacetate preirradiated with gamma rays in air at 0°C. Grafting conditions, 60°C, 20 hr.

Table IX. Monomer Reactivity Ratios of Styrene with n-Butyl Acrylate in the Graft Copolymerization onto Cellulose and Cellulose Triacetate at 50°C.

Trunk Polymer	Copolymer	r_{St}	r_{BuA}	r_{St}/r_{BuA}
Cellulose	grafted	1.38 ± 0.01	0.22 ± 0.01	6.3
	nongrafted	0.90 ± 0.03	0.40 ± 0.01	2.3
Cellulose	grafted	1.16 ± 0.01	0.42 ± 0.01	2.8
triacetate	nongrafted	1.08 ± 0.01	0.54 ± 0.01	2.0
AIBN-initiated				
copolymer		0.76 ± 0.01	0.38 ± 0.01	2.0

the adsorption of styrene or complex formation of styrene with radicals.

(3) Molecular Weight, Molecular Weight Distribution, and the
     Number of Grafted Polymers per Trunk Polymer. Since graft-
ing reaction onto cellulose is usually carried out in heterogene-
ous phase, the termination is disturbed by the gel effect and the
grafted polymer has higher molecular weight than the homopolymer.
In homogeneous grafting onto cellulose derivatives dissolved in
solvents, the molecular weight of the grafted polymer is not much
different from that of the homopolymer.
     The molecular weight distribution of grafted polymers has
been determined by several investigators. It was sometimes wide
(46, 47) or it had bimodal distribution(48). Our results(49) on
the molecular weight distribution of polystyrene grafted onto
cellulose triacetate showed that at least in the initial stage of
the grafting the molecular weight distribution is similar to that
of ordinary polystyrene. It is recognized that as the grafting
proceeds, the molecular weight increases and the distribution be-
comes wider(Figure 20).
     As for the number of grafted chains per trunk polymer, Ikada
et al.(50) showed that in the grafting reaction of styrene in
methanol-water as solvent onto cellulose with simultaneous irra-
diation, the number of branch molecules per trunk polymer is
0.915 after exhaustive extraction of unreacted cellulose and
homopolystyrene. It is usually recognized that the number of
grafted chains does not exceeds 1. New grafting methods which
produce multi-branch grafted copolymers easily are expected to
be developed.

(4) Stereoregularity of Polymers Formed in Graft Copolymeriza-
     tion. Since graft copolymerization onto solid trunk poly-
mers, especially onto fibers, is a kind of organized polymeriza-
tion in matrix, the structure of the polymers formed is expected
to be different from those of the ordinary radical-initiated pol-
ymers, because the solid trunk polymers would give some influence
on the molecular association and orientation of the monomers be-
ing polymerized.
     In our first report(51), methyl methacrylate(MMA) and metha-
crylic acid were grafted onto various fibers such as nylon 6,
cellulose triacetate fiber and polyester fiber with preirradia-
tion techniques using gamma rays from a Co-60 source and the
stereoregularity of the branch polymers isolated by acid hydroly-
sis was determined by proton NMR spectroscopy. The results indi-
cated that the stereoregularity of PMMA and poly(methacrylic
acid) grafted onto viscose rayon and cotton was different from
that of the polymers formed in ordinary radical polymerization.
     In the second report(52), MMA was grafted onto viscose ray-
on, wood pulp, cellophane and poly(vinyl alcohol)(PVA). The
stereoregularity of the polymers grafted onto rayon is different

from that of the polymers grafted onto wood pulp, mercerized wood pulp, cellophane and PVA films and powder.

Recently, the stereoregularity of PMMA grafted onto various kinds of rayons, cotton linters and mercerized cotton linters was investigated in detail(53). The results shown in Table X indicate that the stereoregularity of PMMA grafted onto ordinary viscose rayon filaments and staples and high tenacity viscose rayon staples of tire cord type is clearly different from that of the ordinary radical-initiated polymers. Those rayons which give the different structures have high percentages of skin portion and the structure is different from that of polynosics and cuprammonium rayons. Therefore, it is deduced that the polymerization in the skin structure affects the stereoregularity of polymers being polymerized.

5. Application of Irradiation to Viscose Process

In the manufacturing of viscose rayons, aging of alkali cellulose to lower the degree of polymerization of cellulose is usually carried out. Imamura and Ueno(54) attempted to replace the aging of alkali cellulose with irradiation.

Dissolving pulps were irradiated with gamma rays or electron beams in a range of $10^5 - 10^8$ rad. The degree of polymerization and carbonyl and carboxyl contents after the irradiation depended on the total dose and not on the irradiation source. Irradiation apparatus for large scale production of low DP pulps was investigated and among CO-60 gamma ray source, high voltage accelerator and low voltage accelerator, low voltage accelerator is most suitable for industrial application(55).

Low DP pulps(DP 440) obtained by irradiation with gamma rays or electron beams were processed in viscose process without aging(56). The analysis of the original and the irradiated pulps is shown in Table XI. The mechanical properties of rayon staples produced from the irradiated pulps are shown in Table XII. Although they show tendency to have a little low wet strength, wet elengation and knot strength, the difference is not appreciable. Pulps irradiated with electron beams showed the same results.

6. Cellulose Industries in Japan

As for pulp and paper industries in Japan, Prof. Nakano will write on the problems related to the industries.

As for viscose process several companies already withdraw from the production and this tendency will continue, because the increase of cost is expected due to the increase of prices of wood pulp and caustic soda, investment for pollution problems and the increase in labor wages.

As a new product, Mitsubishi Rayon Co. installed machines for production of viscose rayon spun bonds recently. The products are now being used for diaper linen, liner of paper table

Table X.   STEREOREGULARITY OF POLY(METHYL METHACRYLATES) GRAFTED ONTO RAYONS AND COTTONS

	VISCOSE RAYON FILAMENTS		ORDINARY VISCOSE RAYON STAPLE		HIGH TENACITY RAYON STAPLE (TIRE-CORD TYPE)		(POLYNOSICS)		CUPRAMMONIUM RAYON FILAMENT		STAPLE		COTTON LINTER		MERCERIZED COTTON LINTER		ACID-HYDROLYZED COTTON LINTER	
	G	H	G	H	G	H	G	H	G	H	G	H	G	H	G	H	G	H
S	53.4	59.2	54.6	59.3	54.5	58.1	57.1	59.0	59.1	61.1	57.8	60.5	61.1	61.5	56.8	57.9	62.5	60.8
H	39.5	36.7	39.9	36.6	39.2	36.6	37.6	37.0	36.5	34.7	37.4	35.7	35.6	34.3	38.0	37.2	32.5	35.0
I	7.1	4.1	5.5	4.1	6.3	5.3	5.3	4.0	4.4	4.2	4.8	3.8	3.3	4.2	5.2	4.9	5.0	4.2

Table XI.   Analysis of original and gamma-ray irradiated pulps

Pulps	A		B		C	
	Original	Irradiated	Original	Irradiated	Original	Irradiated
α-cellulose(%)	92.0	88.6	90.1	87.5	88.2	84.9
β-cellulose(%)	4.6	8.3	4.9	7.9	5.5	10.2
Number average DP	750	448	776	465	754	455
Pentosan (%)	3.7	3.7	3.6	3.7	4.8	4.7
Copper number	1.2	1.8	1.2	1.9	1.5	2.3

Table XII. Comparison of properties of rayon staple fibers obtained by conventional and no-aging viscose processes.

Stretch ratio	Properties		Pulp A		Pulp B		Pulp C	
			Conven-tional	No-aging	Conven-tional	No-aging	Conven-tional	No-aging
1.2	Fineness	(d)	1.64	1.67	1.68	1.64	1.64	1.64
	Tenacity Dry	(g/d)	2.92	2.88	2.85	2.77	2.90	2.89
	Tenacity Wet	(g/d)	1.81	1.73	1.68	1.64	1.79	1.63
	Dry/Wet	(%)	62.0	60.1	58.9	59.2	61.7	56.4
	Elongation Dry	(%)	18.0	18.3	18.1	17.2	17.5	17.3
	Elongation Wet	(%)	22.5	23.3	22.0	19.9	20.6	19.7
	Knot tenacity	(g/d)	1.75	1.77	1.80	1.82	1.81	1.72
	Loop tenacity	(g/d)	2.06	2.05	2.03	1.92	2.09	1.95
1.5	Fineness	(d)	1.72	1.75	1.76	1.77	1.74	1.78
	Tenacity Dry	(g/d)	3.37	3.29	3.32	3.10	3.37	3.16
	Tenacity Wet	(g/d)	2.31	2.23	2.24	2.04	2.31	2.03
	Dry/Wet	(%)	68.5	67.8	67.5	65.5	68.5	64.2
	Elongation Dry	(%)	17.4	14.6	15.5	13.8	14.5	14.6
	Elongation Wet	(%)	20.4	16.5	15.6	15.7	15.6	14.9
	Knot tenacity	(g/d)	1.53	1.55	1.56	1.55	1.62	1.53
	Loop Tenacity	(g/d)	1.81	1.62	1.65	1.60	1.77	1.58
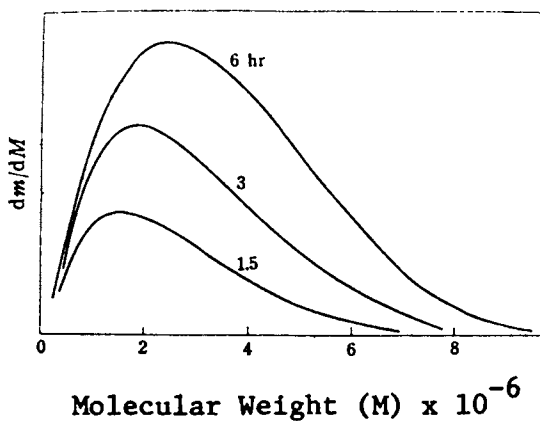
Figure 20. Molecular weight distribution of grafted polystyrene formed in the copolymerization at 75°C
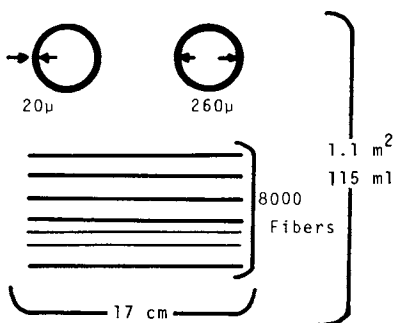
Figure 21. Assembly of artificial kidney
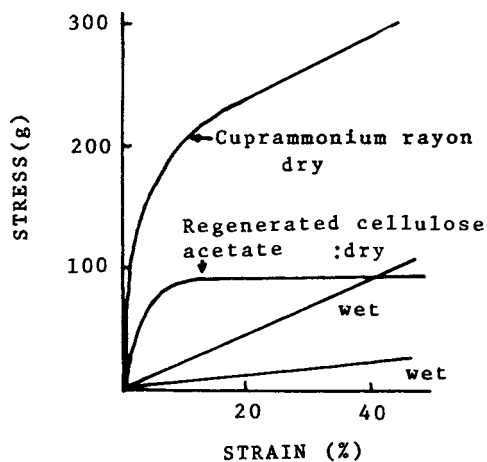
Figure 22. Stress–strain curves of hollow fibers
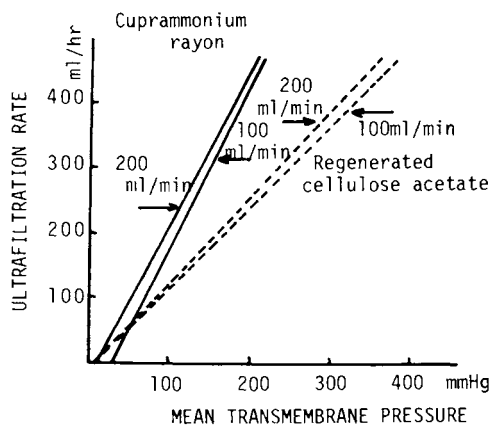
Figure 23. Comparison of ultrafiltration rate

napkins, and packaging fruits.

Cuprammonium process increased its production steadily and developed several new products, such as artificial kidney and spun-bonded fabrics. Asahi Chemical Industry Co. and Asahi Medical Co. developed artificial kidney made of hollow fibers of cuprammonium rayon. The assembly is illustrated in Figure 21. It is made of 8000 hollow fibers(each ca. 300 deniers), of which inside diameter is 260μ. Cuprammonium rayon in Japan is manufactured from cotton linter pulps. It has higher strength than regenerated cellulose acetate hollow fibers as shown in Figure 22. It has higher rate of filtration for water and urea, as shown in Figure 23. Especially, it can be sterilized with ethylene oxide gas, permitting simple and short operations. Improved thrombogenicity permits less heparin dose and less residual blood after dialysis. Present production per month is now 30,000 pieces.

Asahi Medical Co. is now developing disposal system made of hollow cellulose acetate fibers. They are used to prevent dialysis of cancer cells and/or bacillus, but pass proteins of low molecular weight. The system is clinically tested for reinfusement of ascitic fluid.

Cellulose derivative industries are developing steadily. Methyl cellulose(D.S. 1.8-2.0) is mainly used for cement mortar and stabilizing agent for suspension polymerization of vinyl chloride and vinylidene chloride. Other uses are cosmetic. Most of hydroxypropyl methyl cellulose is used in the field same as methyl cellulose, but a low viscosity grade is used in tablet coating.

Hydroxypropyl methyl cellulose phthalate(hydroxypropyl 6-10%, methyl 18-22%, phthalate 27-35%) is used for enteric coating and photo-sensitive polymers. This polymer is superior to cellulose acetate phthalate since the latter has tendency to produce acetic acid during preservation.

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The Relationships between Fibrous Materials and Paper Products. Concepts. Prospects

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1. The concept of relationships between "fibrous materials and paper" in the course of the fundamental processes of paper converting and obtainment. Paper characteristics

For quite a long time, relations which can be established between pulp, as the original fibrous material, and paper, the end product of a series of intermediate technological processes, have been the intuitive concern of paper producers.

Yet the detection of qualitative and especially quantitative relations apt to outline the reciprocal influences between the original properties of the cellulose fibrous material and those of the paper end product (physical, rheological, mechanical strength paper properties) is a matter of future achievement.

In the course of paper-converting a series of operations and processes (which are sketched out in figure 1) come between pulp (the raw material) and paper (the end product).

Modern technologies call for an additional use of auxiliary (non-fibrous) materials having specific functions. The use of adhesives leads to a reevaluation of the above mentioned sketch of influences and thus we get a completed form (figure 2).

From figure 2 we may infer that pulp is likely to be influenced by an addition of adhesives which, in their turn, exert an influence on the fundamental operations.

However pulp has a decisive part in lending paper certain specific characteristics. Similar decisive actions are brought forth by a number of adhesives.

39

Table 1

FACTORS OF INFLUENCE		Influence on factors or operations, determination of paper characteristics, respectively																											
		PULP				OPERATIONS										PAPER CHARACTERISTICS													
		A1	A2	A3	A4	C11	C12	C13	C14	C2	C3	C4	C5	C6	C7	D11	D12	D13	D21	D22	D23	D24	D25	D26	D27	D31	D32	D33	D34
PULP	A1					●●	·	·	●	●	●	●	●	·	●●	▲▲	▲▲	△	▲▲	·	·	▲	▲	·	△	△	▲	▲	▲▲
	A2					●	●●	●●	○	·	○	●	·	·	·	△	·	△	·	△	·	·	·	▲	△	·	·	△	·
	A3					○	●●	●●	●●	·	●●	●●	·	·	·	△	·	·	·	▲▲	△	·	·	△	·	·	·	△	·
	A4					●●	·	·	○	●	●	●	○	●●	●	●●	▲▲	▲▲	▲▲	·	·	·	·	▲▲	·	▲	▲	△	·	▲▲
ADHESIVES	B1	·	·	●	·	·	●●	○	●	·	○	●	·	○	○	△	·	▲	·	▲▲	·	·	△	△	▲	▲	▲▲	▲▲	△
	B2	·	●	●●	·	○	●●	●	●	·	●	●	·	·	·	·	△	·	▲▲	·	·	·	△	△	·	·	△	·
	B3	·	●	●●	○	○	●	○	●●	·	○	●●	○	○	●●	△	△	△	▲▲	▲	▲▲	▲▲	▲▲	△	▲	▲	▲▲	▲▲	▲▲
	B4	·	○	○	·	·	·	·	●●	·	·	·	·	·	·	·	·	·	·	·	▲▲	▲	·	·	·,	·	·	△	·
	B5	·	○	●●	·	·	○	·	●●	○	●	●●	○	·	●	△	·	△	△	△	▲▲	▲	△	·,	·,	▲	▲	▲▲	▲▲
	B6	·	○	●●	○	·	·	·	○	○	●●	●	·	·	·	·	·	△	·	·	·	·	·	·	▲▲	·	△	△	·
	B7	·	○	●●	○	·	·	·	·	·	·	○	○	·	·	▲▲	·	▲▲	·	·	▲	·	·	·	▲	·	▲	▲	·
	B8	·	○	●●	●●	·	○	○	·	●	○	○	·	·	·	·	·	·	·	△	·	△	·	·	△	·	·	·	·
	B9	·	○	○	●●	○	○	○	·	●●	·	○	·	·	·	·	·	△	·	△	·	·	△	·	·	·	·	·	·
FUNDAMENTAL OPERATIONS	C11															▲▲	▲▲	▲▲	▲▲	▲	△	▲	·	△	▲	▲	▲▲	▲	▲
	C12															△	·	▲	·	▲▲	△	·	·	△	△	△	▲	▲	△
	C13															·	⌒	·	·	·	▲▲	▲	·	·	·	·	·	·	·
	C14															▲	△	▲	▲▲	▲	▲▲	▲▲	▲	·	·	▲	▲▲	▲▲	▲▲
	C2															△	·	·	·	·	·	▲	·	·	·	·	·	·	·
	C3															△	·	·	·	▲	·	△	·	·	▲	·	·	△	·
	C4															▲	△	△	▲	▲	▲▲	▲▲	▲▲	·	▲	▲	▲▲	▲▲	▲▲
	C5															▲	△	△	△	△	·	△	·	·	▲	·	△	△	△
	C6															▲▲		▲▲		▲▲	·	·	·	·	△	△	·	·	△
	C7															▲	▲▲	▲▲	▲▲	△	▲	▲	▲▲	·	·	▲	△	▲▲	▲▲

A. Fibrous material
   (Pulp)–by following properties:
   1) Morphological
   2) Chemical (α, β, γ-cellulose, functional groups, lignin, ash)
   3) Electrokinetic (ζ-potential)
   4) Rheological

B. Adhesives
   1) Sizing substances
   2) Coagulants
   3) Filling materials
   4) Dyestuffs
   5) Retention aids
   6) Dewatering aids
   7) Wet strength agents
   8) Dispersibility and flotation agents
   9) Antifoams

C. Operations
    1.   Stock preparation
    1.1. Beating
    1.2. Sizing
    1.3. Dyeing
    1.4. Filling
    2.   Stock delivery on paper machine and
         sheet formation
    3.   Dewatering
    4.   Retention (fibrous material, filling
         material)
    5.   Pressing
    6.   Drying
    7.   Calendering

D. Paper characteristics
    1.   Mechanical and rheological
    1.1. Strength characteristics (in a wet and
         dry state)
    1.2. Compressibility
    1.3. Dimensional stability etc.

    2.   Physical
    2.1. Apparent density
    2.2. Degree of sizing
    2.3. Brightness degree
    2.4. Opacity
    2.5. Smoothness
    2.6. Dielectrical properties
    2.7. Filtrant-porous

    3.   Special
    3.1. Sonority
    3.2. Flatness-dusting
    3.3. Printability
    3.4. Behaviour to final prelucration and
         finishing

Note: Influence   • zero
                       ○ weak
                       ● strong
                       ●● essential

       Determination   • zero
                       △ weak
                       ▲ strong
                       ▲▲ essential

A synoptical representation of the pulp-paper relations having a slight or strong influence within the usual system (pulp-adhesives-operations-papers) is to be found in table 1.

The data mentioned in table 1, though qualitative, may lead to quantitative proportions, by use of mathematical models of simple or multiple correlations. Subsequently, these proportions will enable the optimization of fundamental operations or of paper characteristics up to the limiting values of the fibrous material or of the parameters of fundamental operations. The contributions reported further down come within this range of items.

2. Pulp from annual plants (Reed, Straw)

2.1. Pulps from annual plants as fibrous materials

Pulps from annual plants supply a heterogeneous, fibrous material rich in non-fibrous anatomic elements (epidermal cells, parenchymal tissues) and silica. The comparatively great amount of pentosans and the small size of the fibres lend these pulps specific paper characteristics (1).

The first factor has a beneficial effect upon beating capability, whereas the dimensional factor favours the production of uniformly transparent and even surface paper, having however rather low strength characteristics. Such a behaviour, in the case of writing and printing paper as well as of multi-layer cardboards, requires the association of pulp from annual plants with spruce fir pulp.

2.2. The behaviour of annual plants pulp undergoing the fundamental paper-converting operations

There are many ways of acting upon fibrous elements (fibrillation or shortening the fibres) in the case of spruce for pulp beating, whereas with annual plants pulp, on account of their small dimension, such possibilities are limited. A comparative study (2) of the beating degree in terms of time, medium fibre length changes and specific surface of beated bleached spruce fir, straw and reed pulps has been undertaken. The results are presented in table 2.

From the very beginning of the operation maximum values of the beating rate can be noticed, and they bring about a considerable specific surface growth.

Table 2

Variation of beating degree, fiber length and specific surface in the time of beating of pulps from spruce, reed and straw

Pulp	Beating time	°SR	$\dfrac{\Delta°SR}{\Delta\tau}$	Specific surface	$\dfrac{\Delta S_0}{\Delta°SR}$	Long fibers %	$\dfrac{\Delta\%}{\Delta°SR}$	Medium fibers %	$\dfrac{\Delta\%}{\Delta°SR}$	Short fibers %	$\dfrac{\Delta\%}{\Delta°SR}$
Spruce	0	13		10150		74.5		12.92		12.5	
	10	21	0.80	10800		58.3		20.1		21.46	
	20	41	2	16000	419	47.95	-0.80	28.50	+0.396	23.55	+0.404
	30	60	1.9	27000		42.07		29.80		28.13	
	40	68	0.85			38.62		30.13		31.25	
	50	76		38250		29.16		30.84		40.00	
	60	80	0.35			20.98		39.43		39.59	
Reed	0	19.5		11000				35.00		22.09	
	5	32	2.6	17000				42.77		37.92	
	10	45.5	3.61	19000	576		-0.620	48.54	+0.146	40.63	+0.473
	15	65.0	2.1	24900				45.21		44.59	
	20	67.0	2.2	38500				43.46		48.96	
	25	73.0	1.2					43.75		50.20	
	30	78.5	1.1					43.67			
Straw	0	27		24400				43.55		25.00	
	5	54	5.9	42000				41.29		39.17	
	10	75	1.7		651	3.75	-0.473	42.09	-0.046	42.09	+0.52
	15	80	1.8					41.55		51.25	
	20	85.5	1.4					40.85		55.42	

In the case of straw pulp the last value is best and this brings about a separate beating, different-iated according to types of fibrous materials (spruce fir, reed and straw). The last mentioned type also has a different electrokinetic potential ζ , which determines the degree of sizing, the retention of the filling material, the dyeing capacity, the forming and dewatering of the sheet on the paper machine.

The studies bear evidence (3,4) of a greater ζ potential in reed (-9 mV) and straw (-8,5 mV) pulp, as compared to bleached spruce fir pulp (-6 mV).

This explains the differing behaviour during the paper sizing process in point of colloidal instabi-lization which takes longer in reed and straw pulps than in spruce fir pulp. Thus the degrees of paper sizing observe the following order:

reed   <   straw   <   spruce fir
pulp   pulp   pulp

We arrive at the same conclusions when examining the curves in figure 3. (5)

2.3. Physical-mechanical properties of grades of paper with pulp addition from annual plants

Pulps from annual plants have low strength proper-ties mainly when they are subjected to double folding and tearing. In case when this fibrous material is beated separately down to a high beating degree and gets mixed up in suitable proportions with spruce fir pulp writing and printing paper having proper cha-racteristics can be obtained.

An addition of 15-30 percent of mixture in equal parts of reed pulp and straw pulp to spruce for pulp improves the strength properties of paper obtained from only spruce fir pulp. In case we exceed the 30 percent limit we get lower strength characteristics.

Figure 4 illustrates graphically these conclusions. The addition of pulps from annual plants in the com-position of the fibrous material increases at the same time, the porosity and the absorption properties as can be seen in the figures 5 and 6. The properties already discussed are largely appreciated in printing paper (6).

From the contents of the cited works we may infer, qualitatively a series of influences regarding the pulp-operations-paper characteristics relationships, which depend on the use of annual plants pulp.
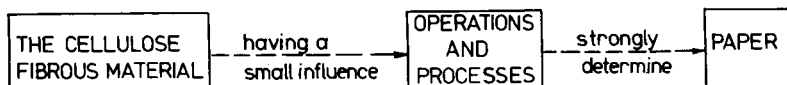
Figure 1. Pulp–paper relations
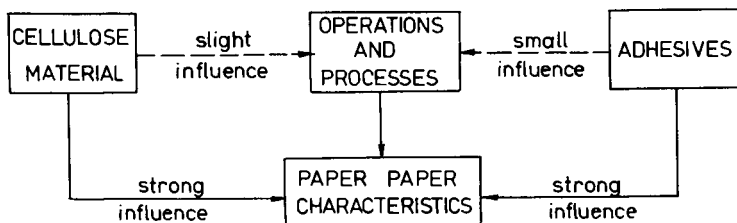
Figure 2. Relations among pulp–adhesives–operations–paper properties
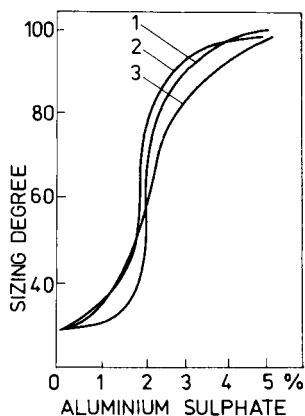
Figure 3. Variation of sizing degree vs. electrolyte quantity. (1) Spruce pulp; (2) reed pulp; (3) straw pulp.
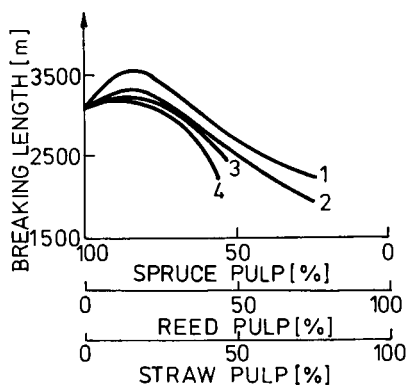
Figure 4. Variation of breaking length vs. fibrous composition. (1, 2) pulps from spruce and reed; (3, 4) pulps from spruce, reed, and straw; (1, 3) separate beating; (2, 4) mixture beating.

Figure 5. Influence of addition of annual plant pulps on paper porosity. (1, 2) pulps from spruce and reed; (3, 4) pulps from spruce, reed, and straw; (1, 3) separate beating; (2, 4) mixture beating.
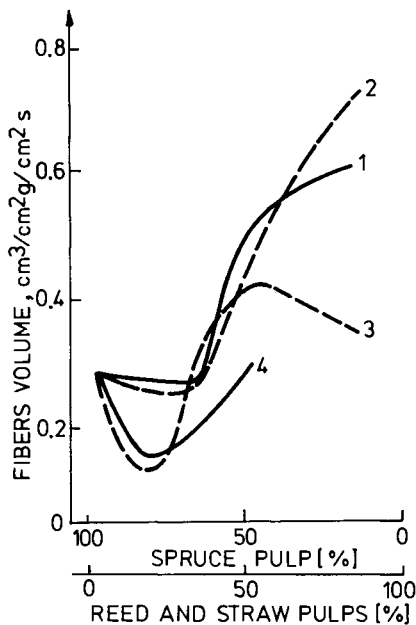
Figure 6. Influence of pulp addition on penetration index; 1, 2, 3, 4 are the same specifications as in Figure 5.
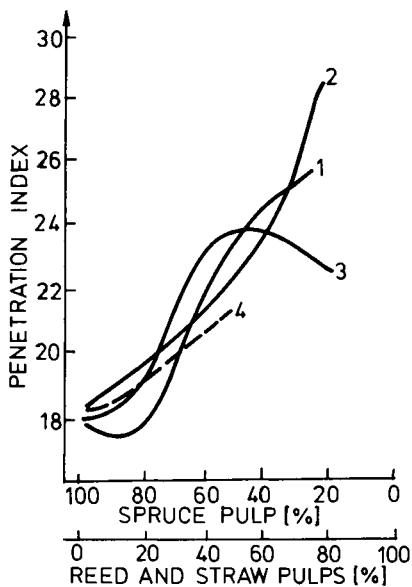
3. Pulps from hardwoods

Beech-pulp lends the paper a series of new characteristics as compared with spruce fir pulp. The lower flexibility characteristic (7) and the different biometry of fibrous elements endow pulp with low paper characteristics. Some values of these characteristics are shown in figure 7 and table 3.
In respect of the chemical composition great differences may be noticed and they are evidenced by the data in table 4.

3.2. The behaviour of beech pulp mixed up with spruce fir pulp in the fundamental paper-converting operations

The investigation was concentrated on the beating rate variation in bleached and unbleached pulps obtained from beech and spruce fir. A much faster beating is to be noticed (8) in bleached beech-pulp as compared with unbleaohed pulp. On comparing with the beating rate of spruce fir pulp, less discernible differences are to be noticed in natural pulps, as can be seen in figures 8 and 9. In this case, as well, a proper means of turning to good account is provided by mixing it up with softwood pulps, by use of method of beating pastes separately.

Supplementary studies refer to the fundamental operations of sizing, filling, forming and pre-consolidating dewatering of the sheet on the paper-machine, by use of a PPE resin adhesive. (9)

The quantitative influences are describes in figures 10-13.
The first two graphs show that the best potential for sizing and filling is of 0-1.0 mV.

The waterproofness characteristics of the wet paper board (see figure 12) are greatly improved by the beech pulp addition to the paper stock composition, diminishing at the same time its compressibility (see figure 13) (10).

3.3. Characteristics of papers from beech pulps mixed up with spruce fir pulps

As regards paper characteristics, beech pulp has a detrimental effect upon the strength properties of paper. (11)
The beating operation may bring forth on improvment of some characteristics.

Table 3

Biometrical data for beech and spruce fibers

Species	Cell wall thickness µ	Lumen diameter µ [1]	Index 2 P/L	Groups repartition by Runkel criterion					Groups repartition by Mühlsteph criterion			
				I	II	III	IV	V	I	II	III	IV
Beech -annual ring 7	2-4;2-5	4-10	0.6 - 2.2	–	–	53.0	43.0	4.0	–	57.1	42.9	–
-annual ring 72	4-5;4-5	2- 8	0.6 - 3.3	–	–	4.3	88.0	7.7	–	13.0	87.0	–
Spruce -annual ring 7	2-3;2-7	9-26	0.14- 0.9	70.0	14.5	15.5	–	–	24.5	65.5	–	–
-annual ring 72	2-9	6-31	0.19- 2.2	25.7	37.0	2.8	20.0	14.5	17.1	51.70	31.5	–

1. radial and tangential
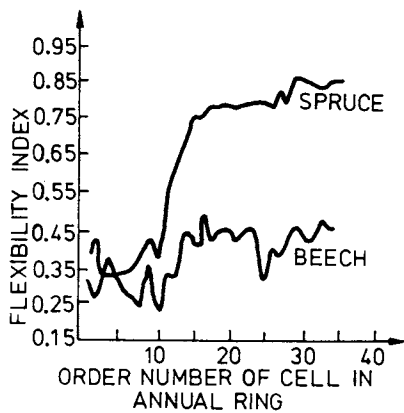
Figure 7. *Influence of cell position on flexibility index*
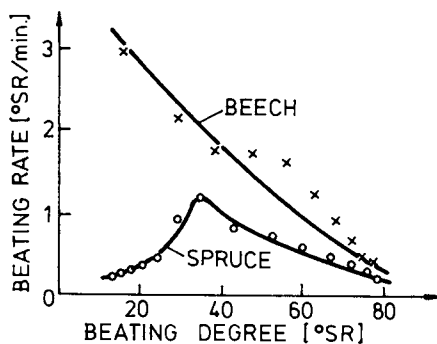
Figure 8. *Variation of the beating rate with the beating degree of bleached spruce fir and beech pulps*
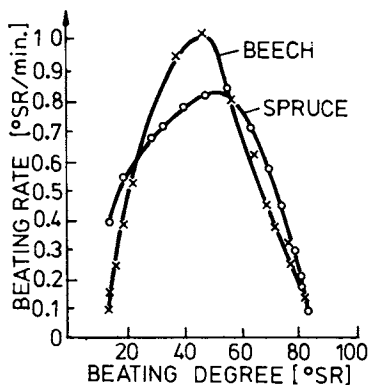
Figure 9. *Variation of the beating rate with the beating degree of non-bleached spruce fir and beech pulps*
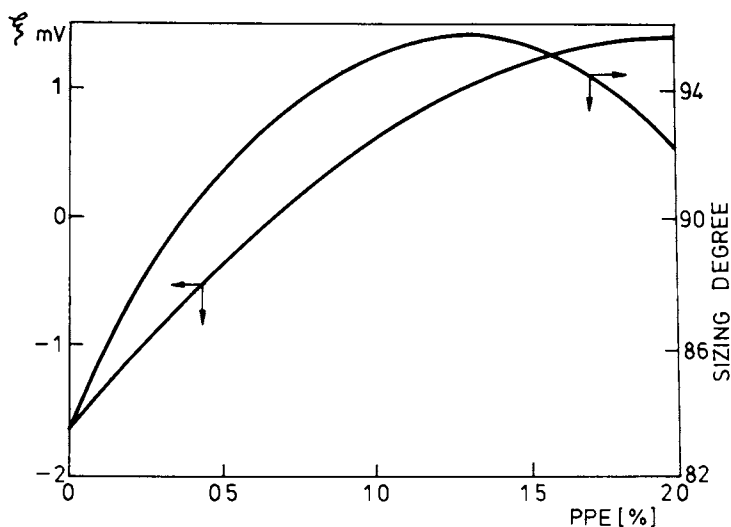
Figure 10. Variation of the electrokinetic potential and of the sizing degree with the addition of soft wood pulps. Fibrous material containing equal parts of beech and spruce pulp, beaten at 40°SR, with the addition of 3% Bewoid glue and 12.5% kaolin.
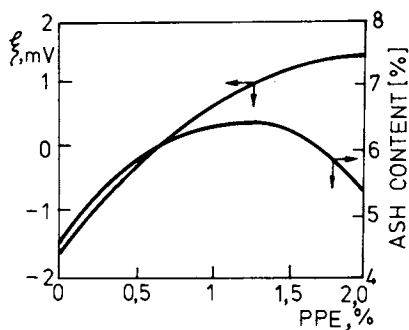
Figure 11. Variation of the electrokinetic potential and of the ash content with the PPE resin addition. Fibrous material containing equal parts of beech and spruce fir pulps, beaten at 40°SR, with the addition of 3% Bewoid glue and 12.5% kaolin.

Many of the existing data outline the existence of determined pulp-paper relations, as well as of influences induced by the fundamental paper-converting operations. (Table 5)

Morphological factors have been reported to have a negative influence upon strength properties; likewise the beating and dewatering operations may act as means of control for the direct pulp-paper correlation.

3.4. Investigations on the ways of obtaining and using PPE as an adhesive in the mass

The influence of adhesives upon the pulp-paper-fundamental operations correlation has been studied. To this end, a polyamidic modified resin, obtained by the reticulation of a polyamide through epichlorhydrine has been prepared. (9) The resin of the poly-amine-polyamide-epichlorhydrine type has been called PPE resin for short.

Because of the cation active character and the strongly electroposition ζ potential, the resin is to be used as an adhesive in the mass (12), retained in the paper paste, on the pulp fibres, having high yields (with or without additional substances). The retention takes place on a wide pH interval limited by 4 ÷ 10. (13)

A small quantity of PPE resin (under 5 percent), added to the fibrous material, displaces the ζ potential of pulp from the range of electronegative values (-9 : -15 mV), passing through the isoelectric point, to the range of electropositive values (+15 : 20 mV) (14). Figure 14 describes this variation.

The PPE resin used as an adhesive in the mass, increases the strength properties of dry and especially wet paper (15,16). It results from figure 15 and 16 that additions of 1-3 percent PPE have been used, causing important increases of strength.

The PPE resin has also effects on the dimensional stabilization and paper band stressing during the drying process (17,18). Figure 17 bears evidence of a reduction of dimensional variations from 15 to 60 percent.

At the isoelectric point of the paste (which corresponds to an addition of 0.15-0.25 percent PPE resin) the values of the breaking length of the suspensions (LRS) reach their maximum, as can be seen in figure 18.

Table 4

Chemical composition of beech and spruce

| Species | Ash % | Extraction with | | | Cellulose | Lignin | Pentosans | Cellulose/lignin ratio |
		Water	NaOH 10%	Alcohol ethylic				
Beech	0.34	1.62	15.70	0.2	47.03	22.37	17.11	2.1
Spruce	0.21	1.68	10.54	0.97	53.53	28.77	8.25	1.86

Table 5

Correlation equations of strength properties of paper obtained with short fibers pulp

Physico-mechanical characteristics	Regression equations
Breaking length, m	$y = 4200 - 43\ x_1 + 40\ x_2$
Burst strength in dry state, Kgf/cm^2	$y = 4.73 - 0.072\ x_1 + 0.00017\ x_1 + 0.00043\ x_1 x_2$
Tearing resistence, g	$y = 78.7 - 0.196\ x_1$
Opacity after calandering	$y = 0.77 + 0.00151\ x_1 + 0.00373\ x_2 - 0.00001 x_1^2$ $- 0.00005\ x_2^2 + 0.00067\ x_1 x_2$

x_1 - beech pulp, %
x_2 - beating degree of beech pulp, ^{o}SR
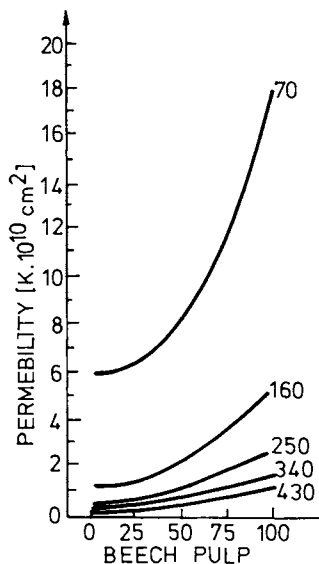
Figure 12. Variation of the waterproofing characteristics of the preconsolidated paper varieties with beech pulp mixed with unbleached spruce fir pulps. Beating degree of the two pulps is 40°SR, with an addition of 3% colophony glue and 1% PPE resin.
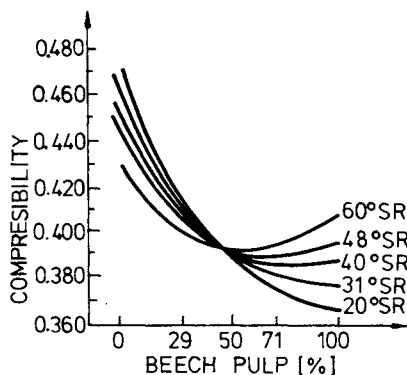
Figure 13. Variation of the compressibility of preconsolidated papers vs. the variation of the bleached beech pulp addition and of the beating degree of softwood, with an addition of 3% colophony glue, 1% PPE resin, and 12.5% kaolin
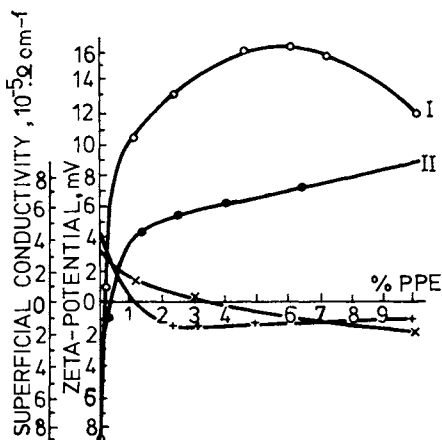
Figure 14. Variation of superficial conductivity and zetha-potential vs. PPE content zetha-potential. (○) Unbeaten pulp, (●) beaten pulp; superficial conductivity (×) unbeaten pulp, (—) beaten pulp.
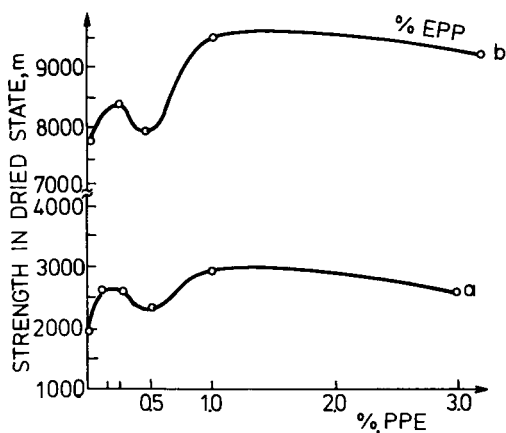
Figure 15. Strength variation of dry papers obtained from (a) unbeaten and (b) beaten bleached softwood sulfate pulps, with an addition of PPE resin
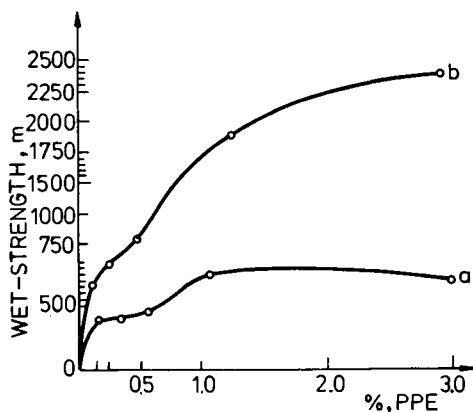
Figure 16. Strength variation of wet papers obtained from (a) unbeaten and (b) beaten ground bleached softwood sulfate pulps with an addition of PPE resin
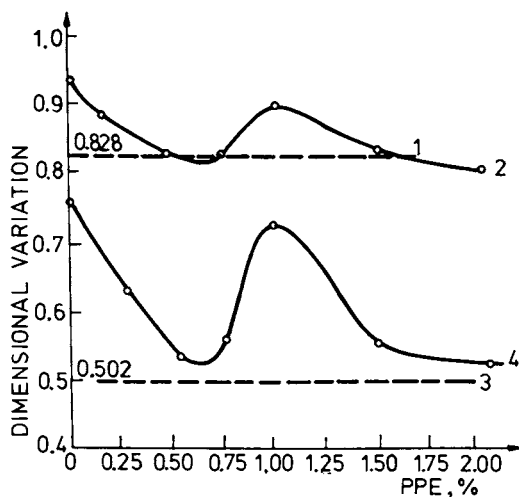
Figure 17. Dimensional variation of two types of paper with the amount of added PPE resin. (1) Dimensional variation of type 1 under the influence of a 2% melamine addition; (2) dimensional variation of type 1 with the addition of PPE resin; (3) dimensional variation of type 2 under the influence of a 5% melamine addition; (4) size variation of type 2 with the addition of PPE resin.
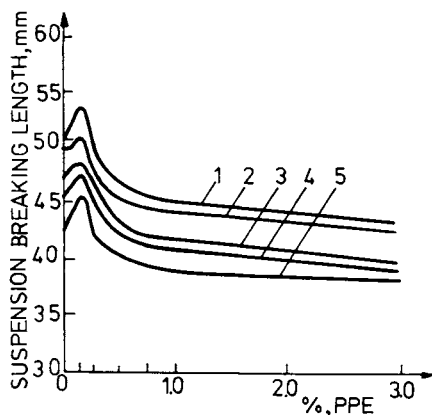
Figure 18. Suspension breaking length variation vs. the addition of PPE resin and consistence in bleached sulfate pulps from unbeaten softwood materials

A similar variation takes place in dry and wet resistances and dimensional stability as can be seen in figure 19.

The changes cited above may be accounted fof by the peculiar rheological behaviour of the fibrous suspension in the region of the isoelectric point, which ensures optimum conditions for the paper formation.

Operations such as sizing, short fibrous materials retention, filling materials retention and even dewatering on the paper-machine are also largely influenced by introducing PPE adhesive into the paste(19).

A maximum degree of sizing is achieved with an addition of only 1 percent PPE resin, when using 3 percent aluminium sulphate, i.e. 80 percent less than in case of the output in usual processing. The papers thus obtained have a pH tending to the neutral value (6,5) and physical-mechanical properties similar to those resulting from the classical reception (14, 20-21). Figure 20 shows the described variations.

As regards the recorded effects upon filling materials retention and short fibres retention, they are to be found in figures 21 and 22.

The study of vallum papers, processed in the presence of the PPE adhesive, resulted in the following correlating equations:

$$F(\%) = 0.5 - 0.5\ x_1 + 0.73\ x_3 - 1.23\ x_2^2 - 1.1 x_3^2 \quad (1)$$

$$\begin{aligned} \mathcal{J}(mV) = 0.12 &- 0.03\ x_1 + 0.934\ x_2 + 1.383\ x_3 - \\ &- 0.105\ x_1^2 - 0.725\ x_2^2 - 0.011\ x_3^2 + \\ &+ 0.116\ x_1 x_2 + 0.262\ x_1 x_3 - \\ &- 0.442\ x_2 x_3 \qquad\qquad (2) \end{aligned}$$

where the dependent variables are:

F - fibrous material retention yield
$\mathcal{J}$ - zetha electrokinetic potential of the suspension

The independent variables are the following:

x_1- colophony glue addition
x_2- aluminium sulphate addition
x_3- PPE resin addition
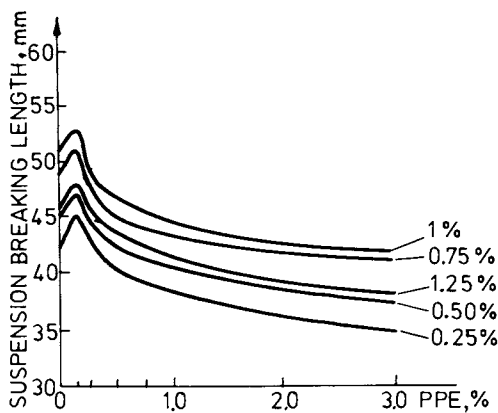
Figure 19. Suspension breaking length variation vs. the addition of PPE resin and consistence in bleached sulfate pulps from beaten softwood materials
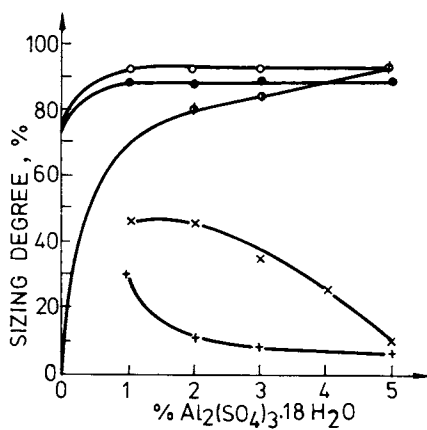
Figure 20. pH of the environment and the sizing degree of the papers obtained with 3% colophony glue with and/or without an addition of 1% PPE resin and rising quantities of aluminum sulfate or natrium aluminate + aluminum sulfate. Degree of sizing: (○) 5% aluminum sulfate; (●) 1% PPE + 1% Al$_2$(SO$_4$)$_3$; (⦶) 1% PPE + 1% aluminum sulfate + natrium aluminate. pH: (×) 5% aluminum sulfate; (+) 1% PPE + 1% aluminum sulfate.
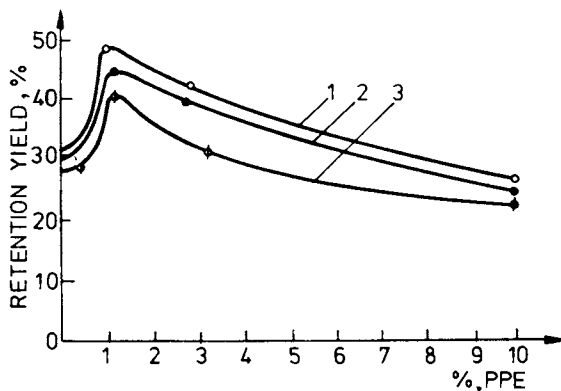
Figure 21. Retention yield variation of the calcium carbonate with PPE resin addition in the case of bleached sulfate pulp which has been beaten for 35 min with an initial addition of 1–10% fillings; 2–20% fillings; 3–5% fillings
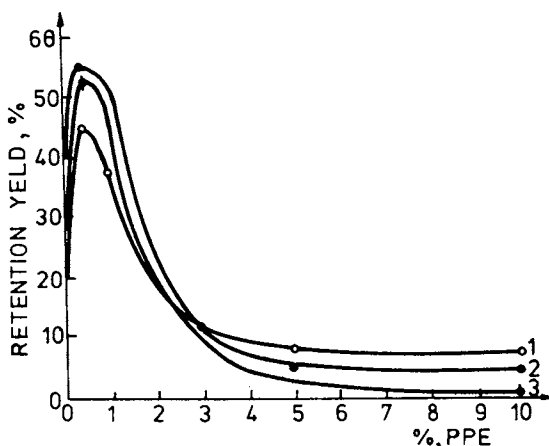
Figure 22. Variation of the titanium dioxide with PPE resin addition retention yield, in the case of bleached sulfate softwood pulp which has been beaten for 35 min in a Jokro mill, with an initial addition of 1–20% fillings; 2–10% fillings; 3–5% fillings

The last values have the following limits:

x_1 = 0-3 percent; x_2=0-8 percent; x_3=0-1.2 percent

In the specific case when in equation (1) we use 3 percent colophony glue (x_1 = +1.682) and 4 percent of aluminium sulphate (x_2 = 0), we obtain equation (3):

$$F = 95.84 + 0.73 \ x_3 - 1.1 \ x_3^2 \qquad (3)$$

The relation describes a curve having a maximum when F = 95.97 percent, corresponding to a quantity of 0.718 percent PPE resin (x_3 = +0.332).

The yield increase regarding the fibrous material retention is F = 9.1 percent.

Under similar conditions, we get equation (4)

$$\zeta = -0.23 + 1.82 \ x_3 - 0.011 \ x_3^2 \qquad (4)$$

where from we find the following value ζ = +0.37 mV, for which the yield is at its highest (region of the isoelectric point).

Similarly influencing factors of the PPE addition in the stock dewatering process on the newspaper-machine have been determined. The following correlating equations have been used:

$$K \ (cm \ s^{-1}) = 9.1 - 1.18 \ x_1 + 0.322 \ x_3 -$$
$$- 0.42 \ x_1^2 - 0.32 \ x_2^2 - 0.294 \ x_1 x_2 \qquad (5)$$

$$\sigma \ (cm^2 g^{-1}) = 2.87 + 0.273 \ x_1 + 0.0167 \ x_2 -$$
$$- 0.1 \ x_3 + 0.04 \ x_1^2 + 0.05 \ x_3^2 +$$
$$+ 0.0146 \ x_1 x_2 \qquad (6)$$

$$\zeta \ (mV) = 1.18 + 0.885 \ x_2 + 2.28 \ x_3 -$$
$$- 0.203 \ x_1^2 - 0.763 \ x_2^2 - 0.763 \ x_2^2 -$$
$$- 0.43 \ x_3^2 - 0.092 \ x_1 x_2 - 0.705 \ x_2 x_3 \qquad (7)$$

As dependent variables the following have been assumed:

K - filtering rate
σ - specific apparent surface of the pulp material and
ζ - electrokinetic potential

The independent variables were the following:

x_1 – proportion of groundwood/total amount of
  fibrous material (60-100 percent)

x_2 – aluminium sulphate addition

x_3 – PPE resin addition (0-1 percent)

If we take x_1 = 0 (80 percent groundwood and 20
percent sulphate pulp) and x_2 = – 1.682, we get
specific equations for K, σ and $\mathfrak{Z}$, resulting in a
maximum filtering rate K_{max} = 8.32·10^{-3} cm s^{-1}, an
increase ΔK = 18 percent and a value of the poten-
tial of +0.11 mV. Thus the hypothesis on maximum
values of dewatering characteristics at a zero $\mathfrak{Z}$
potential, for which the specific apparent surface
is at its lowest. The use of PPE adhesives in
controlling, setting and maintaining the isoelectric
point of the pastes offers an advantageous way of
controlling and optimizing the conditions of dewater-
ing, flowing consolidating and paper forming on the
paper machine realizing in this manner the requested
final characteristics of the papers.

 4. Investigations regarding the obtaining and
utilization of synthetic polymers and of modified
cellulosic fibres in paper converting

 4.1. General aspects of realizing the symbiosis
among the components of the fibrous material

 A series of well-known properties of pulp (among
which we may quote hydrophobic characteristics,
water dispersion and dry state strength) make up the
support in its utilization for paper processing. Such
characteristics are accompanied by certain drawbacks
flows (such as low strength under wet conditions,
sensitiveness to aging and destruction), which can be
compensated or adjusted by introducing into the
fibrous material new types of compounds, such as
modified celluloses and synthetic polymers.

 Thus grades of paper with various technical
functions are processed and they have mechanical
strength, waterproofness characteristics and increased
aging properties.

 New paper products, known under the name of
"synthetic papers" differ from "classical" paper in
proportion as the amount of participation on non-pulp
fibrous elements is more important. The more and more
extensive use of synthetic and artificial polymers in
the paper converting process is due to the limited

amounts of (natural) raw fibrous material mainly in
the developed countries. At the same time there came
up the problem of diversifying paper products, con-
sequent upon the combination of properties specific
to pulp with other categories of polymers. Such trends
have resulted in the collaboration of new procedures
and fundamental operations; even less expensive and
more effective.

Table 6 comprises some of the possible ways of
turning into account synthetic and artificial polymers
in the paper converting industry. In case of modified
pulps and adhesives in the mass, it is suggested that
macromolecular solutions or dispersions should be
used.

The diagram of the fibrous material-fundamental
operations-additive s-paper products has the following
aspect, in accordance with already mentioned data.
(table 6)

The qualitative influences resulting from the
utilization of chemically modified pulps or synthetic
polymers in the fibrous materials are shown in tables
7 and 8.

4.2. Study of papers obtained from cyanoethylated pulp (22-25)

A study devoted to the obtaining and characteriza-
tion in point of paper characteristics of cyanoethyl-
ated pulps, has clearly shown that cyanoethylation
of pulp is effective only at small degrees of sub-
stitution (a maximum of 1.4 percent nitrogen).

The analysis of the simultaneous influence exerted
by the parameters of the reaction between acrylo-
nitrile and bleached resinous sulphate pulp preacti-
vated through alkaline treatments) resulted in the
determination of regression equations of the main
chemical and physical-chemical characteristics of
cyanoethylated pulp, which are comprised in table 9.

The physical-mechanical properties of cyanoethyl-
ated pulp may be compared with the properties of the
witness (spruce fir pulp), there being greater values
of the tensile strength and breaking strength and
bursting strength. There has also been noticed an
increase of the beating rate of modified pulp, because
of the COOH groups.

The regression analysis led to the establishment of
optimum conditions of cyanoethylation, apt to provide

Table 6

Possible ways of using artificial polymers chemically modified celluloses and synthetic polymers in paper technology

Artificial Polymers	
A. Chemically modified pulps	B. Synthetic polymers
(obtained by etherification, esterification and grafting) used as:	Used as:
I Fibrous material utilized as such or mixed up with bleached pulp	I Additives in the mass – used in amount of 0.1-10 percent with the following functions: hydrophobic action, filling, strength increase in dry or wet state, retention agents, dewatering accelerators, protecting agents against aging etc.
II Additives in the mass, to be dispersed or solved in water	II Adhesives utilized in amounts of 10-50 percent in a) coating pastes b) binding of non-woven
	III Films a) for surface treatment of paper b) as paperized sheets
	IV Fibres for obtaining synthetic papers, such as a) non-modified fibres b) modified fibres

Table 7

Influence of pulp derivative (modified pulps) on properties of paper

Characteristics Derivative (modified pulp)	Dimensional (size) stability	Thermo-resistance	Aging resistance	Micro-biological properties	Ions-exchanging properties	Fat-and water-proof properties	Optical properties
Carboximethyl cellulose	-	-	-	-	++	+	+
Hydroxyethyl cellulose	++	-	+	-	-	-	-
Sulphoethyl cellulose	+	+	-	-	-	-	-
Acethylcellulose	+	+	-	-	-	-	-
Xanthate cellulose	·	·	·	·	·	·	·
Aminocellulose	·	·	·	+	+	+	++
Cyanoethyl cellulose	+	++	++	+	·	·	·

· no influence
- negative influence
+ positive influence
++ strong influence

Table 8

Influence of some resins and polymers used as additives on paper characteristics or fundamental operations

Resin or polymer	Hydro-resist-ance	Resist-ance in dry state	Dimen-sional stabi-lity	Aging resist-ance	Dehy-dra-tion accel.	Reten-tion	Sizing Reten-agent	Spec. elec. pro-perties	Resit-tance to chem. agents	Optical pro-perties
Starch	•	+	•	•	•	•	+	•	•	−
Dialdehyde starch	+	+	+	+	•	•	•	•	•	−
Dialdehyde hydrasone	+	+	+	•	•	•	•	•	•	−
CMC	•	+	•	•	+	•	+	•	•	−
Cellulose xanthate	+	−	+	•	•	+	•	•	•	−
Ureoformaldehydic resins	+	•	+	−	−	•	+	•	•	−
Melaminformaldehydic resins	+	+	+	−	•	•	•	•	+	−
Phenolformaldehydic resins	+	•	+	•	+	+	+	++	+	−
Polyamydic resins	++	++	+	+	•	++	•	•	•	−
Sulphonic resins	+	•	•	•	+	•	+	•	•	−
Vinyl-polycetates	+	+	+	+	•	•	•	•	•	−
Polyacrylamide	•	++	+	•	•	++	++	•	•	−
Polyacroleine	+	+	+	•	•	+	•	•	•	−
Rubber latex	+	+	+	•	•	•	+	•	+	−
Ketene dimers	+		•	•	•	•	+	•	•	−
Polyethylenimine	++	−	•	•	+	++	•	•	•	−

Table 9

No	Variable	Regression equations
1.	Nitrogen content	$y = 0.7 + 0.14\ x_1 + 0.22\ x_2 + 0.1\ x_3 + 0.05\ x_4 + 0.15\ x_5 +$ $+ 0.04\ x_1x_2 + 0.05\ x_2x_5 + 0.1\ x_3^2 - 0.15\ x_4^2$
2.	COOH content	$y = 3.0 + 0.1\ x_2 + 0.01\ x_2x_4 + 0.2\ x_4$
3.	Breaking length	$y = 7488 - 265\ x_2 - 201\ x_4 - 217\ x_5 + 262\ x_6 + 353\ x_1x_3 +$ $+ 256\ x_1x_4 - 423\ x_1x_5 + 897\ x_1x_6 - 214\ x_2x_4 - 214\ x_3$ $x_4 - 214\ x_3x_4 - 378\ x_3x_5 + 213\ x_4x_5 + 4639\ x_1^2 +$ $+ 4812\ x_3^2 + 4812\ x_3^2 + 4572\ x_4^2 + 4648\ x_5^2 + 4672x_6^2$
4.	Bursting strength	$y = 4.4 + 0.2\ x_1 - 0.1\ x_2 - 0.07\ x_1x_2 + 0.25\ x_1x_3 +$ $+ 0.3\ x_1x_4 - 0.2\ x_1x_5 + 0.6\ x_1x_6 + 0.15\ x_3x_4 + 0.1$ $x_4x_5 + 3.0\ x_1^2 + 3.0\ x_2^2 + 3.0\ x_3^2 + 3.0\ x_4^2 + 3.0\ x_5^2 +$ $3.0\ x_6^2$
5.	Double folds	$y = 2329 + 164\ x_2^2 + 171\ x_1^2 + 383\ x_3^2 + 209\ x_4^2 + 471\ x_5^2 +$ $175\ x_6^2 + 610\ x_1x_6 + 565\ x_3x_4$

x_1, AN quantity, % x_3, reaction time, min. x_5, beating time of pulp, min.

x_2, reaction temperature, °C x_4, NaOH add, % x_6, consistency, %

a fibrous material resistant against aging. Table 10 comprises these data.

Special investigations have shown that cyanoethylated pulp is also characterized by chemical stability, resistance against microorganisms and improved dielectric properties.

Thus, cyanoethylated pulp mixed up with spruce fir pulp (up to 40 percent) behaves favourably during the fundamental paper-converting operations, leading to the obtaining of a broad range of paper grades with absorbing and thermoresistant properties.

4.3. Synthetic papers obtained from chemical fibres (synthetic and artificial)

Chemical fibres, unlike those of natural pulp, do not have certain essential properties of chemical fibrous materials (hydrophilic characteristics, fibrilization, bonding capacity etc.). When used in the paper industry special consolidating agents have to be added to ensure the binding of the fibres in the structure of the paper sheet.

"Synthetic papers" with a number of valuable properties (mechanical strength, electrical properties, chemical stability, biochemical and dimensional szability, waterproofness) are obtained according to the nature and percentage of chemical fibres in the fibrous composition. To this end new types of chemical fibres (acrylic terpolymers with hydrophilic properties and increased fibrilization properties)(26), physical mixtures of polymers having good dielectric properties (27), modified fibres (28, 29) have been prepared, being extensively used in synthetic papers processing.

The consolidation has been carried out by means of polyamidic, polyvinylic, polyesteric, polyolefinic fibres etc. Copolymers with butadiene or acrylates have been used as adhesives.

When discussing the correlation fibrous material-synthetic papers-fundamental operations we may now infer the following triad : (figure 24)

The following components take part in making up this triad:

    A - fibrous material (pulp or non-pulp +
          consolidating agent)
    B - fundamental operations
    C - paper characteristics

Table 10

No.	Variable	Regression equations
1.	Breaking length, m	$y = 7097 + 225\ x_1x_2 + 225\ x_1x_3 + 478\ x_1x_6 + 182\ x_2x_3 + 381\ x_4x_5 + 609\ x_4x_6$
2.	Bursting strength, kgf/cm²	$y = 4.42 + 0.21\ x_1 + 0.24\ x_1x_4 + 0.47\ x_1x_6 + 0.01\ x_3x_4 + 0.13\ x_1^2 + 0.1\ x_2^2$
3.	Double folds	$y = 2722 + 177\ x_3 + 140\ x_4 + 427\ x_5 + 198\ x_6 + 157\ x_1x_2 + 535\ x_1x_6 + 276\ x_5x_6 + 132\ x_6^2$
4.	α - cellulose	$y = 85.1 + 7.4\ x_1 + 0.6\ x_1x_2 + 5.0\ x_1x_3 + 5.3\ x_1x_4 + 10.5\ x_1x_6$
5.	Brightness	$y = 75.1 + 3.7\ x_1 + 0.5\ x_1x_2 + 4.7\ x_1x_3 + 4.7\ x_1x_4 + 13.8\ x_1x_6$
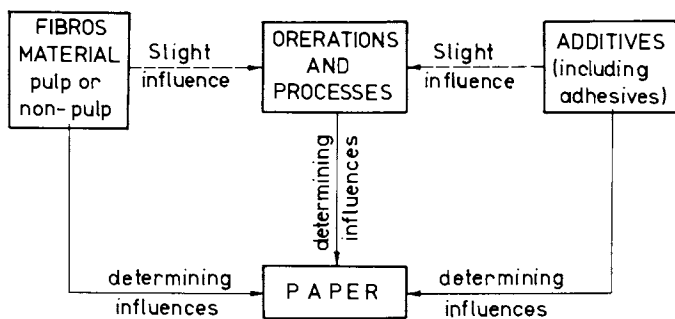
Figure 23. Diagram of the fibrous material–operations–additives–paper product interrelations
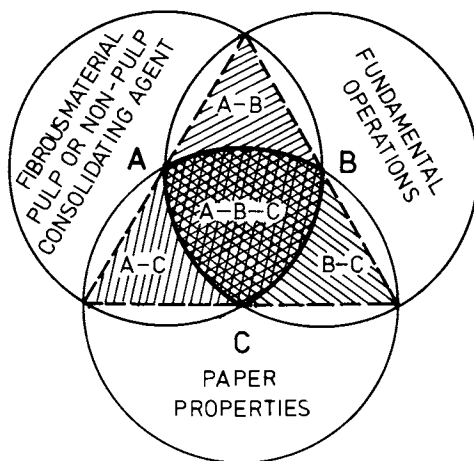
Figure 24

The diagram provides the possibility of systematically exploring the interferences of the three influencing factors.

The concern with using mixtures of chemical and pulp fibres originated firstly in the limited performances of traditional paper in some of its uses and secondly in the high cost of synthetic paper obtained from chemical fibres 100 percent. A competitive evolution of the two types may be foreseen. Economical reasons and improvement of existing technologies will exert a great influence on this evolution.

Conclusions

The interrelations of fibrous material-paper product have been consistently characterized.

The leading general concept asserts the interference of moderate influences or of determining actions resulting from the fundamental operations and the addition of additives, between the properties of the initial fibrous material and those of the final paper product. The investigation has been directed towards the fibrous material-additives-fundamental operations-paper characteristics system in the case of short fibres from annual plants pulp (reed, straw) and hardwoods. Qualitative correlations has been determined in the first place and afterwards quantitative interpretation has been given to them.

Some relations proved apt for being introduced into a mathematic model, the influencing factors enabling the optimization of paper characteristics or of the fundamental operations.

The determining influence of additives has been illustrated by use of the cation-active PPE resin. The resin modifies essentially some fundamental operations and has a direct effect on improving paper properties.

Similar interrelations have been determined in the case of artificial and synthetic polymers introduced in the composition of the pulp fibrous material.

The effects are due to the symbiosis between the properties of the paper properties of the synthetic polymers and of the natural pulp.

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3

History and Future Trend of Synthetic Paper Technology in Japan

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The brief history of Synthetic Paper or Plastic Paper in Japan is summarized as follows:
(1) Until the year of 1967 when Foamed Polystyrene or Polyethylene Sheet was developed.
(2) Until the year of 1970 when the idea of Raw Material Revolution, so to speak, centralizing the utilization of Plastic Paper or Synthetic Paper with Plastic Film Base, was embodied in the form of industrialization.
(3) Until the year of 1975 when White Plastic Sheet for Vacuum Molding, in particular, resulting from a mixture of Mineral Filler in large quantities and Synthetic Pulp, as well, was industrialized.
With the above divisional periods in mind, first of all, I would like to describe the trend mainly from the technological point of view:
Lastly, I would like to introduce the newest type of Synthetic Paper on which we are at present doing research, attempting to sound the technological trend in the future.
(1) <u>Foamed Sheet Age (Up to 1967)</u>
In the wake of Wood Pulp Paper did the second paper, viz., Non-Woven Fabrics come out. The third paper was none other than Foamed Polystyrene Sheet that made its debut in 1960. None-Woven Fabrics are mostly used instead of cloth, while Foamed Polystyrene Sheet could be used in the main for lunch boxes and other sundry items after vacuum molding, being seldom made use of as a substitute for paper.
As regards Foamed Polystyrene Sheet, several Japanese manufacturers such as SEKISUI KAGAKU CO. and KOKUSAI PULP CO. became capable of producing 500 t. - 1,000 t. per year respectively in or about the year of 1960.
This Sheet was aimed at being developed enough to replace paper in uses due partially to its pearl-like beautiful glossy

72

surface and partially to its paper-like rigidity and opaqueness characteristically.

Above all, SEKISUI had established its plant in the United States,too, reinforcing its operation there. Nevertheless, it proved to be insufficient as paper in point of strength, printability, etc., with the result that its sales amount was not as satisfactory as had been anticipated.

It was not until the year of 1960 that NIPPON ART PAPER CO.-R. & D. Division, present JAPAN SYNTHETIC PAPER CO., improved the stength and printability of this Foamed Polystyrene Sheet under the brand of "Q-Foam" of Foamed Polyethylene Sheet.

Subsequently, from 1965 through 1971 this improved type of Foamed Polyethylene Sheet had been produced and offered for sale by JAPAN SYNTHETIC PAPER CO. Then, MITSUI POLYCHEMICAL CO.'s wholly-owned subsidiary, HI-SHEET KOGYO CO. took over the production, producing 3,000 t. per year at the present time. In this connection, its physical properties are as represented by TABLE (1).

(2) Film Base Type Synthetic Paper Age(from 1967 to 1970)
It was in 1966 that JAPAN SYNTHTIC PAPER CO. announced another brand, "Q-Per", a type of Synthetic Paper with only its surface paperized by chemically treating by means of the same film as the Synthetic Paper with the brand of "Q-Kote",finally became the cynosure of all eyes not only in Japan but also all over the world what with its printability and printing effect estimated at the highest quality as printing paper.

If the cost of the biaxially oriented film could reach at 60 cents per kg. through the mass-production of 1,000 ton per month and the new tentering technology being under developing by Dr. Shoei Yazawa or Mitsubishi-Monsanto Chemical Co., the Synthetic Paper "Q-Kote"'s price would be estimated approximately 1.5 times as much as the high quality coated paper.

On the occasion of this technological development, the Japanese Science and Technology Agency in the Japanese Government was strongly convinced that Synthetic Paper would fill in the shortage of pulp for paper in Japan and contribute to development of Japan's Petrochemical Industry, too. As a Government policy, they therefore decided to promote this industry.

Encouraged by this Government policy, on the other hand, JAPAN SYNTHETIC PAPER CO. completed its production facilities for "Q-KoteQ and "Q-Per" capable of producing 3,000 t. per year in 1969 as its 1st term program. Afterward, OJI-YUKA SYNTHETIC PAPER CO. with the brand of "UPO-EF" and SEKISUI KAGAKU CO. with the brand of "Printel" respectively set up their production facilities for their products in 1971. In this regard, "Q-Kote", "Q-Per", "UPO-EF", and "Printel" are as represented in performance by TABLE(1).

Furthermore, practicality of this type of Synthetic Paper was promoted. To cite a few examples, books made only from "

"Q-Kote" and "Q-Per" were published, and some pages of a certain
leading weekly with its weekly circulation of 1,000,000 copies
were composed of this type of Synthetic Paper to say nothing of
Posters, Pamphlets and Writing Paper.

In addition to the above three(3) manufacturers nearly ten
(10) others announced Film Base Type Synthetic Paper along with
their samples.

Meanwhile, UCC, MEAD CORP.(U.S.A.) and XYLONITE CO.(U.K.)
had been developing Pigmented Film Type Synthetic Paper. For
example, the performace of MEAD CORP.'s "Acro-Art" is as repre-
sented by TABLE (1).

Simultaneously in Japan such manufacturers as CHISSO CO.
and NITTO-BOSEKI CO. had been making researches on Synthetic
Fiber or Pulp for paper, though they could not industrialize
this material.

(3) Synthetic Pulp & Highly Pigmented Type-Synthetic Paper
Age (1971 - 1975)

1. Slump in Film Base Type Demand

Development of demand for Synthetic Paper as replacement of
conventional paper has turned out to be extremely difficult
owing to Japan's economic recession on the whole, deep business
depression adversely affecting the high class paper industry in
particular, the "Dollar Shock", raises in petrochemical materials
caused by boosts in oil, etc.

The aforesaid preceding three(3) manufacturers have exterted
every effort to commercialize their products, in the hope that
the products could be applied to users even at high prices, suf÷
fering from their respective low operation.

However, in my personal estimation, their respective produc-
tion in the year of 1974 is as represented by TABLE (2)

2. Debut of Synthetic Pulp

MITSUI-ZELLERBACH CO.(JAPAN), a Joint Venture firm established
by CROWN-ZELLERBACH CO.(U.S.A.) and MITSUI PETROCHEMICAL CO.
built a plant capable of producing 500 t. per month of Synthetic
Pulp under the brand of "SWP"(Synthetic Wood Pulp) in 1973,
throwing light on the Synthetic Pulp Age.

According to the manufacturing method of Synthetic Pulp that
had been practiced until then, in the first place, plastic Poly-
mer was produced, and it was converted into fiber or pulp, though.
"SWP" was prepared by a new process, subjecting Monomer to
Polymerization and converting it into fiber simultaneously.

This Synthetic Pulp was the fruit of exceedingly epochal
technological development, resembling Wood Pulp a great deal in
both shape and quality. For some uses it cou;d blend with Wood
Pulp and be formed properly by the conventional paper machine.
"SWP" only could be subject to paper-forming, however.

As compared with conventional paper made from Woof Pulp only,
this mixture could be characteristic in performance of High Opac-
ity and Brightness, Lighter Weight, Higher Clearness, Dimension

Stability against Humidity, Heat Sealability and Emobossability.
On top of these properties, it is excellent in dehydration and
evaporation. In conclusion, addition of Synthetic Pulp is said
to enlarge the Machine Speed.

Subsequent to MITSUI-ZELLERBACH CO.'s development, HITACHI
KASEI CO., TORAY CO., etc. started developing Synthetic Pulp.
In consequence, the entire production of Synthetic Pulp is
estimated to exceed that of Film Type Synthetic Paper, as
represented by TABLE (2)during the period of 1975 and 1976.

3. Highly Pigmented Film Type

In view of the fact that the cost of Petrochemical Resin
skyrocketed, causing a boost in the price of the product, and
that the combustion furnace is apt to be damaged due to high
calorie when it be burned, several manufacturers have promptly
started to develop Highly Pigmented Film or Sheet containing
more than 60% of low-priced Inorganic Filler that could serve to
lower combustion calorie, since 1971. The largest maker of all,
LION YUSHI CO. has begun to turn out the above in its production
capacity of 10,000 t. per year. Its product under the brand of
"Kalp" is as represented in performance by TABLE (1).

Sulphur emanates from Crude Petroleum when it burns.
This sulphur could be converted into Gypsum, which could be made
in sheetings by means of Polyolefin Resin as Binder in a skillful,
but simple way.

Crude Petroleum imported into Japan contains lots of Sulfur,
and therefore it would be forcibly changed to CaSO4 in order to
prevent air pollution, just after combustion. And,Gypsum in
large quantities could be supplied to us at a low cost, as the
good filler. Probably because of imcomplete engineering in the
field of Paperization only thick sheet for Vacuum Molding has
so far been put on the market here in Japan, though, It is
expected that Paper-like Film would be produced in the near
future.

Aside from the above, Polyolefim Sheet for Vacuum Molding
containing over 60% of such Iorganic Filler as Ca CO3 and CaSO4
is at present manufactured by four(4) Japanese makers. Its density
is 1.4 - 1.6, its combustion calorie, 3,000 - 4,000 Kcal/kg.,
its thickness, 0.5 - 1mm. and it is noteworthy that it could be
deeply molded in almost the same as Clear Resin.

Such improvement of High Filler Plastic Sheet, to the best
of my knowledge, could be ascribed not merely to progress in
Technology on Treatment of Inorganic Material but to betterment
of Engineering in Mixing and Sheeting, yoo.

4. Prospects.

1. It is expected that Synthetic Pulp will be popular
with users at large.

di, In case of recovery of Scrapped Paper, or Spoilage, on the
contion that some per cent of Synthetic Pulp involved in it,
should prove not to interfere, utilization of Synthetic Paper

Table(1) Properties and Printability of each Synthetic Paper Type

Physical properties / Item	Test method	Pigment mixing ACROART (Mead Paper Co)	Surface paperizing Q-PER(QM55) (Japan Synthetic Paper Co.)	Core paperizing PRINTEL (Sekisui Chemical Co.)	Foaming Q-FOAM (Japan Synthetic Paper Co.)	Coating Q-KOAT (Japan Synthetic Paper Co.)	Comparitive tests Art paper (Nippon Kakoseishi Co.)	Highly pigmented modified KALP (Lion Yushi Co., Idemitsu Kagaku Co.)
Weight, g/m²	JIS P-8124	114	75	112	135	130	130	121
Thickness, μ	JIS P-8118	102	115	99	258	117	119	130
Density, g/m³	JIS P-8118	1.12	0.63	1.13	0.53	1.11	1.09	0.93
Whiteness, %	JIS P-8123	79	92	82	82	88	82	96
Opacity, %	JIS P-8138	92	82	94	75	97	97	97
Gloss, front, %	JIS P-8142	13	2	10	20	22	21	—
(60°~60°C) back, %	•	5	2	12	13	24	25	—
Smoothness, front, mmHg	Smoothness tester	320	620	180	185	30	170	—
back, mmHg	•	600	630	160	260	30	240	—
Tensile strength MD, kg/cm	JIS P-8113	2.7	3.2	1.7	2.7	5.3	8.5	3.5
CD, kg/cm	•	2.7	3.5	1.1	1.7	7.4	6.4	0.4
Elongation MD, %	JIS P-8132	630	21	20	580	19	1.8	31
CD, %	•	410	36	2	75	20	4.5	38
Tearing strength MD, g	JIS P-8116	190	28	32	110	79	60	22
CD, g	•	—	25	32	360	49	59	—
Ink luster(indigo), %	JIS P-8142	25	7	27	21	54	36	—
Ink depositing	—	◎	○	◎	◎	◎	◎	—
Ink absorption	—	×	◎	○	○	◎	◎	—
Ink transfer	—	○	○	○	○	◎	◎	—
Ink setting time, min.	—	120	10	75	—	35	60	—

TABLE (2)   PRODUCTION in 1974

MANUFACTURER	PRODUCTION CAPACITY (ton/month)	ACTUAL PRODUCTION (ton/month)	CONSUMPTION FOR PRINTING (t/m)(%)	BRAND	RESIN
SEKISUI KAGAKU	500	200	160 (80)	Printel	PS, PE, PVC
OJI-YUKA	500	150	135 (90)	Yupo FP	PP
MITSUBISHI RAYON	350	100	80 (80)	Miraynart	PE
NISSHIN BOSEKI	50	40	32 (80)		PS, PVC
TOYO TOUGHPER	200 (500)	100	60 (60)	Toughper	PP, PE
OTHERS	30	20	10 (50)		

PS = Polystyrene
PVC = Polyvinyl Chloride
PE = Polyethylene
PP = Polypropyrene

might increase by leaps and bounds from now on. This is because
its mixture with Wood Pulp would be expected to exceed in point
of productivity and commercial value the difference in price
between Synthetic Pulp and Wood Pulp insofar as its effect is
concerned.

2. It is understood that Nonpolymer Syntheic Paper will make
its debut in a few years.

We doubt if Paper which contains, for instance, more than
70% of Inorganic Material would be called Synthetic Paper. We
regard use of Mineral in large quantities being found in abun-
dance and causing less pollution instead of Wood Pulp as the
same purpose of developing Synthetic Paper.

As a matter of fact, we have been doing research under the
theme of "Inorganic Paper" for some years. We are of the view
that development of this "Inorganic Paper or Nonpolymer Paper"
could be made in the following four (4) ways:

a. Pigmented Film Type

To start with, we could think of improving LION-YUSHI CO.'s
"Kalp". We presume that there would be much demand for this
type of paper provided its process cost and performance for
printing and wrapping paper, when made thin, would prove to be
satisfactory.

For instance, there is much possibility that its Composite
Structure by a combination of Split Yarn piled up crosswise
would be commercialized.

b. Clay Coated Type

In case of conventional Clay Coated Paper, High-Grade White
Paper is in use for its Substrate. This is because its Coating
Layer is not thick enough, and its Covering Power is small.

Should we succeed in selecting and combining Inorganic
Filler and Binder serving to increase, Covering Power and Stiff-
ness in the Coating Layer and in developing Process Engineering
capable of uniforming Heavy Coating at a low cost, we could make
its Substrate Paper or plastic films thinner, or use Fiber (
Whisker), as mentioned later, as Substrate being rich in inorganic
Filler. Needless to say, if we should make use of such thin
Biaxially Orientated Film as "Q-Kote" in the same case, we
would be able to turn out the Highest-Grade Printing Paper
superior in smoothness.

c. Mineral Fiber Type

A type of paper, composed of Glass Fiber and Wood Pulp in
mixture and formed by machine, is practically put to use in the
field where Dimension Stability against humidity is required.
Instead of Glass Fiber, we should think of making use of Mineral
Fiber available at a lower cost and having the particular
qualities of paper,too, either by itself or by Mixed Forming
with Wood Pulp.

It is notable that the way of recovering Gypsum (Ca SO_4)
against Lime (Ca CO_3) out of SO_2 Gas in the smoke when Heavy

Petroleum is burnt is forcibly carried out in Japan for preven-
tion of Air Pollution. What with control of reaction valocity in
this Gypsum manufacturing process and addition of Catalyzer for
crystallizatio μ, there would be available alpha-Type-CaSO4 1/2H2O,
about 10 micron in diameter and 100 - 150 micron in length, in
the form of Needle-Shaped Crystal. When burnt in 200 - 800 C,
the Crystal would remain nearly unchanged in shape and intact and
be transferred to II-Type Ca SO4, when it would be less soluble
in water and stabilized. This technical know-how is the fruit
of the recent development at Hyogo Prefectural Industrial Re-
search Laboratory in Japan. It is reported in this connection
that they made a type of paper by mixing this material with 10-
25% of Wood Pulp, and that Water Separation proved to be good
in paper-forming on the wire-screen, and that only less than 10%
of the Used Gypsum weight dropped out through the screen, with
the result that the obtained sheet was as soft and the same
in touch as ordinary paper.

We could clearly see through the Electro-Microscope that
a lot of Gypsum Fiber (Whisker) stuck in the long Wood Pulp.
Becoming aware of the fact that it might cause some trouble in
the form of powder, but if changed to Whisker no matter how
narrow and short it might be, it would serve to put an end to
such trouble. In my opinion, this fact would contribute a great
deal to development of Non-Polymer Synthetic Paper.

d. <u>Type of Forming by Absorption of Powder on the Surface of
   Pulp Fiber</u>

In a nutshell, all Non-Polymer Powder should be absorbed or
adhered mainly by Zeta (ζ) potential force to the surface of
each wood pulp fiber and subsequently it could be formed by
paper machine without trouble caused by powder leakage through
the screen even though wood pulp content might be less than 10%
in weight.

The aforesaid Gypsum could be formed by this method, as well,
but in order to have the powder fixed on the fiber after it dries
up, Hot Pressing with the help of Synthetic Pulp, or Resin Coat-
ing on the surface would be required. This method also would
be effectively applied to the formation of the aforesaid Gypsum
Whisker. Not only Gypsum but also nearly every other kind of
Mineral, Polymer, etc can be absorbed on the surface of Wood
Pulp, and formed by Paper Machine.

Moreover, as an example of its application, in case Clay for
Ceramic Tile be changed into green sheets containing about 10%
pulp in weight by this method, and burned in 1250°C, 10% of Wood
Pulp would vaporize in CO2 and H2O, and be of the same quality as
that of Ceramic Tile made in the conventional process.

Accordingly, we have recently announced at a meeting of the
Ceramic Society in Japan that this Method would facilitate the
Manufacture of the Large-Sized Thin Tile.

ABSTRACT:

In the event that we forecast the technological trend of
Synthetic Paper in the future, judging from what has so far
brought about its development, we cannot help but assert that
Synthetic Pulp will enter much acceleratively into the field of
Wood Pulp, in line with development of the technical know-how
on much use of such materials as Non-Polymer Powder, Fiber, and
Whisker on or in each type of Synthetic Paper brought to light
heretofore.

4

Efforts in Latin America to Develop or Adapt Technology for the Production of Newsprint from Typical, Regional Cellulosic Raw Materials

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Introduction and Scope

The trend towards growing imports of pulp, paper
and forest products in Latin America has been a source
of ever-increasing concern to the regional paper indus-
try, as well as to local governments. Particular in-
terest has been focussed on newsprint, as it repre-
sents about a third of these imports to the mentioned
area. In other words, newsprint constitutes the main
deficiency in production of the Latin American pulp
and paper industry. Solving this problem of newsprint
supply from within Latin America has captured the in-
terest, not only of the regional paper industry and
governments, but also of international organisms and
other organizations as well.

In the Regional Consultation on Pulp and Paper
for Latin America, organized in May of 1970 by FAO,
ECLA and UNIDO, in combination with the 10th Annual
Convention of ATCP, FAO presented a secretariat paper,
analyzing the possibilities of developing the news-
print industry in Latin America. At this Regional
Consultation, it was pointed out that Latin America
possesses extensive cellulosic resources, close to a
fourth of the world's forest area, but that, neverthe-
less, it is a net importer of pulp, paper and forest
products. The importance of newsprint as a source of
deficit was again emphasized.

Latin American newsprint consumption at that time
was estimated by FAO at 1.06 million metric tons per
year, the local production being slightly over 300,000
metric tons per year, leaving close to 760,000 tons

per year to be imported, which represented around 72%
of the regional demand for this commodity.

Newsprint production capacity in Latin America,
according to FAO, was concentrated in 1970 in four
countries, as follows:

Argentina	20,000 tons	(1 mill)
Brazil	127,000 tons	(1 mill)
Chile	131,000 tons	(2 mills)
Mexico	50,000 tons	(1 mill)
TOTAL	328,000 tons	

It should be pointed out that although FAO assign-
ed 20,000 MT/Y of newsprint capacity to Argentina, the
Canadian Pulp and Paper Association does not register
any newsprint production in this country for 1970 or
any subsequent year.

Low newsprint prices prevailing at that time,
combined with what was defined at the mentioned Region-
al Consultation as "unfair commercial practices",
frequently adopted by exporting countries, did not
stimulate growth of the existing newsprint mills in
Latin America, and this, in turn, could only result in
increasing imports of this product, unless a decided
effort could be carried out to develop this industry,
based on the efficient use of local resources.

In view of this situation, FAO dedicated consid-
erable effort to evaluating the potential of projects
for new newsprint mills that were under study or being
contemplated at that time, as well as looking care-
fully into the resources available for this purpose.

One of the first conclusions that was reached in
this study was the obvious lack of traditional or con-
ventional raw materials for newsprint manufacture,
particularly spruce and balsam, which are the usual
species used in Scandinavia and some other areas for
this purpose. In other words, there was no availabil-
ity whatsoever of low resin conifers, on the one hand,
and, on the other, there existed a wide variety of
resources from Mexico all the way down to Argentina,
Brazil and Chile, varying from natural coniferous for-
ests of high resin content to a great variety of broad
leafed species, plantation pines and sugar cane
bagasse.

However, in the analysis of this situation, FAO

was not too optimistic regarding the technical feasi-
bility of many projects, nor of the quality or cost of
newsprint obtainable from the rich abundance of fiber
resources available, most of which were classified by
FAO as "secondary fibers". Hence, FAO recommended
considerable caution regarding the implementation of
new projects, emphasizing the convenience of develop-
ing plantations of more conventional species, particu-
larly spruce and balsam, classified as "primary
fibers".

Representatives from many of the Latin American
countries were not in agreement with the opinions ex-
pressed by FAO, particularly regarding the priority
assigned to developing the supply of more conventional
species of conifers, as it was felt that decided em-
phasis should be given to the use of local resources,
which should not be classified as "secondary fibers",
but rather as alternate fibers, in any case. This
reasoning was based on the ever-increasing effort to
develop adequate technology within Latin America,
which would permit the efficient use of local cellulo-
sic resources for the production of a wide variety of
pulp and paper grades, including, of course, newsprint.
This effort has resulted in a marked growth of the
pulp and paper industry in several of the Latin Ameri-
can countries, which it is hoped will stimulate in-
creased efforts in further development work, not only
in these countries, but also in others of the region
that have had to face more problems or limitations in
this respect.

ATCP, which is the technical association of the
Mexican pulp and paper industry, feels that the men-
tioned effort has considerable merit and in June of
1975 organized the First Latin American Pulp and Paper
Week, in conjunction with its Fifteenth Annual Conven-
tion, having in mind the following objectives:

1) To present examples of some of the main tech-
nological development efforts in Latin America, with
the expectation that the results obtained so far would
lead to a better understanding of the problems of re-
search and development and, of course, to stimulating
increased efforts in this field; and

2) To bring together representatives of industry,
research centers, international organisms, financial

institutions and government to present and discuss the
situation and problems of the regional paper industry,
as well as its possibilities for growth on the basis
of increasing technological interchange and collabora-
tion.

To this end, ATCP selected what was felt to be
outstanding examples of the mentioned development ef-
fort and obtained the collaboration of many distin-
guished authorities in this field to present the re-
sults of their work at the mentioned Latin American
Pulp and Paper Week, held in Mexico City in June 1975.

The present paper is, then, a summary of those
presentations made during said week, with specific
reference to newsprint manufacture, complemented with
additional information to give a more complete picture
of the newsprint situation in Latin America.

However, on doing this, full recognition is given
to the authors of the mentioned presentations. It is
not the intention of ATCP to infringe in any way on
the rights of these authors. Rather, as mentioned,
the objective is only to summarize the main efforts re-
garding newsprint production and give a picture of the
present situation in this field in Latin America.

Specifically, cases on newsprint manufacture from
the following fibrous resources are summarized:
     1) Pinus Radiata plantations in Chile.
     2) Natural coniferous forests in Mexico.
     3) Eucalyptus plantations in Brazil.
     4) Willow and poplar plantations in Argentina.
     5) Sugar case bagasse in Mexico and Peru.
Reference is also made to a de-inking plant which is
presently under construction in Mexico, based on tech-
nology developed in the U.S.

The present paper, therefore, constitutes a sum-
mary of the effort behind the newsprint mills in
Latin America, either in operation or presently under
construction. It does not pretend to cover all the
efforts in this field, but only those mentioned, al-
though reference is also made to several projects now
under serious consideration in order to give as com-
plete a picture as possible.

Newsprint from Pinus Radiata Plantations (Chile)

Newsprint production in Latin America was first
started in Chile around 1936, but it was not until
1957 that they entered this field on a sustained basis
with the production of one paper machine. In 1964
another newsprint machine was put into operation bring-
ing the installed capacity up to 144,000 MT/y.

Said capacity was considerably greater than the
local demand for newsprint, which forced the Chilean
mills to look towards other markets in Latin America.
Exporting to other countries, even in Latin America,
was certainly not an easy task, but little by little
exports were increased, based on competitive prices
and quality, to the point where Chile now exports most
of the newsprint manufactured in the country.

One of the key factors behind the entrance of
Chile into the newsprint market, both local as well as
export, was the development of extensive Pinus radiata
plantations, which constituted an important and econom-
ic source of good quality wood, as required for
groundwood production. The story behind this develop-
ment is, indeed, an interesting one.

A basic factor was the fact that Chile possesses
very particular climatic and soil conditions, which
proved to be extremely favorable for the growth of
certain species of conifers, especially Pinus radiata.
These conditions, together with favorable legislation,
led to an extensive forestation program which today
covers close to 350,000 hectares with the following
distribution:

Region	Forested Area (Ha)
Valparaiso	10,500
Maule	75,000
Bio-Bio	236,000
Valdivia	25,000
TOTAL	346,500

As can be seen, these plantations have been con-
centrated mainly in the Province of Bio-Bio, where
the most favorable conditions exist. In fact, recent
studies in the eastern side of the Nahuelbuta Moun-
tains of Bio-Bio have shown that this area has the
most favorable growth conditions for Pinus radiata in

all of the country. Growth rates reach as high as
26 m^3/Ha/y or even more in this area for trees between
21 and 25 years of age, as compared to half this fig-
ure for some other areas. Growth rates in the men-
tioned area can be better appreciated from the fol-
lowing information.

Age (yr.)	Height (M)	Density (Trees/Ha)	Volume(M^3/Ha)
10	17	1,500	180
15	22	1,300	350
20	26	1,080	510
25	28	900	650

Forestry legislation in the country has been
gradually improved over the years so as to protect and
promote Pinus radiata plantations as much as possible
and to take the best advantage possible of the favor-
able situation that prevails in Chile for development
of the pulp and paper industry. Under these circum-
stances it is expected that 80,000 hectares of new
forests will soon be added to those already indicated.

As previously mentioned, newsprint is produced on
two paper machines in Chile, one operated by Compania
Manufacturera de Papeles y Cartones, S.A. (CMPC), lo-
cated in Bio-Bio and the other by Industrias Foresta-
les, S. A. (INFORSA), located in Nacimiento. The
CMPC machine was supplied by Voith of Germany. It has
a 505 cm. wire and operates with an overall efficiency
of 85% at 625 meters per minute. The INFORSA machine
also operates at 85% efficiency but runs at 762 MPM.
It is a John Ingles-Dominion machine, having a 551 cm.
wire.

The combined groundwood capacity installed at
these two mills is around 130,000 MT/y. The CMPC mill
has 9 Voith grinders, consuming 11,600 KW, while the
INFORSA mill has 6 Koehring-Waterous Great Northern
grinders, requiring 16,500 KW. Most of these grinders
use 67 inch by 54 inch stones.

CPMC uses semi-bleached kraft pulp as its rein-
forcing stock, which is produced at its modern complex
of Laja. Unbleached sodium sulphite pulp is used by
INFORSA. However, this last company has been care-
fully studying the high yield sodium bisulphite proc-
ess with very encouraging results. In all probability
future expansions in this area by INFORSA will be made

based on this process.

Considerable effort has gone into establishing the most favorable conditions for groundwood production from Pinus radiata. Careful consideration was given to such factors as stone properties, sharpening cycles, etc. The result of this effort has been a good quality groundwood, as can be appreciated from the following comparison with a typical Scandinavian groundwood.

Fiber Classification (Bauer-McNett)	P. Radiata	P. Abies
28	14	17
28-48	25	16
48-100	21	19
100-200	13	13
200	27	35
CSF	105	100
Breaking Length, Km.	2.8	2.5
Tear Factor	52	40
Stretch, %	2.0	1.9
Brightness, Elrepho	60	62
Scattering Coef. $Cm^2/Gr.$	630	700

From the above figures, it can be seen that Pinus radiata groundwood has excellent strength properties, as compare with Picea abies groundwood from Scandinavia, but optical properties are somewhat lower.

Considerable effort has also gone into such areas as chemical pulping, stock preparation and papermaking so as to obtain the most favorable paper properties, with the lowest requirement of chemical pulp. INFORSA presently uses about 22% of sulphite pulp, while CMPC uses 17% of semi-bleached kraft with a breaking energy of 0.35 Kg-Cm/Gr. and 0.38 Kg-Cm/Gr of the wet sheet, respectively.

Operating efficiencies of the two newsprint machines in Chile compare well with machines of Scandinavia of more or less the same date of installation. This reflects the tremendous overall effort that has gone into all aspects of newsprint production in Chile so as to take advantage of the favorable wood growing conditions prevailing in the country and, thus, consolidate their position in Latin America as a supplier of this commodity. Future expansions, particularly

that considered by INFORSA, will undoubtedly improve
efficiencies and costs and further enhance Chile's
position in the Latin American market.

Newsprint from Natural Coniferous Forests (Mexico)

Newsprint production in Mexico was first consid-
ered on the basis of utilizing the natural coniferous
forests. In 1952 a feasibility study was carried out
which eventually led to the establishment in 1960 of
the first newsprint mill in Mexico by the government.
This mill was established close to the town of Tuxte-
pec, in the State of Oaxaca, at the junction of the
Valle Nacional and Santo Domingo Rivers, which togeth-
er form the Papaloapan River.

Wood from the near by Sierras, which separate the
Papaloapan River Basin on the Gulf side from the Paci-
fic coast, is brought to the Tuxtepec Mill, partly by
the road which leads over these mountains to the City
of Oaxaca on the Pacific side and partly by railroad
through a roundabout route.

It should be kept in mind that these are natural
or cloud forests with trees of mixed species and ages
of up to 300 years, the predominating species being
Pinus patula, Ceodustrobus oaxacana, Ocarpa and
Ayacaguite.

In fact, there are very few plantation forests in
Mexico. At these latitudes, conifers grow spontane-
ously on the sides and tops of the mountains at 1800
meters and above, where they find the natural moisture
and other conditions needed for their development.
These natural forests can be found as far south as
Honduras and Nicaragua and then completely disappear
and do not reappear in South America. The coniferous
forests in South America are practically all planta-
tion forests.

These natural forests were first used in Mexico
for pulp and paper production by the mills located a-
round Mexico City, and it was only natural that they
were the resource for the supply of raw material for
the first newsprint mill. However, the production of
groundwood from these trees posed very serious problems,
among other things due to the high resin content as
well as the very large percentage of dark heartwood

present, especially in the older trees.

Additionally, due to the forest situation, the
Tuxtepec Mill was forced from the very beginning to
use wood that was cut and debarked in the forest. Un-
fortunately, a good part of the moisture was lost dur-
ing transportation, and this, of course, constituted
another source of problems.

However, technical assistance was obtained in the
early years from a mill in Texas, Southland Paper
Mills, Inc., which had developed considerable experi-
ence in producing groundwood from southern pine trees
which also have a high resin content. Problems owing
to the high resin content were overcome to a consider-
able degree using caustic soda and alum in the shower
water of the grinders. Nevertheless, considerable at-
tention and effort was devoted to the stones used, un-
til the optimum combination of grain, porosity and
hardness was found which allowed obtaining the best
properties of the groundwood and of the final sheet.
However, the use of caustic soda led to foam problems
for which adequate solutions had to be found.

Furthermore, the large percentage of dark heart-
wood resulted in low brightness of the groundwood,
which inevitably required bleaching to bring the
brightness up from around 50% to 58%. Zinc hydrosul-
phide is used for this purpose.

The original capacity was 30,000 MT/Y, which was
reached after two or three years of operation, basical-
ly with four ring-type grinders and one paper machine.
No chemical pulp facilities were or have been install-
ed. Between 18% to 22% semi-bleached kraft is requir-
ed. This pulp is obtained locally or imported.

Around 1964, capacity was increased to about
45,000 MT/Y, adding on two more grinders, a disc re-
finer for the rejects, a poor-man pick up for the pa-
per machine and more dryers, plus other equipment and
modifications. Later on two ponds were installed to
keep the wood from losing additional moisture, and a
decculator was also installed. A converflo type head-
box was put on the paper machine, which helped consid-
erably in improving the moisture profile. These and
other modifications allowed reaching a production of
56,500 MT in 1974. In late 1975 a new expansion was
started up, involving basically chip groundwood

facilities, plus further paper machine modifications,
which is expected to bring the newsprint capacity of
this mill up to 70,000 MT/Y.

　　After fifteen years of operation, considerable
experience has been built up in this mill in process-
ing wood from natural coniferous forests in Mexico for
the production of groundwood and newsprint, under spe-
cial conditions not found in the main newsprint manu-
facturing countries. This experience could be of con-
siderable value to other areas, either in Mexico or in
Central America, where quite similar conditions can be
found.

　　Future expansions of this mill are presently un-
der study, based on sugar cane bagasse which is quite
abundant in the Papaloapan River Basin, as well as
plantation pines. This company has also been studying
several fast growing pines with the idea of developing
large-scale plantations closer to the mill. After
several years of effort, 4500 hectares have been
planted, containing close to 9 million trees. The
main species selected for this purpose are Pinus trop-
icalus, Pinus caribaea and Ocarpa.

　　In accordance with this forestation program, the
company expects to reach 15,000 hectares in the next 3
or 4 years. The yields as well as the time required
for cutting are expected to improve dramatically. The
present yield in the natural forest is about 1 M^3/Ha,
and 25 years are required for cutting. With the new
species, this time should be between 10 and 12 years,
and the yield will be considerably higher than that
which is presently being achieved.

Newsprint from Eucalyptus (Brazil)

　　Quite a lot has been written in the past few
years about Brazil as the new frontier of the pulp and
paper industry, and not very much can be added in this
respect. The tremendous forestation program underway,
together with an extremely favorable investment climate,
has drawn the attention of many countries, including
the U.S., Canada, Japan and others. Besides, many
large multi-national paper companies have already been
operating in Brazil with considerable success.

　　Just to give some idea of the tremendous

potential involved, estimates have been made which in-
dicate that about 3.5 million hectares of plantation
forests should be reached by 1987 at the present rate
of forestation. Considering an average yield of 20
M^3/Ha., for both Eucalyptus and Pine, the production
of wood should reach about 70 million M^3/year by 1987,
which is, indeed, a considerable figure.

The interesting thing is that this forestation
program covers many areas and species, not just Euca-
lyptus and Parana Pine, which have drawn more atten-
tion, but also Southern Pine, such as Pinus elloiotti
and taede and Tropical Pines, among others, Pinus ca-
ribaea and cocarpa.

In mentioning this tremendous forestation effort
going on in Brazil, reference must be made to the Jari
Project, one of the most daring developments that can
be found in any country, covering such aspects as in-
fra-structure, agriculture, animal husbandry and, of
course, forestry. The Project is located in the Jari
River area of the lower Amazon basin. With regards to
the forestry effort, very ambitious studies are being
carried out to appraise the possibility and conven-
ience of clearing present tropical species and replac-
ing them with fast growing species, like Pinus cariba-
ea and Gmelina arborea. The project covers a total
area of about 80,000 hectares and has been approved by
the SUDAM government department. However, it will take
about 25 years to reach any conclusions about the
health of third generation trees and the general effect
of the program on the regional ecology.

Attention was first drawn to Brazil from the
point of view of pulp and paper as a result of the
rapid development of Eucalyptus plantations, their
tremendous growth potential and the surprising a-
chievements derived from the resulting pulp, i.e., ex-
cellent quality writing and printing paper from 100%
Eucalyptus stock.

The first Eucalyptus plantations in Brazil were
made in the State of Sao Paulo by Edmundo Navarro de
Andrade in 1904 with the idea of obtaining fuel and
sleepers for the railroads. Close to a hundred
species were introduced from Australia, and, as a re-
sult, not many years later Eucalyptus plantations were
successfully established in various regions of the

country.

It did not take long to make the jump from fuel
and sleepers to pulp and paper. The next step was the
combined use of Eucalyptus and Parana Pine for the
production of newsprint, which had been started by the
Klabine organization around 1946, based on Parana Pine.
Today this organization uses up to 55% Eucalyptus
chemi-groundwood in the newsprint furnish of their
Monte Alegre mill (Industrias Klabin do Parana de
Celulose, S.A.) the rest being a mixture of groundwood
and long fibred pulp from Parana Pine.

The story behind this development is well worth-
while looking into, as Klabin has been one of the
pioneering groups behind the development of Eucalyptus
pulping technology in Brazil. The main motive for us-
ing Eucalyptus for newsprint stems from the interest
in replacing, at least partially, groundwood from
Parana Pine, which has a harvesting cycle of over 25
years, as compared to less than a third for Eucalyptus.

This partial replacement of Parana Pine with Eu-
calyptus, not only leads to lower costs, but also to a
better utilization of the mentioned pine resources,
the availability of which has been decreasing.

However, groundwood and even high yield semi-chem-
ical pulp production from plantation Eucalyptus species
poses special problems, as compared to the situation
in Australia, where natural Eucalyptus forests having
trees up to 400 years old have been successfully used
for newsprint manufacture for many years.

The use of Eucalyptus for newsprint production in
Brazil dates back to 1954 when a laboratory investiga-
tion program was started aimed at producing chemi-
groundwood by the cold soda method from local species
(Salegna and Alba). These studies were continued
through 1958 when a pilot plant was set up on a semi-
commercial basis, which eventually led to the instal-
lation in 1965 of the first full-scale operation hav-
ing a capacity of 220 tons per day. This unit is
still in operation today.

One of the key aspects involved was developing an
adequate impregnation stage. Impregnation with and
without pressure was studied, as well as temperature,
chemical concentration and other factors, until the
optimum set of conditions was finally established.

Depending on the conditions of the wood, soda concen-
tration was varied between 40 and 120 gr./lt., temper-
ature between 40 and 80° C and impregnation time be-
tween 30 and 45 hours.

    After impregnation under the mentioned conditions,
defibration could be carried out in a stone grinder,
yielding an adequate quality groundwood, together with
a low rate of rejects, i.e., about 1%.

    Impregnation conditions have to be adjusted to
the varying properties of the incoming wood, taking
into consideration, among other things, species, age,
diameter, density, moisture content and brightness.
Additionally, stone properties have to be closely con-
trolled so as to obtain the best combination of
groundwood properties. This requires carefully watch-
ing the sharpening procedures and cycles, as well as
the stone properties. With proper control of impreg-
nation and grinding conditions, power requirements for
grinding can be reduced to 0.85 KW/KG of commercial
Eucalyptus chemi-groundwood, as compared to 1.43 KW/KG
of conventional, commercial Parana Pine groundwood,
with 50% less rejects.

    As a result of the impregnation, a two-stage
washing operation is required, whereby the pH of the
chemi-groundwood is brought down from a level of 9.5
to 10.5 to within 6.0 to 6.5.

    Single stage bleaching, as presently applied us-
ing zinc hydrosulphide as the bleaching agent, gives a
brightness increment of 6° to 7° GE, which is suffi-
cient for local newsprint requirements when the initial
brightness of the chemi-groundwood is between 47° to
50° GE.

    Bleaching conditions are reported as follows:
        Temperature   60-70° C
        Retention Time   60-90 minutes
        Initial pH   6.0 - 6.5
        Consistency   4%

    However, initial brightness levels can drop as
low as 43° GE and for this reason a bleaching sequence
using hydrogen peroxide in the first stage and zinc
hydrosulphide in the second has been successfully
studied, which ensures a final brightness of 60° GE.

    The final cost of the Eucalyptus chemi-groundwood
is reported by the Klabine group to be around 30%

lower than that of Parana Pine groundwood, even con-
sidering the bleaching chemicals. This has led to an
 increasing use of Eucalyptus chemi-groundwood in the
newsprint furnish, reaching levels of up to 55%, with
quite satisfactory strength properties, combined with
good brightness (58-61°GE) and opacity (92-94%).

        Further studies are being made regarding the use
of Eucalyptus for the production of bleached sulphite
pulp, and tests in this connection show that 30% long
fibered pulp can be replaced by Eucalyptus without any
appreciable effect on the quality of the final sheet.
Kraft pulping of a mixture of wood chips from 70% pine
and 30% Eucalyptus also shows considerable promise.

        It can be safely concluded that the use of plan-
tation Eucalyptus species has been definitely estab-
lished for newsprint production in Brazil, both from a
technical as well as an economical point of view, and
that the use of these species for the mentioned pur-
pose has allowed reaching a more efficient use of the
local wood resources available.

Newsprint from Willow and Poplar (Argentina)

        Once again, another very interesting situation can
be found in Latin America for pulp and paper develop-
ment. As in the case of Pinus radiata in Chile and
Eucalyptus in Brazil, the Parana River Delta in Argen-
tina possesses very favourable soil and climatic con-
ditions for the growth of willow and poplar.

        These conditions, plus other factors, such as
favourable government tax exemption policies and spe-
cial import duties on pulp, paper and forest products
from countries not pertaining to the Latin American
Free Trade Association, combined to promote the devel-
opment of extensive forest resources of willow and
poplar in the mentioned Delta area.

        This region contains a forestable area of not
less than one million hectares, which is not presently
subject to extensive agriculture, cattle raising or
any other important utilization. Under the prevailing
legislation, the forestation program in this area has
already covered 110,000 hectares with willow and poplar
species obtained originally from the U.S. and Europe,
constituting one of the most important forestation

program with said species that can be found anywhere.

This program has been integrated with a national forestation program, in combination with the National Forestry Institute which includes long fibered species (pines), as well as willow and poplar and some other species.

According to said program, 60% of the plantations will be made of conifers and will be concentrated in the province of Missiones and part in Entre Rios. About 20% will be devoted to further developing the willow and poplar plantations of the Delta area, and the remaining 20% will cover other regions of the country, based on various species.

Of the species planted in the Parana River Delta, 83% correspond to willow and 17% to poplar. Willow is generally planted in the low lands subject to frequent flooding and even in the marshy areas of the Delta Islands, while the poplar species have been planted on the higher lands and coastal regions of these islands.

The following average yields has been calculated for these species: Willow: 16 m^3/HA/Year, including bark, yielding 12.9 metric tons of wood. Poplar: 19 m^3/HA/Year, including bark, yielding 15 metric tons of wood.

By 1968, an excess of 120,000 m^3 per year of wood was available in this region that could not be absorbed by the relatively small local lumber operations. This fact together with the increasing deficit of newsprint in the country gave birth to the newsprint drive, which finally led to the establishment of Papel Prensa, S.A. and the implementation of one of the most interesting pulp and paper projects that can be found today.

A key aspect in this development effort was constituted by Law 18.312 and Decree 4,000, outlining a national program for the development of an internal supply of newsprint.

The first step in this program was the execution of a number of economic and technical studies and surveys which, in turn, allowed establishing basic parameters for a step-wise development program, that included, of course, research into the particular processing conditions required for the production of a suitable groundwood type pulp from the wood available in the Delta.

As required by Argentina legislation, consulting
and investing groups were constituted to organize and
supervise the work program that was required. Both
these groups were selected by the government in 1971
on a bid basis, the Papel Prensa group having been
selected as the investor and Proinpa as the consultant.
In 1972, the government authorized the installation of
the first newsprint manufacturing unit of 100,000 MT/Y
capacity by Papel Prensa, S. A., conditioned to the
satisfactory completion of all the studies and tests
required.

This unit was authorized as the first part of a
three-stage program, involving two additional units of
100,000 MT/Y capacity each, which would be licensed or
authorized by the government, also on a bid basis, ac-
cording to the development of the market and other
factors.

The technical studies were entrusted to the Cen-
tro de Investigacion de Celulosa y Papel (CICELPA),
pertaining to the Instituto Nacional de Ciencia Indus-
trial. The mentioned research center began to look
into the process that could be used in converting the
wood available in the Delta into a groundwood pulp
suitable for newsprint production. Stone grinding
procedures were discarded at an early stage due to the
wood properties, and a chip grinding process was se-
lected. Many trials were carried out and the need of
a chemical pre-treatment was definitely established.
The conditions and chemicals for this pretreatment were
also studied.

As required by the government, pilot and commer-
cial trials had to be carried out. The assistance of
several technical and equipment manufacturing groups
in Finland was obtained for this purpose, and tests
were carried out on a pilot, as well as a commercial
scale, using the facilities of the KESKUS Laboratories,
OY (Central Pulp and Paper Laboratories), Tapiola,
Helsinki and the ENSO-VALMET paper machine installation
at Imatra, Finland.

For these trials, wood was ocean freighted to
Finland and processed under the studied conditions,
and the newsprint was produced on the mentioned ENSO-
VALMET Fourdrinier machine, using 80% chemi-groundwood
from willow and poplar and 20% coniferous semi-bleached

kraft.

This kraft pulp was obtained from Chile since the
project is envisaged, at least in the first stage,
without any chemical pulp production, the long fibered
pulp requirements to be imported from Chile.

Successful pilot-scale runs were made with only
15% chemical pulp, but 20% has been considered for com-
mercial-scale production to be on the safe side.

The paper produced in the commercial run was
printed on high speed presses in both Finland and Ar-
gentina with very good results. Excellent printing
properties were obtained, and the runnability of the
sheet in the presses was also good.

The key to reaching these results was, then, the
proper processing of the wood to obtain an adequate
quality groundwood type pulp. In essence, the proc-
ess involves a pre-treatment of the chips with soda
(NaOH) and sodium sulphite (Na_2SO_3). About an hour of
impregnation with said chemicals is required at 90° C.
Chemical consumption averages around 25 kg. of caustic
and 30 kg. of sulphite per ton of wood, and the yield
is reported at 90%. However, chemical consumption is
varied according to the variation of the properties of
the wood. Impregnation is followed by two-stage refin-
ing. No bleaching is required, and the brightness of
the final sheet is reported at 60% and above.

Based on these results, the government granted in
October 1972 final authorization to Papel Prensa to
proceed with the implementation of the project. engi-
neering for the mill was started, and the equipment
supply was contracted from Finland. Construction has
now been completed. The first stage will cover one
Foudrinier paper machine, plus the chemi-groundwood e-
quipment and auxiliary services required. The capac-
ity will be 100,000 MT/Y, as mentioned.

The pulp mill equipment includes basically a con-
tinuous M and D Bauer type inclined digestor, with a
heat exchanger for the liquor; two impressafiners to
remove excess liquor; four double disc refiners in
the first stage and two in the second stage, operating
at 25) inlet consistency in the first stage and the
necessary screening equipment (pressure screens and
centricleaners). The screened pulp will be thickened
on deckers and then stored in high density chests. A

refiner is included for the rejects.

Outdoor chip storage will be used, the effects of this storage having been studied by CICELPA, with favorable results.

The paper machine is a Valmet standard Foudrinier with a 7.70 M. trim, designed to reach a speed of 850 M/Min. Moisture content, basis weight and thickness will be computer controlled.

In 1974, Papel Prensa acquired 20,000 hectares in the neighboring province of Entre Rios and has been developing new hybrid clones, which have been under evaluation by CICELPA. The objective in mind has been the selection of the most favorable clones from the point of view of both forestry as well as pulping and papermaking. The results so far indicate that wood yields can be sharply increased, maintaining good pulp properties, particularly tear, breaking length and brightness.

The main species or hybrids planted so far in this new development program by Papel Prensa are sauce americano and species 131-25 and 131-27. Up to 2000 trees per hectare have been planted and cutting can be staggered every 10 years, with wood yields as high as 120 tons per hectare.

The design of the mill takes into consideration a future expansion that would double the capacity by adding on a second module. In fact, Papel Prensa has already presented a bid to the government for said purpose and may be granted authorization to install a second paper machine and the corresponding pulp equipment and auxiliary services. This expansion program seems quite logical in view of the considerable technological development behind the project and the tremendous wood potential of the area.

Furthermore, the development of pine plantations in the province of Missiones should give additional support to the project, as the need for importing the long fibered pulp requirements could be eliminated.

Besides, further research into processing will be continued, and any expansion of the mill will certainly take into consideration new developments, including thermo-mechanical pulping as applied to the mentioned wood species.

Newsprint from Bagasse (Mexico and Peru)

Basic Considerations. Undoubtedly bagasse is the
most controversial raw material for newsprint manufac-
ture of all those mentioned so far. Much has been
said against and now and then in favor of its use for
newsprint production. In this connection, some arti-
cles have been published containing totally unfounded
and even wild claims, both technical as well as econom-
ic, that never could be demonstrated in practice.
This situation, together with other negative factors,
which include the poor condition or economics and even
failure of many bagasse pulp and paper mills in sever-
al countries, has contributed in giving bagasse a bad
reputation, particularly for newsprint manufacture.
        However, the fact remains that bagasse is produc-
ed in many countries where conventional wood species
are either scarce or completely lacking, and its use
in the pulp and paper industry is continually increas-
ing. It is the by-product of a basic and well estab-
lished industry. Furthermore, its planting, harvest-
ing and collection costs are written off against the
sugar manufacturing operation. It is so bulky that it
poses a serious disposal problem. Hence, it is used
in almost all the sugarmills all over the world as a
fuel, constituting the basic energy source in these
mills, complemented in most cases with some supplemen-
tary fuel, either coal, gas or fuel oil.
        Therefore, its basic cost is that of the fuel
needed to replace it in the production of the steam
and power required by the sugarmills. But, consider-
ing that bagasse is not a very efficient fuel and that
the thermal efficiency achieved in most bagasse burning
installations is generally low, its replacement by some
other fuel like those already mentioned should lead to
higher overall efficiencies and certainly to a better
utilization of resources, both fiber and fuel.
        This is particularly important considering that
many sugarmills use a substantial amount of supplemen-
tary fuel. This is certainly the case in Mexico. Fur-
thermore, this fuel is not burned efficiently in many
of the mills. Therefore, low thermal efficiency is de-
rived not just from bagasse.
        This leaves open a number of interesting possibi-
ities for more efficiently utilizing the mentioned

resources. Some are already being applied, but there
is certainly room and definite possibilities for im-
provement. The idea would be to reach the highest
thermal efficiency possible in each case, the particu-
lar conditions for which vary considerably from country
to country and, of course from project to project.

The basic consideration that must be kept in mind
is that bagasse can be efficiently replaced with some
other fuel in many cases, thus liberating large quan-
tities of by-product fiber which can constitute a very
attractive source of raw material for a large-scale
pulp and paper operation, as required for newsprint.

It must also be kept in mind that the availability
of bagasse under the mentioned circumstances is imme-
diate, not requiring large investments in forest devel-
opments, species selection, hybridization, infrastruc-
ture development, years of waiting for trees to grow,
etc. In fact, the sugar mill operation is equivalent
to the forest for a bagasse pulp and paper mill, and,
in this case, the raw material is taken off a conveyor
that comes from the crushing rolls. Cane varieties
selection work is already carried out by the sugarmill,
and the infrastructure required for the operation of
the sugarmill is generally sufficient and adequate for
the needs of a paper mill.

This is quite important, as the development of
wood resources inevitably requires large investments
in infrastructure in many countries where sugar cane
is grown and bagasse could be made available.

Another important requirement for a successful
and competitive newsprint operation from bagasse is a
proper processing technology that would allow obtain-
ing a satisfactory pulp, at low costs that could be
used as the basic stock, i.e., in the highest possi-
ble proportion. This basically has been the stumbling
block for many attempts in this field.

In view of this situation, a brief description
will be made of some of the efforts to develop a satis-
factory pulping process, as needed for newsprint, be-
fore summarizing the work that has led to the engi-
neering and construction of the first two bagasse news-
print mills in the world.

<u>Background on Bagasse Newsprint Production Efforts.</u>
The first attempt to manufacture newsprint from
bagasse that drew considerable attention was the De La

Roza mill that was built a number of years ago in Cuba
(Tecnica Cubana). This mill was established on a com-
 mercial basis and operated for several years, produc-
ing newsprint of a more or less acceptable quality.
The process basically involved pre-hydrolysis of whole
bagasse, followed by sulphate pulping and conventional
three-stage bleaching. However, numerous problems were
encountered to which satisfactory solutions were not
found in all cases.

     First of all, there were considerable and uncon-
trollable losses in bulk storage of whole bagasse under
the existing conditions. Secondly, bleaching of the
pre-hydrolized pulp was very difficult and expensive.
Additionally, despite the fact that whole bagasse was
used, yields were low, and the paper was obtained at a
high cost, thus rendering it non-competitive with the
international market.

     The general conclusion that can be drawn from this
and other similar efforts is that chemical pulp is too
expensive to be used as the basic stock for bagasse
newsprint production. Besides, chemical pulp is gen-
erally too low in opacity for this type of application.

     Another approach was oriented towards the produc-
tion of a mechanical type pulp, trying to follow as
closely as possible conventional procedures for ground-
wood manufacture. However, the results obtained varied
greatly from those that could be expected for wood,
naturally, due to the entirely different properties and
morphology of bagasse, as compared to wood. Wood is a
selected tissue obtained from trees, while bagasse con-
tains all those tissues that were present in the cane
stalk prior to grinding in the sugarmill rolls. Anoth-
er important aspect is the fact that trees accumulate
wood in annual growth rings, while sugarcane is an an-
nual plant, and the fiber that is equivalent to the
wood fiber is not accumulated. Furthermore, sugarcane
stalks are harvested immature, i.e., when juice produc-
tion is at the maximum point, long before the vegeta-
tive cycle is completed.

     Therefore, bagasse contains tissues which are e-
quivalent to the leaves, bark and other cells which are
eliminated before pulping in the case of wood. On top
of that, there is no sharp division or separation be-
tween the different types of cells present in bagasse,
a situation which makes it impossible to separate the

fibrous tissues from the non-fiber elements by simple
mechanical means. Furthermore, even if all the non-
fiber elements could be efficiently separated, the re-
maining fibrous portion would still be quite heteroge-
neous, considerably more than wood fibers.

Under these circumstances it can be readily under-
stood why the various tissues present in bagasse, react
differently to the mechanical and/or chemical treat-
ments generally applied for pulping wood.

Therefore, in the case of bagasse, conventional
stone grinding techniques cannot be applied as, obvi-
ously, the structure of bagasse is quite different from
wood. Attempts to produce a mechanical type of pulp
from bagasse were circumscribed, then, to disc grinding
or refining procedures, but even these techniques en-
countered very serious problems due to the excessive
heterogenity of this raw material. For instance, in
the case of pith, these cells would collapse on passing
through the disc mill and then expand afterwards with-
out grinding.

Besides, they interferred with the proper grinding
of the fibrous portion. Therefore, strong depithing
was required, prior to disc milling, generally up to
50%, which rejected a large percentage of useful fiber.
This automatically eliminated the basic advantage of a
mechanical type pulp which, obviously, is a high yield.
Incidentally, strong depithing is also a basic require-
ment for conventional chemical pulping of bagasse, as
applied in almost all the mills in operation today.

In addition, two stage disc milling was required,
consuming an excessive amount of power, far more than
needed for producing conventional groundwood. On top
of this, due to the structure of bagasse fiber, the
end product was a flour, lacking adequate fibrous or
pulp characteristics. It must be kept in mind that
bagasse fiber tends to grind to a flour when disc mill-
ed without any chemical pre-treatment. This flour can
be used as a filler type pulp but lacks the wet
strength and formation properties needed to be used as
the basic ingredient or stock for newsprint production.
Furthermore, bleaching is extremely difficult and
expensive.

Up to now there has been no practical and impar-
tial demonstration of the technical and economic feasi-
bility of producing a high yield mechanical type pulp

from bagasse, having adequate brightness as well as wet
strength and formation properties, that could be used
as the basic stock for high speed newsprint production.
Rather, the results available in connection with this
work confirm that a mechanical type pulp cannot be used
as the basic stock for bagasse newsprint and that if
adequate properties are to be obtained, a chemical pre-
treatment is required, which combined with proper me-
chanical defibering could yield a satisfactory type
pulp that could have a relatively high yield, a low
cost and acceptable bleaching properties to reach the
brightness levels that are presently required for news-
print.

Several attempts have been made in various coun-
tries and by different organizations to develop a semi-
chemical process to meet the previously mentioned re-
quirements. However, only one of these processes, the
Cusi process, has been selected for use by the first
two commercial bagasse newsprint mills that are pres-
ently under design and construction, one in Mexico and
the other in Peru. A brief description is made of the
effort behind the mentioned development.

Process Selected for Commercial Bagasse Newsprint
Manufacture. A different approach to pulping bagasse
was developed by Dr. Dante S. Cusi and his collabora-
tors at the San Cristobal pulp and paper mill, just
outside Mexico City. The process, as applied by San
Cristobal, is used for the production of bleached mar-
ket pulp, as well as writing and printing paper, plus a
considerable amount of creped paper for facial and san-
itary tissues and napkins.

However, Dr. Cusi and his group modified this ba-
sic process so as to adapt it to the production of a
high yield pulp that could be readily bleached to a-
round 60% brightness, maintaining the physical and op-
tical properties that are required for high speed news-
print production and printing. This effort was started
in the late 1950's and continued through the first half
of the following decade. Numerous trials and produc-
tions were involved, including high speed printing runs
on most of the commercial presses in Mexico City. The
economics of the process were evaluated with extremely
encouraging results, and, in 1964, it was felt that the
process was ready for promotion.

The Mexican Government and local private invest-
ment groups became interested and joined together with
Dr. Cusi and his organization in programming and exe-
cuting the most extensive evaluation and testing pro-
gram of any process in this field. This program cover-
ed nine years of testing, i.e., from 1965 to 1974, in-
cluding trials, tests and production runs in several
mills in Mexico, the U.S., Canada and Europe. Large
scale trials were carried out on newsprint machines in
the U.S.and Canada, and high speed printing runs were
made on presses, not only in the mentioned countries
but also in Europe and in Mexico.

The assistance and collaboration of numerous inde-
pendent and highly qualified groups were obtained
throughout the entire program in planning, organizing
and supervising all the work, as well as in evaluating
the results and preparing the corresponding reports.
These advisors and consultants included large newsprint
manufacturing organizations from the U.S., the United
Kingdom, Canada and Germany, as well as various equip-
ment manufacturing organizations, engineering, and con-
sulting organizations from Europe, the U.S., and Mexico.
The services of the two main government research organ-
izations in Mexico were also used in supervising and
checking results throughout the entire program.

Tables 1, 2, 3, and 4, together with Figures 1, 2
and 3 (Special Appendix), show the participation and
function of the various groups that took part in the
last set of trials organized by the Mexican government,
lasting from 1972 to 1974. These tables and figures
were taken from the report of one of the consultants
(Atkins Planning), specially contracted to supervise
the trials and prepare an overall or consolidated re-
port of the results. They also show the vast scope of
this technical testing and evaluation program.

After completing the technical testing program,
covering laboratory, pilot and commercial scale tests,
the technical information was then used by other inde-
pendent groups in preparing manufacturing cost esti-
mates and evaluating the economics of this production,
using computer models specially developed for this pur-
pose. Based on this work, a final feasibility report
was prepared by the Mexican Government. However, before
reaching a final decision as to the implementation of
the project, the Mexican government sponsored additional

tests in Peru with another process developed by a U.S.
multinational organization.

It should be mentioned that, simultaneously, an-
other project for bagasse newsprint production in Peru
was reaching a similar degree of progress, and the de-
cision regarding process selection was also delayed un-
til the results of the mentioned trials in Peru for the
Mexican government were available. Hence, the decision
regarding both the project in Mexico as well as the one
in Peru depended on the results of the evaluation of
the U. S. process versus the Mexican process.

After completion of the demonstration of the U.S.
process in Peru, the Peruvian government decided to go
ahead with its project, based on the Mexican process
and entered into contracts with the Cusi group, as well
as with Mexican and U.S. engineering organizations (Bu-
fete Industrial and Rust Engineering) for the supply of
the technical information and knowhow, the basic engi-
neering, the detailed engineering and the construction
management.

The decision of the Mexican government took more
time to reach, but was also favorable to the Mexican
process, and a new company, Mexicana de Papel Periodico,
S.A., was organized in June of 1974 by the government
to implement the project. This company entered into
contracts with the Cusi organization and the mentioned
Mexican engineering group to provide all the technical
information and engineering services required for the
installation of the mill, including construction
management.

To-date, the basic engineering of both of these
mills has been completed, civil works have been started
and most of the equipment, including the paper machines,
has been ordered.

However, before entering into a detailed descrip-
tion of these projects, reference is made to the basic
pulping technology and differences that can be found
with respect to the conventional bagasse pulping tech-
nology used in most bagasse pulp and paper mills pre-
sently in operation.

The basic features of the Cusi Process cover the
following points: (1) a selective wet-depithing sys-
tem, having a low but controllable rate of pith rejec-
tion (15% to 30%); (2) a multi-stage pre-impregnation
system, whereby all or practically all, the pulping

chemical or chemicals are added, prior to digestion
(any adequate chemical system can be used, either acid,
neutral or alkaline);   (3) a mild short-cycle digestion
(total chemical consumption, based on NaOH is between
8% to 9%);   (4) fractionation after cooking to separate
the easily pulped fibers from the harder to cook frac-
tionation, which is only partially pulped or softened
by the chemical treatment; and (5) mechanical defiber-
ing of only the partially cooked fraction in a thermo-
mechanical disc mill, with very low horse power con-
sumption (5 to 8 Hp per daily ton).

The rest of the operations are conventional and
involve combining the mentioned pulp fractions and sub-
jecting them to washing, screening and a two-stage
bleaching sequence, using hypochlorite or any other
convenient combination of chemicals.

In this way, maximum flexibility can be obtained,
as depithing is adjustable, as is the intensity of the
chemical and mechanical pulping operations. In other
words, more or less pulping chemicals and power can be
applied to meet varying conditions and properties of
the bagasse, as well as brightness requirements of the
final sheet, which has shown a tendency to increase o-
ver the years. This is extremely important as present
brightness levels for newsprint unavoidably require
bleaching, and this, in turn, establishes the need for
a chemical treatment to ensure satisfactory and econom-
ic bleaching conditions. Besides, the chemical treat-
ment, as previously mentioned, is needed to ensure
proper defibering properties of the bagasse and thus
avoid excessive grinding of the fiber, together with
high power requirements.

Therefore, the chemical treatment, not only allows
conserving the strength properties of the original fi-
ber during disc milling, but also obtaining adequate
bleaching properties of the resulting pulp.

Fractionation of the easily pulped tissues, prior
to disc milling avoids unnecessary over-treatment of
these cellular elements which are very sensitive to
either chemical or mechanical action. If they were to
be subjected to disc milling, as in conventional semi-
chemical pulping, their properties would be consider-
ably lowered, particularly tear, opacity and freeness.
Therefore, pre-impregnation and mild cooking allow

pulping these delicate tissues with minimum damage to
their original properties, while fractionation allows
separating and further treating (disc milling) those
fiber cells which require a more energetic processing
for pulping.

The aforementioned principles are independent of
the chemical system used for the pre-treatment. As
mentioned, any convenient system can be used. However,
it should be pointed out that alkaline systems have
shown the most favorable results with bagasse, either
alkaline sulphite, sulphate or straight soda. Hence,
in the case of the Cusi Process, any one of these sys-
tems can be used. Selection should depend on the eco-
nomics of each project.

Therefore, it can be seen that this type of dif-
ferential pulping reduces the need for strong depithing,
as required in the conventional approach; minimizes
the use of chemicals and power for pulping, yet con-
serves the intrinsic properties of the fiber; renders
the highest possible yield at the lowest cost and pro-
vides the greatest operating flexibility.

This last aspect is particularly important, as
bagasse properties and supply conditions continually
vary over the year, and newsprint quality requirements
have also been changing, showing a trend towards higher
brightness and lower basis weight. Obviously, in-built
flexibility is a basic requisite for any new mill com-
ing into this field. The Cusi Process is particularly
suited to this purpose, as its inherent flexibility al-
lows producing form a straight mechanical pulp to a
full chemical pulp or any point in between, as may be
required, thus reducing the underlying technical risk
to a minimum. This has been a basic consideration in
its selection for the first two commercial bagasse
newsprint mills.

Characteristics of the Mexican and Peruvian
Projects. The main characteristics of the Peruvian and
Mexican bagasse newsprint mills are summarized in Table
5, (special Appendix). However, it would seem perti-
nent to mention that, while the mill in Peru is design-
ed for a capacity of 114,000 MT/year of newsprint with
one paper machine, the mill in Mexico is going ahead on
the basis of two modules, each of 100,000 MT/year news-
print capacity with one paper machine and the

corresponding bagasse pulping facilities, recovery, power generation and other services per module. Construction of the first module is underway, and the start-up of the second module will be staggered from one to two years after the first module enters into production. Provision has been made to add on a third module, depending on how the demand for this commodity develops.

Bagasse Newsprint - Special Appendix

Introduction. Tables 1, 2, 3, and 4, as well as Figures 1, 2 and 3 have been taken from the Report, "Manufacture of Bagasse Newsprint", specially prepared by Atkins Planning of Epsom Surrey, England for Promotora de Papel Periodico, S. A. de C. V. of Mexico City, dated September, 1973.

This information summarizes the scope of the testing program carried out under the sponsorship of Promotora de Papel Periodico, as well as the main results obtained and the suitability of the plan to impartially evaluate the technical and economic feasibility of producing newsprint from sugarcane bagasse.

Promotora de Papel Periodico, S. A. de C. V. was formed in 1972 with the participation of Nacional Financiera, S. A. of the Mexican Government, the International Finance Corporation, Mr. Romulo O'Farrill and Cia. Industrial de San Cristobal, S. A. The objective of Promotora was to finance, organize and direct a complete technical testing and economic program that would allow: (1) finalizing all the work carried out previously by the promoting group, based on the successful production of bagasse pulp and paper by San Cristobal; (2) evaluating the technical feasibility of producing bagasse newsprint by the Cusi Process; and (3) preparing up-dated manufacturing cost estimates and equipment and plant costs, as well as economic projections that would permit the promoting group to adequately appraise the economics of bagasse newsprint production for the Mexican market and reach a final investment decision regarding the establishment of a 190,000 - 220,000 MT/y mill.

Technical Program. A complete testing program covering laboratory, pilot and mill scale tests and runs was organized and executed with the assistance of

several consulting and equipment manufacturing organi-
zations, including the main newsprint manufacturing
group of Continental Europe and the two principal gov-
ernment research organizations.

The list of participants and their functions, the
scope of the work and the reports prepared are shown in
Tables 1, 2 and 3 and Figures 1, 2 and 3.

Atkins Planning, planning and management consul-
tants of the United Kingdom, were specially contracted
to observe and appraise all the technical work in order
to prepare a comprehensive technical report which would
include not only the views of Atkins but also of all
the other consultants. The assignment of Atkins also
covered the preparation of manufacturing cost estimates
based on the results of the technical testing program.
The Atkins Planning team engaged in this program con-
sisted of members of their Process Planning Department,
working in close association with Dr. Julius Grant, a
world authority on pulp and paper manufacture, and Mr.
Albert Kirk, M.B.E., a printing expert.

Suitability of the Plan. Regarding the suitabil-
ity of the program to properly assess the technical
feasibility of producing bagasse newsprint, Atkins com-
mented the following in their report to Promotora: ¨It
is undeniable that the numbers and qualifications of
observers of the trials were adequate to enable full
appraisal to be made of the technical feasibility of
the process¨. ¨Finally, the objective of the trials
(namely assessment of the technical feasibility of
manufacturing newsprint from bagasse on the commercial
scale), is considered by Atkins Planning to have been
achieved¨.

Manufacturing Cost Estimates. These were prepared
by Atkins and are summarized in Table 4.

Conclusions.¹ Overall conclusions reached by
Atkins were as follows: ¨The trials have shown that
the Cusi Process is technically feasible. In-works
manufacturing costs will be in the range of M$1,247 to
M$1,421 per ton of newsprint; depending upon plant
modifications, by-products recovery and ancillary e-
quipment installed in the final complex. Apart from
above, these costs are likely to be affected signifi-
cantly only by variations in the costs of bagasse,
other raw materials and energy.

The process concepts and equipments are based upon

those used and established in the pulping of agricul-
tural fibres, and a long history of process development
by Dr. Cusi and his associates".
    <u>Final Report and Investment Decision.</u> Based on
the manufacturing cost estimates prepared by Atkins
Planning, other independent groups elaborated and pre-
sented economic projections for a 190,000 - 220,000
MT/y bagasse newsprint mill, that were used by Promo-
tora in putting together a Final Feasibility Report
that was presented to the Government Authorities in
February, 1974. The Mexican government decided to im-
plement the project and in June, 1974 formed Mexicana
de Papel Periodico, S.A. for this purpose.
    ACKNOWLEDGEMENT. The author wishes to express his
gratitude to Promotora de Papel Periodico, S.A. de C.V.,
for its authorization to publish the mentioned tables,
figures and conclusions obtained from the Report by
Atkins Planning.

<div align="center">TABLE 1</div>
<div align="center"><u>List of Participants</u></div>

    The parties invited by the Promoters to partici-
pate in the trials can be broadly classified into four
groups namely:
A. Parties providing trial facilities or consultancy
    and having financial or equipment supply interest
    in the project.

Cia. Industrial San Cristobal	providing the pulping and slow speed papermaking facilities.
Beloit Corporation (U.S.A.)	providing high speed twin-wire experimental paper-making facilities.
Voith J. M. GmbH (Germany)	providing high speed single- and twin-wire experimental papermaking facilities.
Simon Carves (U.K.)	providing a capital and manufacturing costs esti-mate based upon data col-lected during the trials and incorporating their past work and association

| | with San Cristobal. |
| Bufete Industrial (Mexico) | providing capital cost estimates for local engineering and equipment. |

B. Parties providing trial facilities and having no
    financial or equipment supply interests in the
    project.

Novedades (Mexico, D.F.)	providing high speed, production letterpress and web offset printing facilities.
Stars and Stripes (Germany)	providing letterpress, production speed printing facilities through the organization of Haindl Papier.
Gebr. Schmidt GmbH (Germany)	providing ink formulation to specifically suit bagasse papers printed at the Stars and Stripes, working through the organization of Haindl Papier.

C. Parties providing testing and consultancy services
    and having no financial or equipment supply inter-
    ests in the project.

Haindl Papier GmbH (Germany)	newsprint manufacturers producing about 1,500 tonnes per day, of which more than 900 tonnes per day is newsprint; acting as papermaking technical advisers; providing process and specifications consultancy, together with modern paper and pulp testing and printability facilities.
Instituto Mexicano de Investigaciones Tecnologicas (IMIT)	providing a complete laboratory process check to confirm the process conditions for reference in the present series of trials.
Laboratorios Nacionales de Fomento Industrial (LANFI or Fomento)	providing a technical audit of the trials, testing results and reports for the executive committe

of Promotora. Also con-
sultancy on the sampling
procedures and testing
procedures to be adopted
for the trials and a full
confirmatory or reference
testing programme inde-
pendent of all other par-
ties.

  Atkins Planning   providing a comprehensive
    (United Kingdom)   technical report and manu-
facturing costs analysis
based upon all partici-
pants' views as reported.

D. Parties observing the trials only and having finan-
cial interest in the project. These parties will
report only to their own interest on the Promotora
Board. Their influence will therefore be direct
and not through the comprehensive technical report
being prepared from this trial series.

    International Finance Corporation (Washington)
    National Financiera, S. A. (Mexico)
    Mr. Romulo O'Farrill (Mexico)

TABLE 2
Reports Submitted by Participants

No.	Participant Submitting	Report Title(Date)
1	Instituto Mexicano de Investigaciones Tecnologicas, A.C.	Experimental laboratory program covering the preparation of pulpfrom sugar cane bagasse and the determination of the characteristics of mixtures incorporating commercial pulps.
2	Cia. Industrial de San Cristobal, S.A.	Report on the production of semi-bleached bagasse pulp and bagasse newsprint (30.4.73)
3	Cia. Industrial de San Cristobal, S.A.	Bagasse Cost Study (25.5.73)
4	Laboratorios Nacionales de Fomento Industrial	General terms of reference (Annexe to First Report) (25.5.73)

5	Laboratorios Nacionales de Fomento Industrial	First Report. Mill scale production of bagasse pulp at San Cristobal. (25.5.73)
6	Laboratorios Nacionales de Fomento Industrial	Second Report. Bagasse Newsprint manufacture at low speed at San Cristobal (25.6.73)
7	Laboratorios Nacionales de Fomento Industrial	Third Report. Printing trials on high speed letterpress and offset presses at ¨Novedades¨ (6.7.73)
8	Laboratorios Nacionales de Fomento Industrial	Fourth Report. Bagasse newsprint - high speed trials on the experimental paper machine of the Beloit research centre at Beloit, Wisconsin, U.S.A. (13.7.73)
9	Laboratorios Nacionales de Fomento Industrial	Fifth Report. Bagasse newsprint high speed Fourdrinier and duoformer trials and San Cristobal newsprint calendering tests at the Voith research centre at Heidenheim, Germany Appendix. Visit to Haindl Papier, GmbH, at Schongau (20.7.73)
10	Haindl Papier GmbH	The evaluation of newsprint trials with bagasse furnish. Volume I. (10.7.73)
11	Haindl Papier GmbH	The evaluation of newsprint trials with bagasse furnish. Volume II. (10.7.73)
12	Beloit Corporation Machinery Division	Newsprint from bagasse pulp trials at Beloit Corporation. (13.4.73)

13   J. M. Voith GmbH   The experimental production
                                     of newsprint from bagasse
                                     on a fourdrinier and duo-
                                     former. (13.4.73)
14   Simon-Carves Ltd.   Report on preliminary en-
     Bufete Industrial   gineering capital and ma-
                                     terials and services re-
                                     quirements for a bagasse
                                     newsprint mill in Mexico.
                                     (Sept. 73)
15   Atkins Planning   Comprehensive technical
                                     report covering the com-
                                     plete testing programs,
                                     plus a manufacturing cost
                                     analysis. (Sept. 73)

TABLE 3
Summary of Papermaking Trials

Trial	Machine Type	Maximum Speed (m./min.)	Trim Width (cm.)
San Cristobal	single wire	100	152
Beloit	twin wire	800	32
Voith	single wire	800	48
Voith	twin wire	800	48
Proposed plant	twin wire	650	(a)
		750	(b)

(a) 4 1/2 roll trim for 95,000 tonnes per year output.
(b) 4 1/2 roll trim for 110,000 tonnes per year output.

TABLE 4

Manufacturing Costs

Item	Cost Type	Cost per tonne of newsprint at 220,000 tonnes output			
		Strategy			
		1	2	3	4
Bagasse Materials	Variable	290.05	290.05	252.06	252.06
and power	Variable	789.54	683.61	901.52	813.01
Management and staff	Fixed	147.11	149.95	147.11	149.95
Labour	Fixed	91.67	94.82	91.67	94.82
Insurance, admin. and central office	Fixed	28.95	29.00	28.95	29.00
					1,338.84
TOTAL MANUFACTURING COSTS (in Mexican pesos)		1,347.32	1,247.43	1,421.31	

TABLE 5

Main Characteristics of the Peruvian and Mexican Projects

	Peruvian Mill	Mexican Mill
Location	Santiago Cao, Peru Adjoining the Trupal Mill, near the City of Trujillo	Tres Valles, Veracruz
Capacity	114,000 MT/y	200,000 MT/y
Cane Milling Season	11 months	6 months
Type of Bagasse to be Used	Depithed at the Sugarmill	Whole bagasse to be depithed at the Papermill

Bagasse Storage System	Moist bulk storage of depithed fiber	Wet bulk storage of depithed fiber
Depithing System	Moist vertical depithers at the Sugarmill followed by wet depithing at the Papermill	Moist depithing in vertical machines at the Papermill prior to storage, followed by wet screening after storage
Bagasse Pulping Capacity	1 module of 350 MTBD/day	2 modules of 240 MTBD/day each
Pulping Chemical	Sodium Hydroxide (8.5% on dry depithed fiber)	Sodium Hydroxide (8.5% on dry depithed fiber)
Bleaching Sequence	Two-stage sodium hypochlorite with washing after each stage	Two-stage calcium hypochlorite with washing after each stage
Chemical Recovery System	None for the present	Copeland Fluidized Bed System
No. of Paper Machines	1	2
Additives	9% retained clay, Alum, Dyes (News Blue and Rhodamine)	9% retained clay, Alum, Dyes (News Blue and Rhodamine)
Paper Machine	Valmet(Finland)	Beloit (USA)
Forming Section	Sym Former (Twin Wire)	Bel Bae II (Twin Wire Former)
Trim(reel)	305"; 774.7 cm.	246"; 624.8 cm.
Press Section	Tri-Nip with granite central roll	Tri-Nip with granite central roll
Dryers	1-60" Baby Dryer and 40-72" Dryers	1-48" Baby Dryer and 45-60" Dryers in 5 sections
Machine Calendar	6 Rolls	4 Rolls with possibility for adding on 2 more rolls
Guaranteed Speed	900 MPM	3000 FPM

Figure 1. Functions of participants

Figure 2.   Materials throughput for trials
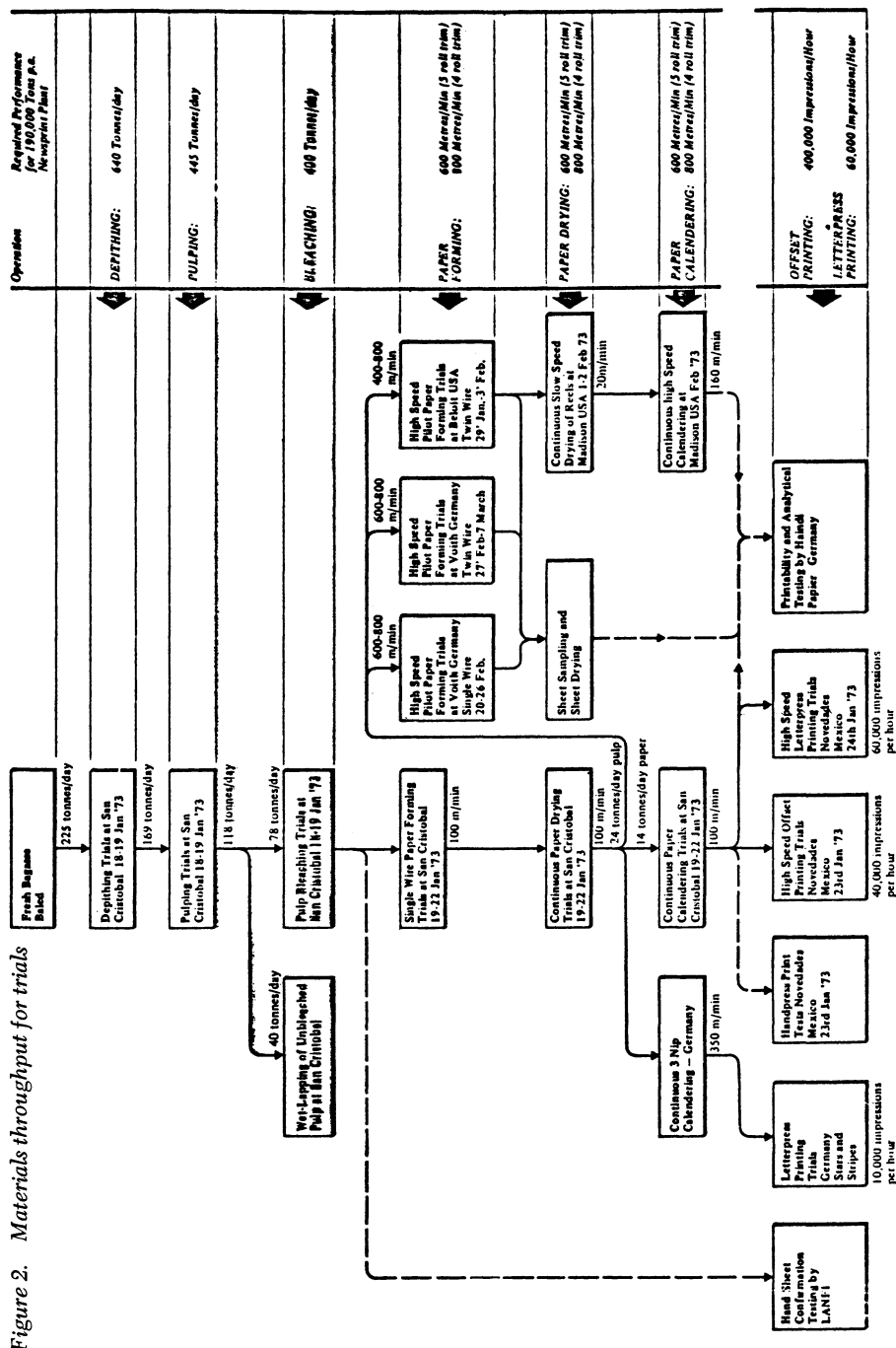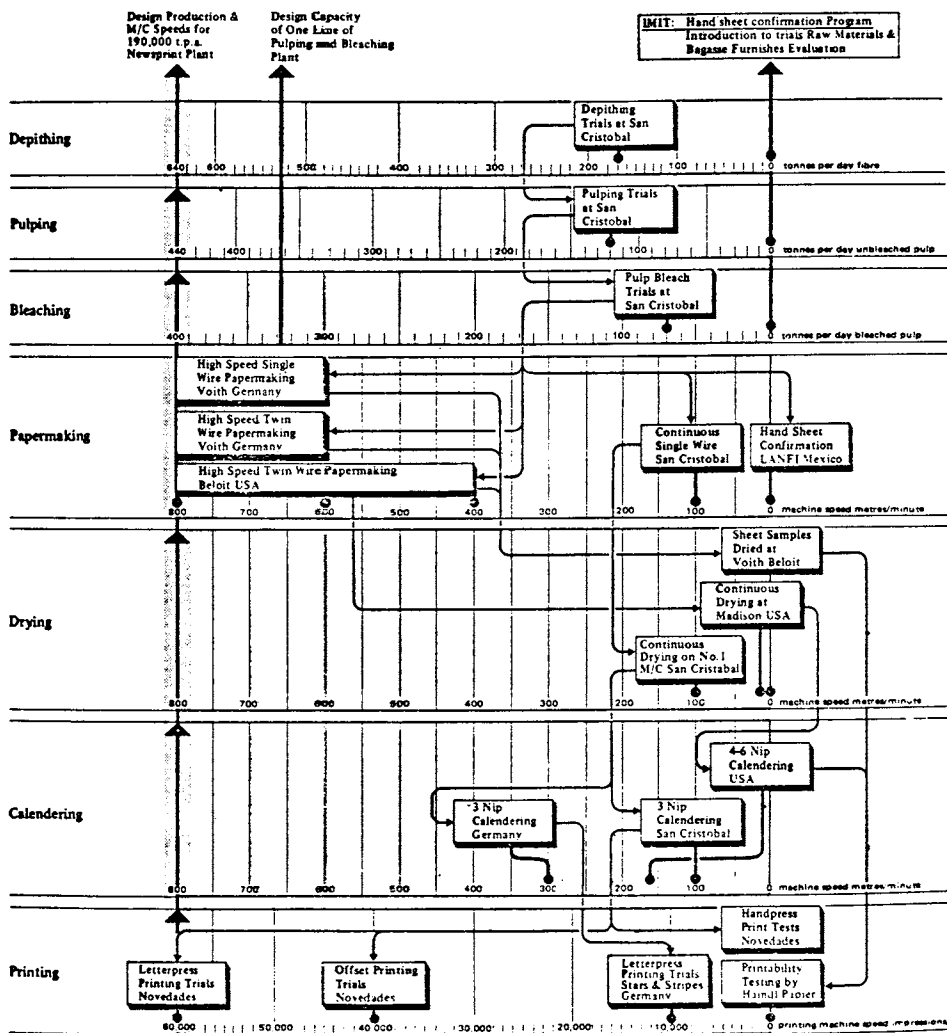
Figure 3.   Comparison of trials and typical commercial speeds and outputs

Newsprint from De-Inked Stock (Mexico)

The construction of a de-inking mill for newsprint production in Mexico is now nearing completion. This mill is being established by Productora e Importadora de Papel, S.A. (PIPSA), in combination with Garden State of the U. S.

PIPSA is a Mexican government organization which centralizes the importation and distribution of newsprint, rotogravure and some other types of paper in Mexico. This organization recently joined forces with the Garden State group to set up a newsprint-de-inking operation, which is in the final stages of construction.

The initial capacity of the mill will be 60,000 MT/Y of finished newsprint, using imported waste paper from the US as the raw material.

This plant is located in Villa de los Reyes in the State of San Luis Potosi, about 60 km. from the city of San Luis Potosi, which is more or less midway between the U.S. border and Mexico City, the main paper consuming area in Mexico.

A new company, Productora Nacional de Papel Destintado, S.A. de C.V. (PRONAPADE), was jointly established by PIPSA and Garden State for the implementation of the project and operation of the mill. The process to be used will be that developed by Garden State in its mills in the U.S. Garden State has collaborated with local engineering organizations in supplying the technical information needed for the engineering and design of the mill and will also assist in the start-up. The operation and administration of the mill will be the responsibility of PRONAPADE.

Equipment for the mill has been obtained basically from the U.S. and Mexico. However, the paper machine is a used Walmsley machine, purchased from Bowater, U.K. It trims 245 inches, and, considering the reconstruction of the headbox, forming and press sections, plus a new drive, the operating speed is expected to reach 1800 FPM. As mentioned, construction of the mill is presently nearing completion, and start-up should begin around May, 1976.

Future Projects and Potential

The previous summaries cover the newsprint mills

in Latin America, either in operation or under con-
struction, giving the following capacity:

TABLE 6
Newsprint Capacity in Operation or Construction

Mill	Country	MT/Y	MT/Y
CMPC	Chile	65,000	
Industrias Forestales	Chile	79,000	144,000
Tuxtepec	Mexico	70,000	
PRONAPADE	Mexico	60,000	
Mexpaper	Mexico	100,000	230,000
Klabine	Brazil		127,000
Papel Prensa	Argentina		100,000
Induperu	Peru		114,000
TOTAL			715,000

Since the newsprint demand in Latin America is
slightly over 1.0 million metric tons per year, there
will still be a need for more installed capacity even
after the mills under construction reach rated produc-
tion levels. Therefore, it would seem of interest to
analyze future growth potential in this field, looking
at some of the more viable projects or expansions now
under serious consideration in several of the Latin
American countries.

Argentina. The newsprint development program in
this country calls for a total production of 300,000
MT/Y of which Papel Prensa has been assigned 100,000
MT/Y. As mentioned, this unit should be starting up
during the early part of 1976. Furthermore, Papel
Prensa has already presented a bid to the Government
for a 100,000 MT/Y expansion, i.e., a second module,
which would bring the capacity of this mill up to
200,000 MT/Y. The raw material for this expansion
would also be willow and poplar from the Parana River
Delta. There is every reason to believe that this
project will be approved by the government and will be
implemented at a reasonable time after start up and
satisfactory operation is achieved of the unit now
reaching completion.

Additionally, another project presently under
study by the Tucuman Province Goernment, the central
government and private investment groups has been
granted preliminary authorization to go ahead. This

project contemplates the use of sugarcane bagasse pro-
duced in the Tucuman province, the main sugar area in
Argentina, and would also have a capacity of 100,000
MT/Y. The location would be in the vicinity of San
Miguel de Tucuman, which is the seat of the Provincial
government. Natural gas, which is piped through this
province to the Buenos Aires area, would be used to re-
place the bagasse in the generation of steam and power
needed by the supplying sugarmills. As in the case of
the mills in Peru and Mexico, the Cusi Process would be
used.
       There is every indication that this project will
also go ahead, subject, of course, to meeting all the
government requirements, and, together with the expan-
sion of the Papel Prensa Mill, would bring the total
newsprint capacity in Argentina up to 300,000 MT/Y, as
per the original program established for this purpose.

       Bolivia. The Bolivian government authorities have
been studying, with the assistance of various organiza-
tions from other countries, the possibility of estab-
lishing a 25,000 - 30,000 MT/Y newsprint and writing
and printing paper mill for the local market. The raw
material under consideration is bagasse, which would be
replaced with natural gas, which is also abundant in
this country.
       The results obtained in the mentioned studies were
optimistic regarding the viability of the project, and
the Bolivian government Development Agency even granted
a letter of intent to a consortium of companies from
Europe, Argentina and Mexico for the engineering and
construction of the mill and also the equipment supply.
       However, the project has not proceeded as per the
mentioned letter of intent. Apparently, new studies
are being made, and the implementation will depend on
the results that will be derived from this work. But,
in view of the abundance of bagasse and replacement
fuel, there seems to be good possibilities for this
project to go ahead in the near future.

       Brazil. Despite the local production based on Eu-
calyptus and Parana Pine, already described, Brazil
still shows an important deficit of newsprint. There
are a number of possibilities for covering said deficit,
and various projects are being subjected to careful

analysis. Wood is the main source of raw material con-
templated for this purpose, but very serious considera-
tion is also being given to bagasse, particularly by
the government agencies, as Brazil is now the leading
can sugar producer in the world. The possibility of
using both wood and bagasse also seems to be of consid-
erable interest.
     Whatever the alternative or alternatives finally
adopted in reaching the goal of self-sufficiency in the
supply of newsprint, there will be the need for estab-
lishing about 200,000 MT/Y of additional capacity in
the not too distant future. Considering the tremendous
wood and bagasse potential of the country, it should
not bee too long before one or two of the projects now
under study get off the ground.

     Chile. Industrias Forestales, S.A., one of the
two newsprint manufacturers in Chile, is considering a
130,000-156,000 MT/Y expansion of their newsprint fa-
cilities. Apparently, the decision to implement this
project will be taken very shortly. Projected start-up
is for the early part of 1973. It has a very solid
basis, as it is backed by the considerable experience
in this field of INFORSA, plus an ample supply of Pinus
radiata. The prject contemplates the production of
about 90 MT/day of chemical pulp using a high yield
sodium bisulphite process and around 320 MT/day of
thermomechanical groundwood. Both of these production
processes have been under study by INFORSA with very
favorable results. This expansion, involving the in-
stallation of a 5 roll machine (300" trim), will bring
the total newsprint capacity up to 274,000 - 300,000
MT/Y and should enhance Chile's position in the Latin
American export market.

     Cuba. The Cuban Government has been sponsoring
through several of its agencies a very ambitious re-
search and development program in connection with
bagasse utilization and sugar by-products in general.
This program is called Cuba 9. Part of this program
covers newsprint production from bagasse, and several
studies have been carried out using basically a mechan-
ical process. The idea behind this processing stems
from the experience of a UNIDO adviser, commissioned in

Cuba during the past few years, with the Ritter ba-
gasse storage method and the unsuccessful efforts of
Crown Zellerbach and the Hawaiian Sugar Planters' As-
sociation to develop a satisfactory process for a me-
chanical type pulp from bagasse.

At the UNIDO conference held in Vienna in Septem-
ber of 1971 on non-wood fibers, the mentioned adviser
obtained the backing of UNIDO, FAO and the Cuban gov-
ernment to establish a pilot plant to follow up the
possibilities of developing a process for producing a
mechanical pulp from bagasse and also to evaluate,
technically and economically, all processes for bagasse
newsprint. This last aspect was proposed as a service
of the mentioned UN organizations to parties interested
in this area.

UNDP and Cuban government funds were obtained to
establish said pilot plant. The equipment has been or-
dered, and the program considered for its use has been
incorporated within the Cuba 9 program. The pilot
plant is expected to be operational by late 1976 or
1977, and the Cuban government is already advertising
technical and advisory services, based on this unit.

The process under consideration involves the fol-
lowing sequence: preliminary depithing; storage of
bagasse by the Ritter method, using the biological
fluid; a second stage depithing; a mild chemical pre-
treatment; disc milling and bleaching. The process de-
pends heavily on the pre-hydrolysis effect which is
supposed to be produced during storage with the biolog-
ical fluid. Depithing requirements are in the 40 to
50% range. No results have been publicly made avail-
able to appraise the potential of this production
method for use in obtaining either the basic stock or a
filler type pulp for bagasse newsprint.

However, if the mentioned process proves to be
successful for either purpose, its promotion poses
several problems. Considerable United Nations funds
are involved, and the first question that naturally
arises is, what country and what organization would be
granted the wrights to commercialize said process?

The Cuban government has also provided funds and
definitely feel that the results will belong to Cuba.
Nevertheless, as mentioned, the whole scheme depends
heavily on the Ritter storage process, developed and

patented a number of years ago by Dr. Ritter, now de-
ceased, at the Ngoye Mill in South Africa. The patent
and commercial rights to this method are held by the
Aschaffenburger group of Germany. How will this situ-
ation, then affect both the commercialization and pat-
entability of the process under study in Cuba?

Furthermore, the installation of a pilot plant by
FAO, UNIDO and the Cuban Government unavoidably brings
into the open the intention, willingly or not, of the
mentioned organisms to establish themselves as the max-
imum judges of bagasse newsprint technology in the
world. This is quite questionable in the opinion of
the author, who emphasized this matter at the 1971
UNIDO Conference at Vienna, but was overruled at that
time.

Under these circumstances, a further question a-
rises regarding the impartiality of the evaluation of
any other process that could be carried out in the fu-
ture in the mentioned pilot plant, especially consider-
ing that the groups behind the operation of this unit
have a definite axe to grind with their own process.

Independently of this situation, which at best is
quite complicated, the fact remains that Cuba has its
own program for newsprint, and it should not be too
long before a concrete project is established for this
purpose, which could be not only for the local market,
but also for export.

Ecuador. Studies are now underway to establish
the viability of a newsprint and writing and printing
paper mill for the local market, based on bagasse.
There is also a strong demand for corrugating medium in
this country, which is presently imported for the local
box plants, together with the linerboard used in manu-
facturing boxes for the export of bananas.

Ecuador is the main exporter of bananas in the
world. Studies are being made to appraise the favor-
able conditions in this country for bagasse pulping and
papermaking, which include the possibility of combining
some newsprint production with that of other types of
paper now imported.

There seems to be a reasonably solid basis for a
project of the mentioned nature, which should material-
ize in the not too distant future.

Mexico. The possibilities of increasing newsprint
in this country are quite ample, particularly consider-
ing that there is already one mill that has been oper-
ating for 15 years (Tuxtepec), based on wood and two
are under construction, one based on waste paper (PRO-
NAPADE) and the other on bagasse (MEXPAPER). All of
these mills have expansion programs, as follows:

> Tuxtepec: 100,000 MT/Y, based on wood and bagasse,
> PRONAPADE: 50,000 MT/Y, based on waste paper, and
> Mexpaper: 100,000 MT/Y, based on bagasse. (2nd
> module)

This means that there is a 250,000 MT/Y expansion
capacity of this industry on a medium term basis, which
could allow doubling the capacity presently installed
or in construction. Since it seems doubtful that the
local market could absorb all this capacity within the
next several years, the government will have to estab-
lish priorities for the mentioned expansions or make
arrangements for exporting any surplus production.

Therefore, growth of the local newsprint produc-
tion will depend on the evolution of the demand for
this commodity in the country over the next years and
on the priorities that the government will inevitably
have to establish for the expansion of the mentioned
mills, which are all government controlled.

Peru. The possibility for expansion of the ba-
gasse newsprint mill now in construction in Peru, ad-
jacent to the Trupal Mill, is quite good, as Peru has a
year round sugar season and said mill is close to the
Casa Grande Sugarmill, the largest in Peru. Therefore,
it is felt that capacity of the newsprint mill could be
doubled in the future, depending on market growth in
Peru and/or export possibilities.

Venezuela. A very interesting project is being
studied involving bagasse newsprint production in Vene-
zuela. This country has an important sugar industry
and an ample supply of fuel oil. Besides, newsprint
imports have reached a level which justifies looking
closely into the possibility of establishing a local
source of supply, which could also include production
of part of the pulp that is also imported.

Various local groups, together with a Mexican

engineering and consulting firm, are preparing the nec-
essary studies, which will lead to an investment deci-
sion on a relatively short term basis. The possibil-
ities of this project going ahead look very good in
view of the favorable circumstances surrounding it.

   Summary of Project Potential. The preceding anal-
ysis of projects covers those which, in the author's
opinion, have a relatively sound basis for future im-
plementation. The potential for future newsprint proj-
ects in Latin America, as herein described, is sum-
marized in the following table.

TABLE 7
Future Newsprint Potential in Latin America

Country	Projected Capacity MT/Y	Raw Material Considered
Argentina	200,000	Wood and Bagasse
Bolivia	20,000	Bagasse
Brazil	200,000	Wood and Bagasse
Chile	156,000	Wood
Cuba	Pilot Plant	Bagasse
Ecuador	Not established	
Mexico	250,000	Wood, Waste Paper and Bagasse
Peru	114,000	Bagasse
Venezuela	100,000	Bagasse
TOTAL	1,040,000	

   As can be seen from the above figures, there is an
excellent growth potential for newsprint production in
Latin America, just considering those projects which
have reasonable possibilities of being implemented in
the not too distant future. These projects, together
with the mills indicated in Table 6, would place in
reach a total capacity of about 1.8 million tons, suf-
ficient to cover the regional newsprint demand in the
next 10 to 15 years at present growth rates.
   The undertaking of these projects will be strongly
influenced, among other things, by market growth, the
newsprint price situation, further escalation of equip-
ment costs, availability of financing and government
policies. Since availability of raw material is no
problem and the technology barrier has been overcome,
the main factors for future development of this

industry in Latin America will depend, in the author's
opinion, mainly on market growth and government poli-
cies. This last aspect is of particular importance,
as generally low profit margins in newsprint manufac-
ture, combined with excessively high investment re-
quirements, together with other factors of a national
political and economic nature, make government partic-
ipation a necessity.

In fact, government policy can make or break any
of the mentioned projects, and this has been an under-
lying factor behind the strong participation of Latin
American governments in this field and a probably
stronger participation in the future.

Newsprint Supply Situation and Perspectives

It can, then, be seen from the previous summary of
development efforts, that the newsprint supply situa-
tion in Latin America is changing rapidly. As a result
of this endeavor, several mills are presently under
construction, two with start ups scheduled in early
1976. Undoubtedly this should result in a marked in-
crease in the regional supply of newsprint.

However, to better appreciate this situation,
Table 8 has been prepared summarizing figures on capac-
ity, production, imports and demand, which include the
newsprint mills that have been operating for many years,
as well as those under construction.

It can be seen from the mentioned Table that news-
print production in Latin America added up to only
295,000 metric tons in 1974, practically the same level
estimated by FAO in 1970. Furthermore, due to the re-
duction in basis weight and the general economic reces-
sion, Latin American newsprint demand was slightly low-
er in 1974 than that estimated by FAO for 1970, i.e.,
1.04 million metric tons in 1974, as compared to the
estimated 1.06 million metric tons for 1970.

Further examination of the available statistics
shows that newsprint demand in Latin America is concen-
trated in relatively few countries as shown in Table 9.
The main newsprint consuming countries are only seven,
i.e., those having a demand of over 40,000 MT/Y in 1974,
and these seven represent approximately 83% of the
entire regional newsprint demand for the mentioned year.
Additionally, newsprint production is concentrated in

TABLE 8
Newsprint Situation in Latin America

Countries	Newsprint Capacity MT/Y (1975)	Newsprint Production MT/Y (1974)	Newsprint Imports MT/Y (1974)[1]	Net Demand MT/Y (1974)[1]
Argentina	100,000[2]	---	150,150	150,150[3]
Belize	---	---	228	228
Bolivia	---	---	3,640	3,640
Brazil	127,000[1]	118,300[1]	145,600	263,900
Chile	144,000	120,120[1]	910	47,000
Colombia	---	---	54,600	54,600
Costa Rica	---	---	12,740	12,740
Cuba	---	---	24,570	24,570
Dominican Republic	---	---	8,918	8,918
Ecuador	---	---	16,380	16,380
El Salvador	---	---	11,373	11,375
Guatemala	---	---	11,830	11,830
Guayana	---	---	1,638	1,638
Haiti	---	---	273	273
Honduras	---	---	2,730	2,730
Jamaica	---	---	10,920	10,920
Mexico	230,000[4]	56,500[5]	154,700	211,200[6]
Nicaragua	---	---	4,550	4,550
Panama	---	---	4,095	4,095
Paraguay	---	---	3,640	3,640
Peru	114,000[7]	---	46,410	46,410
Puerto Rico	---	---	35,490	35,490
Surinam	---	---	478	478
Trinidad and Tobago	---	---	6,825	6,825
Uruguay	---	---	16,380	16,380
Venezuela	---	---	84,630	84,630
Others (8)	---	---	2,275	2,275
TOTAL	715,000	294,920	805,975	1,036,865

[1] Information taken from "Newsprint Data: 1974", published in July, 1975 by the Canadian Pulp and Paper Association.
[2] This figure refers to the newsprint mill presently under construction in the Delta area of Argentina by

Footnotes to Table 8 continued ---
 Papel Prensa, S. A., based on willow and poplar.
[3]The figure given by the Technical Association of the
  Argentine Pulp and Paper Industry (ATIPCA) for news-
  print demand in the country during 1974 amounts to
  187,425 Mt.
[4]This figure includes the following mills:

Tuxtepec:	70,000 MT/y	(1975 expansion)
Pronapade:	60,000 MT/y	(under construction, based on de-inked stock)
Mexpaper:	100,000 MT/y	(under construction, based on sugarcane bagasse)(1st module)
TOTAL	230,000 MT/y	

[5]1974 Production figure given by Tuxtepec in June 1975.
[6]Net demand obtained by adding Tuxtepec, production
 figure to import figure given in "Newsprint Data:
 1974".
[7]This figure refers to the capacity of the bagasse
 newsprint mill presently under construction by
 INDUPERU, near Trujillo, Peru.
[8]Includes Barbados, Netherlands Antilles, West Indies
 and others.

TABLE 9
Main Newsprint Consuming Countries in Latin America

Country	Newsprint Demand in MT/y[1]		
	1960	1970	1974
Brazil	185,807	262,890	263,900
Mexico	99,813	286,256	211,200
Argentina	144,287	259,291	150,150
Venezuela	23,590	84,119	84,630
Colombia	33,181	56,599	54,600
Chile	26,855	47,523	47,000
Peru	18,139	49,532	46,410
TOTAL	531,672	1,046,210	857,890

[1]Source: Canadian Pulp and Paper Association

still fewer countries, even considering the mills pres-
ently under construction.

Available figures also show that the peak for
newsprint demand in Latin America was reached around
1970, then diminished considerably in subsequent years,
showing some increment in 1974.

With regard to the sources of supply of newsprint
imports by Latin America, Canada has been the main ex-
porter to this region. According to figures from the
Canadian Pulp and Paper Association, Canadian exports
to said region amounted to around 190,000 MT in 1960,
580,000 MT in 1970 and 590,000 MT in 1974. This last
figure represents about 73% of all the newsprint im-
ports by Latin America. Scandinavia constitutes the
other main newsprint supplier to this area, although it
must be kept in mind that Chile exports close to 60% of
its present newsprint production to other Latin Ameri-
can countries.

However, the main conclusion that can be drawn is
that despite newsprint production having remained prac-
tically static for many years in Latin America, this
situation is rapidly changing with new mills scheduled
to start operations in 1976, 1977, and 1978, which, on
reaching rated production, will more than double the
present capacity of this industry.

Furthermore, the potential for new projects is
quite good. In fact, projects totalling over a million
metric tons per year of capacity are presently under
serious consideration in several countries, as describ-
ed in the preceding chapter, providing ample possibil-
ities for future development of this industry in this
area.

A fundamental consideration in this dramatic
change is the fact that this new capacity is based on
technology developed within the region for the exploi-
tation of local cellulosic resources, once classified
as ¨secondary fibers¨.

Obviously, this is the result of the work of many
dedicated specialists in several countries to find the
most economic approach to newsprint manufacture, under
the particular circumstances and conditions prevailing
in each case. This endeavor has turned what seemed to
be a distant dream in 1970, that of reaching self-suf-
ficiency in the regional supply of newsprint, into

practically a reality. Considering the new mills under
construction, plus those already operating, as well as
the projects now under study, the mentioned goal should
not be very far away.

In fact, taking into account the large availabil-
ity of fiber resources in Latin America, as well as the
herein described technological development effort, who
knows where this situation could eventually lead?

SUMMARY

Despite the fact that Latin America possesses con-
siderable fiber resources, it has traditionally been
deficient in the production of pulp, paper and forest
products and has had to import these products from
other areas, such as the U. S., Canada and Scandinavia.
Newsprint represents the single most important item of
these imports.

However, there has been a considerable effort over
the past years to develop technology within Latin Amer-
ica, especially adapted to the nature of the fiber re-
sources available in this area. This effort has re-
sulted in a considerable growth of the paper industry
in some of the countries of the mentioned area, based
on an ever increasing use of local raw materials.

ATCP organized the first Latin American Pulp and
Paper Week in conjunction with its XV Annual Convention
with the main purpose of presenting examples of the
mentioned technological development·efforts. A group
on newsprint was organized during said convention, and
papers on development efforts related specifically to
newsprint were presented by several countries, such as
Argentina, Brazil, Chile and Mexico.

This endeavor has led to the construction of three
new newsprint mills, one in Argentina, based on poplar
and willow, one in Peru and another in Mexico, both of
these based on bagasse. Additionally, there is another
mill in final construction stages in Mexico which will
produce newsprint from de-inked stock, based on techno-
logy developed in the U. S. and which will be importing
waste paper also from the U. S.

Newsprint production in Latin America has been
based for many years on the operation of four mills,
two in Chile, one in Mexico and the other in Brazil.

The capacity of these mills has not increased signifi-
cantly over the past years and has allowed covering
roughly 30% of the regional demand for newsprint. How-
ever, when the new mills under construction come on
stream, installed capacity will be more than doubled,
which is, indeed, an important change with respect to
previous years.

Therefore, the present paper has been prepared
with the object of describing the development effort
behind the newsprint mills already in operation in
Latin America, as well as those now under design and
construction, using as a basic reference the papers
presented on this subject at the mentioned Latin Amer-
ican Pulp and Paper Week.

Furthermore, an analysis is made of the market and
supply situation and also of the potential for future
newsprint projects in this area. These potential proj-
ects, together with the mills presently in operation or
construction, could contribute enormously to the goal
of covering Latin American requirements for this com-
modity, based on technology developed within this regin
for the most efficient use of local raw materials.

Acknowledgments

3. ¨Utilizacion de Fibras Cortas en la Fabrica-
cion de Papel Imprenta¨, Ing. Claudio Lobe, ABCP
(Brazil).
4. ¨El Proyecto Argentino de Paperl para Diario¨,
Ing. Carlos Baques, ATIPCA (Argentina).
5. ¨Analisis de Madera y Pastas de Alto Rendi-
miento de Nuevo Clones Hibridos de Sauces¨, Dr. Edmundo
Fiano y Colaboradores, ATIPCA (Argentina).
6. ¨Consideraciones Tecnico-Economicas en las
Fabricacion de Papel Periodico a partir de Bagazo de
Cana de Azucar¨, Dr. Dante S. Cusi, Compania Industrial
de San Cristobal, S. A.

The author would also like to express his appre-
ciation to ATIPCA of Argentina, ABCP of Brazil, ATCP-
Chile, Fabricas de Papel Tuxtepec, S.A. and Compania
Industrial de San Cristobal, S.A. for additional in-
formation and special assistance received in the prep-
aration of this paper.

Special mention is made of Promotora de Papel
Periodico, S.A. de C. V. for having permitted the
author to use information contained in reports prepared
for said company, covering the testing and verification
program carried out by Promotora on bagasse newsprint
manufacture.

The author would like to especially thank Mr.
Samuel K. Miran of Compania Industrial de San Cristobal,
S.A. for his help in reviewing and correcting the text.

5

Australian Developments in Paper Science and Technology

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Progress in the pulp and paper industry in Australia has been largely connected with the development of appropriate technologies for processing the indigenous raw materials, particularly *Eucalyptus* woods, which form the main base of our pulping and papermaking economy. Eucalypts and a few other hardwoods are used for kraft, soda, neutral sulphite, cold soda, chemigroundwood and groundwood pulps, and for hardboard manufacture. Plantation-grown pines also provide a significant part of the pulpwood resources, particularly *Pinus radiata*, which is used for kraft, neutral sulphite, bisulphite and refiner groundwood pulp, and to a lesser extent *Pinus elliottii*, which is used for chemimechanical pulp.

Eucalypts

The eucalypts, of which there are hundreds of species, vary widely in respect to their pulping and papermaking characteristics, with age, species and growth rate controlling essential properties such as basic density and extractives content. *Eucalyptus* plantations are not extensive in Australia, most of the pulpwood being drawn from virgin forests or from naturally regenerated forests which have been cut over in previous procurement cycles, mostly for sawmilling. The wide diversity in wood quality within the genus does not appear to be fully appreciated outside Australia, and a minimum definition of a pulpwood resource must include tree age, or at least whether old growth or regrowth, species composition and basic density. It has been shown (1) that alkali requirements, yield and pulp strength may be explained in terms of species, age, basic density and extractives content.

As pulpwood the young low-density hardwoods are to be preferred to older and denser woods on most grounds - low chemical consumption, higher pulp yields, easier chemical recovery, minor extractives problems, higher bonding strength, and smaller vessels with less picking in off-set printing. When these advantages are considered alongside the rapid growth rates attainable with some

134

eucalypts it is not surprising that some pulp and paper
manufacturers are showing increasing interest in plantations.
Recent experiments (2) have shown that nitrogen and phosphorus
fertilizers at a rate of application of 200 kg/ha (N) and
90 kg/ha (P) give a 5-fold increase in biomass production of
Eucalyptus globulus after four years, showing that there is
immense potential for increasing the productivity of native
species on our low fertility soils.

A considerable amount of work is also in progress on the
genetic improvement of *Eucalyptus* species (3), interacting with
provenance studies, hybridization, vegetative propagation and the
breeding system of *Eucalyptus regnans*. Significant differences
in wood basic density have been revealed between families (4) and
we have shown (5) that these are sufficient to have an appreciable
effect on paper properties, bonding strength being higher and tear
lower for wood of lower density.

Research relevant to the development of our hardwood
resources has been concerned with quite complex relationships
between the properties of wood, fibre, pulp, paper, pulping
liquors and effluents. Over the last 25 years work in various
countries, including Australia, has led to a sharper picture of
the basic requirements of papermaking materials, particularly in
relation to hardwoods; the essential features of this picture are
as follows.

Basic Requirements of Papermaking Materials

In the cellulose fibre we have a relatively cheap, renewable
raw material which is well suited to form the basis of the paper
industry because of its molecular and anatomical characteristics.
Lateral association between the long cellulose molecules through
hydrogen bonding provides the essential components of strong
fibres. Similarly, in the usual types of paper the fibres are
held together by hydrogen bonds which develop between them as the
wet sheet is dried. These interfibre bonds are also largely
reversible under conditions which are sufficiently mild to permit
easy reclamation of the fibres for further use.

In the relationship between the properties of paper and the
wood of other plant material from which it is made, we regard the
lateral conformability of the fibres as occupying a central
position (6, 7). Lateral conformability may be defined as the
reciprocal of the load required for fibre collapse. On the wood
side it is largely dependent on the ratio of fibre diameter to
wall thickness, which is normally the principal morphological
factor in basic density, and on the paper side it controls the
relative bonded area of the sheet and hence a range of sheet
properties. Conformable fibres can collapse during pressing and
drying of the paper web in such a way as to provide a high bonded
area which makes best use of the hydrogen bonding potentiality of
the hydroxyl groups in the pulp.

Extraneous materials, or extractives, occur in varying amounts in wood, often in the cell cavities, or lumens, or in the vessels of hardwoods. The extractives content is strongly dependent on the species, the age of the tree, and the position in the tree, being higher in the heartwood and in the older trees. The occurrence of ellagitannins in eucalypts may give rise to problems not encountered with the gallotannins present in most hardwoods (8). If present in the wood in large quantities the extractives can be extremely troublesome in various ways: by increasing the consumption of chemicals during pulping and bleaching, by giving rise in some instances to residual pulping liquors of high viscosity and poor swelling and burning properties (9), by sometimes causing deposits to form on various pieces of equipment in the pulp mill, and by affecting paper quality because of their colour or that of their degradation products.

Other anatomical features of the wood are significant for its utilization in papermaking. The vessel elements of hardwoods survive the pulping and bleaching processes and may often lie flat in the surface of the paper sheet. If the paper is used for offset printing the vessel segments tend to lift out or "pick" leaving white areas, and destroying print quality to an extent which is dependent on the size and concentration of the vessels.

Post-War Technological Changes

The NSSC process has been particularly successful as applied to Australian eucalypts. Both old and regrowth wood is used for corrugating medium and regrowth pulp is also suitable for inclusion in furnishes for wrapping and bag papers (10). Eucalypt NSSC papers behave very well on corrugating machines and give rise to fibreboard with high flat crush. Cold soda pulps from eucalypts have been used successfully as components of newsprint, fine papers and magazine grades. The suitability of eucalypts for the production of cold soda pulps is related to their sensitivity to swelling agents. Experiments conducted by the late R.S.T. Kingston and B. Budgen (11), along the lines of similar work by Lagergren et al on Scandinavian woods (12), have shown that when eucalypt wood is treated with cold caustic soda at a concentration of 5 to 10 per cent, the tensile strength is reduced to about 30 per cent of its original value, whereas a similar treatment applied to radiata pine only results in a reduction to about 85 per cent. The higher hemicellulose content of hardwoods would be expected to contribute to the swelling behaviour and to give rise to separation between the S_1 and S_2 layers of the cell wall (13).

The manufacture of newsprint from eucalypts at Australian Newsprint Mills Ltd. (ANM) is an interesting story (14). The principal constituent of the newsprint furnish from the outset has been stone groundwood. The preferred grinding wood was that

from the very old trees, up to several hundred years, whereas the young eucalypts were found to have poor grinding properties (15). This effect is thought to be the result of prolonged acid hydrolysis facilitating the process of mechanical fibre separation (16). As supplies of the most suitable grinding wood declined and as higher machine speeds were required, the cold soda process (17) and alkaline grinding were introduced, and more recently eucalypt groundwood with improved properties has been produced from impregnated billets of younger wood (18).

Other technological innovations include the development by Associated Pulp and Paper Mills Ltd. (APPM) in association with Kamyr AB, of a successful countercurrent continuous digestion system for the manufacture of hardwood soda pulps (19), the successful operation by the same company of the wet oxidation recovery process for soda black liquors (20), the manufacture of tissues at the Apcel mill of Kimberly-Clark of Australia from bisulphite pulps from plantation-grown pines and the development of novel methods of pitch control in that operation. It is reported that an Australian company, Smorgon Consolidated Industries (SCI), has taken up the first foreign licence of Sonoco's sulphite recovery process, which involves pelletizing of the spent waste liquors with alumina and subsequent exposure to high temperature, resulting in the recovery of make-up chemicals for pulping.

On the papermaking side of the industry there has perhaps been a more ready acceptance of imported technology than on the pulping side, which is closer to the indigenous raw material and its peculiarities. However, reference can be made to the early introduction by Australian Paper Manufacturers Ltd. (APM) of Inverform - Fourdrinier machines, which proved to be very successful, and to the application of computer control (21). In Australia liner- and boxboards are predominantly of multiply structure with a large waste paper component (ca. 80%). Solid Fourdrinier kraft boards are used only for special applications. Thus APM has installed Fourdrinier - Inverform systems, and SCI has recently commissioned a Dorries machine with three Fourdrinier formers. Improvements have also been made by APM in headbox design, and wet web evaluation has been successfully applied at ANM to the control of papermaking processes (22). Useful contributions have been made in the control of cockling, associated with a short laboratory study of the rheology of the drying web (23), and in the application of wet end additivies, having regard to the electrokinetic properties of the fibres and other furnish components (24, 25).

Pilot equipment has been developed (26) for a process (27) which involves addition of a starch solution between the newly formed plies at the wet end of a machine making multi-ply board, with the result that it should be possible to increase machine speed by eliminating the starch application at the size press. To the extent that product quality is also improved by this technique,

it should be possible to increase the proportion of waste paper
and still meet the previous strength specifications. If white
liner boards are required, suitable pigments may be incorporated
between the outer ply and the remainder of the board (28) thereby
whitening and opacifying the waste paper substrate and reducing
the requirements for bleached virgin pulp in the outer layer.

Other process improvements include the development by APM of
satisfactory methods for pelleting NSSC pulp for interstate bulk
transport; simple modifications to pulp washers, based on an
appreciation of the mechanism of incipient interfibre bonding,
which greatly increased their efficiency; and the development by
CSIRO and ANM of a greatly simplified technique for removing
ellagic acid deposits from pulp mill equipment by using
hypochlorite bleach liquor in a specific pH range, instead of
concentrated nitric acid (29).

A new bleach plant at our largest pulp mill (APM Maryvale)
has a number of novel features in process and plant design. The
4-stage bleaching sequence is not unique but is unusual. The
sequence employs a calcium hypochlorite pre-treatment before first
stage chlorination, followed by caustic extraction, chlorine
dioxide and calcium hypochlorite stages. The sequence eliminates
washing between the chlorine dioxide and hypochlorite stages, and
is therefore accomplished with only three washing steps.

In the converting field there have been a number of
interesting developments. In a period of resorcinol shortage, a
starch-tannin corrugating adhesive was developed which provided
adequate water resistance (30). New methods of waxing corrugated
fibreboard containers have emerged and have been applied
industrially.

Possibilities for Utilizing Denser Woods

The development of the wood chip export industry in Australia
has taken place within the last few years, the first plant, in New
South Wales, commencing to export in 1970, another in Tasmania the
following year, two more in Tasmania in 1972 and another in
Western Australia in 1976. The industry has stimulated a
considerable amount of research into the relationships between
wood and pulp properties, particularly in relationship to the
requirements of the industry in Japan, which is the sole market
at present.

The relationship between wood density and paper properties is
of considerable economic interest in Australia and in other
countries concerned with hardwood pulping or with chip export. A
wide range of density is encountered within the genus *Eucalyptus*
and throughout the large number of genera occurring in the tropical
rain forests which will probably yield increasing quantities of
pulpwood in the near future. An understanding of the effect of
wood density and structure on paper properties is already
contributing to the wider utilization of hitherto unused species,

either individually, as components of heterogeneous chip mixtures, or as pulps with special properties for inclusion in appropriate proportions in papermaking furnishes.

High density is a reflection of a relatively thick fibre wall. When the wall thickness is low in relation to the fibre diameter, the fibres can collapse into flat ribbons during the papermaking process, thus providing a highly bonded structure with high strength and a smooth surface suitable for writing or printing. If however the fibre wall is thick as in dense woods, the fibres retain their cylindrical shape during the papermaking process, with the consequence that the interfibre bonding is most imperfect, the bonding strength of the paper is low and the surface of the paper comparatively rough. The tearing strength of such paper can however be quite high. Furthermore, fibres from dense woods can provide a bulky sheet which in some circumstances could be an economic advantage in that paper meeting a particular thickness specification can be made from a smaller amount of fibrous material, providing that the strength level is adequate. High bulk can also be a desirable physical property insofar as it is associated with compressibility characteristics which may facilitate certain printing operations.

For Australian eucalypts, wood basic density, which ranges from 300 to 1000 kg m^{-3}, and extractives content are considered to be the main determinants of their pulping and papermaking properties. Unscreened pulp yield has been found (31) to pass through a maximum at a basic density of about 450 kg m^{-3}, with a serious decline in yield above 600 kg m^{-3}. Strength properties directly associated with interfibre bonding (breaking length and burst factor) decline steeply as wood density rises from 500 to 650 kg m^{-3}, but much more gently at higher densities (32). This behaviour can be largely correlated with that predicted from a simple model involving the effect of cell wall thickness on the number of fibres in a sheet on constant basis weight, and on the extent to which the fibre collapses in the papermaking process. Pulping studies on about thirty individual tropical hardwoods from Papua New Guinea (33) also indicated that with increasing wood basic density there is a highly significant decline in paper strength properties associated with interfibre bonding. Bulk and freeness were significantly higher for pulps from the denser woods.

Although high density is an advantage for some purposes - in providing bulk, opacity and compressibility in the paper sheet, in reducing freight costs in bulk chip transport, and in increasing digester production efficiency - very dense woods are not generally favoured as pulpwood, on account of wear on chipper knives, lower pulp yields, and inferior pulp strength. They are unsuitable for some end uses, although laboratory work (34) indicates that bleached kraft pulps from dense hardwoods should be acceptable as a component of papermaking furnishes for the higher grade printing and writing papers. It is most unlikely that paper made predominantly from very dense woods could meet the

normal specifications for these grades, but when blended with
pulps from low density hardwoods, or with softwood pulps,
considerable proportions - up to about 30 per cent - could be
tolerated. Such pulps could probably be used also as components
of tissue papers.

The vessel picking problem in off-set printing tends to be
worse with paper from dense woods than from woods of low density,
even at the same vessel:fibre ratio, as has been shown by
comparing a very dense eucalypt (*E. tetrodonta*) with one of low
density (*E. regnans*). The greater bonding capacity of the
laterally conformable fibres from the wood of low basic density
results in the vessel segments being bound more firmly into the
paper surface than is possible with the uncollapsed fibres from
the dense wood (35).

The use of wood species which are not pulped commercially at
present, such as those of higher density, could allow improved
management techniques to be practised in established forests, and
could open up a number of remote areas for development as well as
increasing the availability of the raw material supply. The
studies of the effect of wood density on paper properties have
provided basic information of considerable use within the
Australian pulp and paper industries, to sawmillers interested in
the chipping of mill residues, in the development of export
industries in Australia and in Papua New Guinea, and in
international assistance programs in Asia and South America.

Recent Research

Mixed Tropical Hardwoods. Much work has been done in
Australia on the pulping of mixed tropical hardwoods from SE Asia,
particularly Papua New Guinea. These have been found to be
suitable for the preparation of unbleached pulps for use in
linerboards, bag and sack papers, wrapping paper and corrugating
medium, and bleached kraft pulps from some forest areas appear to
be suitable also for high-grade printing and writing papers (33,
36). Kraft pulps from the mixed tropical woods when compared with
established eucalypt pulps require more alkali in their
preparation, are usually of lower yield, have a higher initial
freeness, require more beating to reach a specified freeness, and
show comparable strength properties at a given freeness.
Bleaching requirements and optical properties are similar. In the
use of mixed hardwood pulps for papermaking, the range of wood
density and fibre types does not appear to be a major problem.

Tests on composite samples from different areas of Papua New
Guinea have shown little variation in pulping properties, even
when the species composition of the forests has differed markedly
(37). However, it is quite invalid to conclude that all tropical
forests will be equally suitable as pulpwood resources. The mean
basic density of potential pulpwood resources in S.E. Asia and
N.E. South America, for example, may differ by more than 200 kg/m^3,

with consequent effects on pulp yield, paper quality and processing costs. Some forests may contain certain species which cannot be economically processed on account of high silica content or some other undesirable feature. In PNG, however, it seems likely that species exclusion can be kept to a very low level.

Trees of Small Diameter. A major advantage of pulpwood plantations is that they may be mechanically harvested at an early age. With species which coppice easily, mechanical harvesting can be particularly effective. Coppice-regenerated *Eucalyptus viminalis* with a period of rotation of 6-8 years can provide a useful source of chip material (38). After removal of leaves and twigs during the harvesting operation, the remainder of the material above ground can be utilized for pulp and paper or fibreboard production.

A recent study (39) has shown that young trees of *Eucalyptus sieberi* can be pulped quite satisfactorily without removing the smooth inner bark. Work on young *Eucalyptus globulus* has shown that the use of unbarked wood has only a slight influence on pulp quality (40). Similar studies have been carried out on young *Eucalyptus regnans* and on branchwood from *Eucalyptus diversicolor*, again with very good results. Thus the fibre supply can be substantially increased from a given area, thinning of regrowth in fire-affected areas can be made more economic, and waste can be reduced. Even the stringy bark of species such as *Eucalyptus muellerana* can be converted into pulp, but with a rather high chemical consumption and low pulp yield.

It has recently been shown (41) that pulping of 8-12 years old *Eucalyptus globulus* and *Eucalyptus delegatensis*, with bark present, by the cold soda process had no significant deleterious effects on pulp strength properties when compared with the same trees with bark removed, but pulps from *E. obliqua* showed some deterioration in strength due to the large amounts of dead bark associated with this species.

Sawmill Residues. In the United States the pulp produced from wood residues rose in the quarter century 1945 to 1970 from zero to nearly a quarter of the total fibrous material used in domestic paper and paperboard mills. Although we have made a start in Australia we have a long way to go in the utilization of sawmill residues. On the north coast of New South Wales some 400,000 tonnes of dockings, slabs and edgings are produced by local hardwood sawmills and would provide an excellent basis for industrial development in this region. In southern N.S.W. and eastern Victoria, large-scale utilization of hardwood sawmill residues is already being achieved. Environmentally residue utilization has many advantages, including elimination of smoke pollution where the waste is disposed of by burning.

Sawdust. Interest in sawdust for pulping has increased
rapidly because of the rising cost of pulpwood and its decreased
availability, compared with the ready availability of huge
quantities of sawdust as a waste product of the timber industry.
Softwood sawdust has been found to be more suitable for pulping
than that from hardwoods because of the greater fibre length of
softwoods, which results in a lower proportion of very small
fibre fragments after sawing. The total amount of softwood
sawdust available in Australia is of the order of 100,000 tonnes
(o.d.) per year and there are several locations where softwood
sawmills and pulp mills are in reasonably close proximity and
sawdust utilization for pulping would be feasible because of low
freight costs. Work with various types of radiata pine pulp (42)
has led to the conclusion that sawdust pulps may be added to pulps
prepared from wood chips in proportions up to about 10 per cent
without rendering these unsuitable for many of their present uses.

Forest Residues. Very large amounts of sound wood suitable
for conversion to fibre are being left in hardwood logging areas
in the form of felled trees which are defective for sawmilling
purposes, stumps, tops, branchwood and overmature derelict trees.
In addition, many forests urgently require thinning of pole-size
trees to achieve satisfactory growth in the remaining trees. An
immense volume of potential pulpwood is available, and even if
utilization were restricted to the most favourable circumstances
a very significant addition could be made to the total residues
available for chipping. This could lead to reduced fire hazard,
improvement of existing stands, both by removal of felled waste
and by thinning, and of course to better utilization of the
forest resource. The removal of old logs from the forest floor
would also facilitate subsequent harvesting operations. Attention
is being paid, however, to the problem of nutrient loss.

Non-Wood Fibres. Fibre sources other than wood have received
some attention, and in particular a study has been made of the
possibilities of establishing a pulp and paper industry based on
kenaf grown under irrigated conditions (43). This work forms part
of a program directed towards the possible development of
integrated photosynthetic product industries (44), and envisages
production of protein from the crushed stems, stock feed from the
green tops and vegetable oil from the seeds, as well as long and
short fibres, from the bark and woody stem respectively.

Pulping. A considerable research effort is being put into
the pulping field. The value of sequential pulping has been
advocated (45) and it has been shown (46) that when *Eucalyptus
delegatensis* is pulped by a two stage process - sodium
hydrosulphide followed by sodium hydroxide - yield, strength and
chemical consumption relative to a single-stage kraft cook are
improved when the sulphur uptake is achieved in the first stage,

the second stage representing an alkaline extraction of the already formed thiolignins.

Much of the early work on holocellulose pulps was carried out in Australia, and somewhat in this tradition cold soda pulps have been used at APPM as a starting point for the preparation of delignified, hemicellulose-rich pulps for greaseproof papers by treatment with sodium chlorite, chlorine dioxide and by multistage chlorination (47).

Eucalyptus regnans has been successfully pulped with concentrated sulphur dioxide solutions and with saturated sulphur dioxide vapour (48). High pressure carbon dioxide solutions have been used to produce explosion pulps from *Pinus elliottii* (49). In addition to these approaches a new look is being taken at hydrotropic pulping (50). The effects on kraft pulping of electron beam pre-irradiation of the wood, and of simultaneous pulping and gamma-irradiation have been evaluated (51). Two-stage oxygen pulping has been studied in some depth at APPM (52).

In respect to the possible replacement of chemical pulps by high-yield pulps, some success has been achieved by the production on a laboratory scale of a new type of high-yield pulp - eucalypt CTMP (chemithermomechanical pulp) - with a well-balanced range of properties (53). Considerable interest is also being shown in the potentialities of thermomechanical pulps from pine.

Conclusion

Australia appears to be on the threshold of technological advances connected not only with the utilization of her traditional raw materials, but also with the identification and establishment of new resources, and with their development. This situation may be expected to lead to the better use of cellulosic materials, in ways which are both industrially efficient and socially acceptable.

Abstract

Progress in the pulp and paper industry in Australia has been largely connected with the development of appropriate technologies for processing the indigenous raw materials, particularly *Eucalyptus* woods. Relevant research has been concerned with the relationships between the properties of wood, fibre, pulp, paper, pulping liquors and effluents. Industrially, major post-war technological changes include the application of neutral sulphite and cold soda pulping to indigenous hardwoods, the development of continuous countercurrent soda pulping, the development of methods of utilizing regrowth eucalypts for newsprint manufacture, the early introduction of Inverform-Fourdrinier machines, the manufacture of tissues from plantation-grown pines, the application of the wet oxidation recovery process and the development of wood chip export projects. Currently considerable attention is being

paid to possibilities for the economic development of a small-scale non-polluting pulping process, thermomechanical pulping of pines and chemithermomechanical pulping of hardwoods, residue utilization and the possible development of integrated photosynthetic product industries.

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No attempt has been made in this brief review of technological
developments to present a comprehensive account of scientific
work connected with the pulp and paper industry. Nor has any
description been given of the structure of the industry in
Australia. However, a report has been prepared (54) which
includes an economic review and discussions on future
requirements, environmental problems, and changing technologies,
together with descriptions of the various sectors of the industry,
including individual companies.

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      Working Party 4 (Pulp and Paper) - Australian Forestry
      Council, Canberra (1974)

Technological Change in the Canadian Pulp and Paper Industry

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Just as necessity is the mother of invention, so
economic and social pressures are the parents of
technological development. Thus, to understand the
developments taking place in the Canadian pulp and
paper industry, it is important to first view the econ-
omic environment affecting this industry.

Canada appears on the map as a huge land mass of
some 3,850,000 square miles, over 200,000 square miles
greater than the United States and approximately 22
times the size of Sweden.

Of this land area, about one-third is forest and
about one-quarter of it, or 950,000 square miles, is
suitable for timber harvest. About 80% of it is soft-
wood.

Most of this wood occurs in the boreal forest
region which is 4,000 miles in length and about 500 to
600 miles wide. This strip is a continuation of the
similar softwood forest that stretches from the Scandin-
avian Peninsula to the Bering Sea. It consists predom-
inantly of spruce, balsam, fir and pine. In its
southern reaches, the softwood forest is interspersed
with aspen and birch.

Of great commercial importance is also the special-
ized rain forest of the coast forest region, which
covers the lower slopes of the mountains facing the
Pacific Ocean. These forests, which are a continuation
of the coastal strip that runs north through Oregon and
Washington, consist principally of Douglas fir, western
hemlock, red cedar and sitka spruce. This region
supplies the world with structural timbers. In this
region, the pulp and paper industry grew up entirely as
a scavenger to absorb the residues of the sawmills,
while in the eastern boreal regions, wood is harvested
principally as pulpwood.

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Canada has a population of about 23 million people, most of whom live in a narrow strip along the southern border. In commercial terms, Canada can be envisaged as a small country, surrounded by three great trading blocks: the European Common Market (population 250 million); the United States (population 215 million); and Japan (population 110 million), as shown in Figure 1.

Each of these trading blocks is to some extent dependent on Canadian fiber, and is willing to buy large amounts of it, provided that Canadians do not add too much value first. Thus, commodities such as newsprint and kraft pulp can be exported tariff free, but fine papers and linerboard have to cross tariff barriers. Consequently Canada produces about ten times as much newsprint for export as it uses domestically, and ten times as much market pulp [1]. But fine paper and other higher value grades are produced on a scale that is only about 30% greater than domestic consumption. (Figures 2,3,4).

Although both pulp and newsprint have to meet fairly rigid quality specifications, their prices are based not so much on quality as they are on world market prices, which in turn are dependent on the balance between supply and demand. The profit margins of companies that supply world market commodities are determined to a large degree by the extent to which raw material costs, labor and transportation costs can be minimized. Thus, market pulp and newsprint are typical cost minimizing industries. This is in sharp contrast with industries such as computer manufacturers, which compete, and hence price their products on the basis of performance, or industries such as consumer goods which compete on the basis of sales maximization [2]. These three categories of industrial behavior can also be applied to pulp and paper products, as shown in Figure 5.

It is therefore not surprising that technological change in the newsprint and pulp industries is heavily weighted towards processing efficiencies rather than towards new product development.

Another major factor that shapes Canadian industry as a major supplier of the world's newsprint and pulp demand is that Canada, like Scandinavia, is faced with the environmental problems associated with wood procurement and manufacturing (particularly air and water pollution) rather than the problem of consumption (solids waste disposal and recycling).

A further characteristic of the Canadian pulp and paper industry is that Canada is not wood limited.
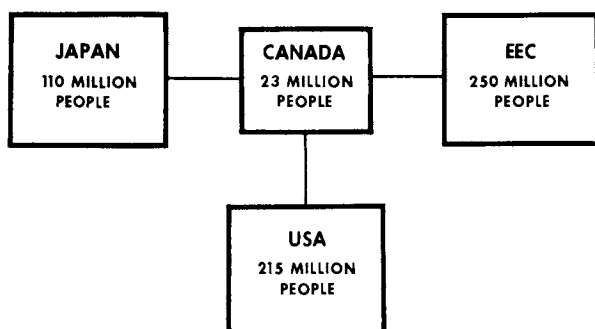
Figure 1.   Canada's neighbors
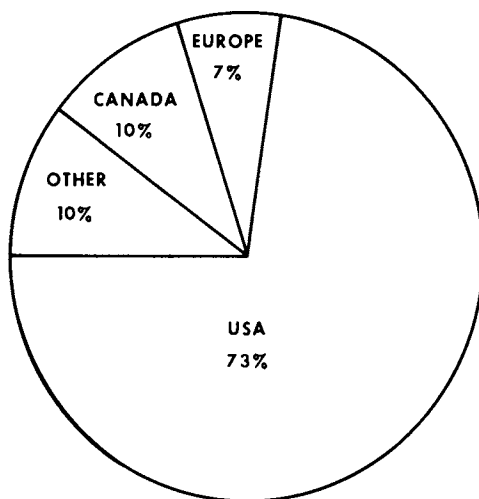
*Figure 2.   Destination of Canada's newsprint
production, 1974*
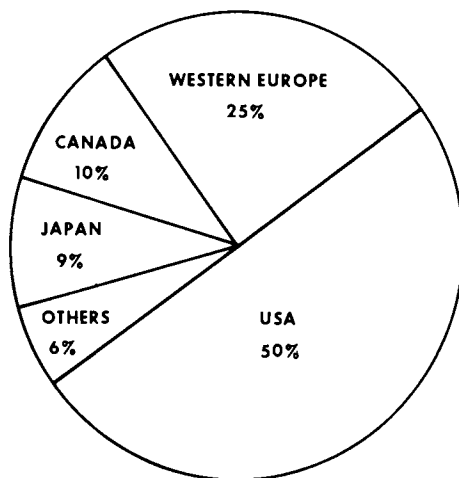
*Figure 3. Destination of Canada's paper
grade market pulp production (both chemi-
cal and groundwood), 1974*
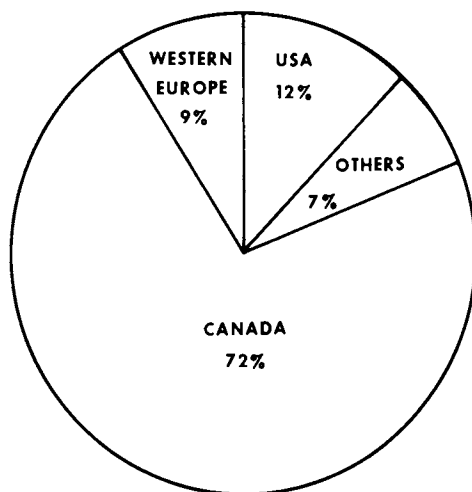
*Figure 4. Destination of Canada's other
paper and board products (excluding news-
print), 1974*

There are enough suitable sites in Canada to support an additional 10 or 11 kraft pulp mills of 1000 ton per day (another 3 million tons per year, or one-half again the present tonnage of market pulp). This differentiates Canada from Sweden, which has reached the limits of its domestic wood supply. Nevertheless, growth in Canada's productive capacity is limited by other economic factors, especially capital cost, cost and availability of labor, access to markets, and decreasing political influence of the primary manufacturing sector.

To summarize, then, the thrust of technological change in the Canadian pulp and paper industry is concentrated in the areas of raw material cost reduction and operating efficiency improvement.

In the following section, some trends in response to these pressures will be reviewed by examining the rate of exploitation in Canada of refiner mechanical pulp, twin wire formers for newsprint machines and continuous digesters.

Refiner Mechanical Pulp

Mechanical pulp is the main raw material in the manufacture of newsprint. Traditionally, it has been manufactured by the grinding of barked logs held against a revolving grindstone, in the presence of water. This process results in a high opacity, low strength wood pulp with a yield based on wood of about 95%. Because of the low strength of "groundwood", both as a wet web on the paper machine and as finished paper, it is necessary to add usually between 20% and 30% long fibered chemical pulp to the furnish. This chemical pulp serves as a reinforcing material increasing the efficiency of the newsprint machine.

In the late 50's, a new process for producing mechanical pulp was introduced -- almost simultaneously in Canada and in the U.S. [3]. This was the manufacture of mechanical pulp from wood chips or other wood residues using disc refiners.

Refiner mechanical pulp has three cost minimizing advantages compared to stone groundwood: reduced labor, cheaper and more readily available fiber, and reduced paper furnish costs. This latter advantage is a result of refiner pulp being considerably stronger than stone groundwood.

Initially refiner mechanical pulping grew rapidly in Canada, but quickly lost momentum in its move to replace stone groundwood (Figure 6). The promise of major savings in chemical pulp with the use of chip
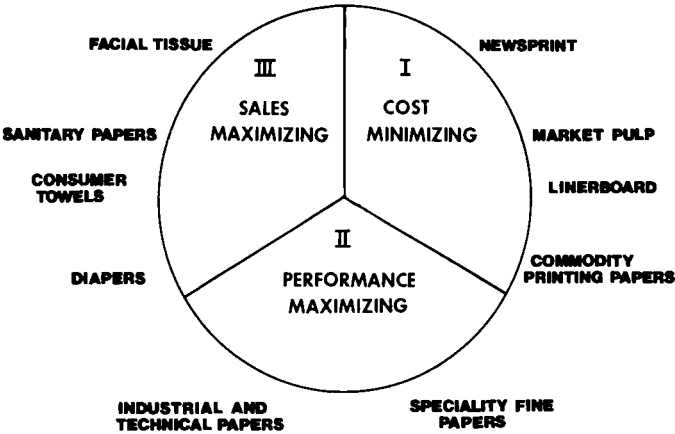
Figure 5.   Classification of pulp and paper products
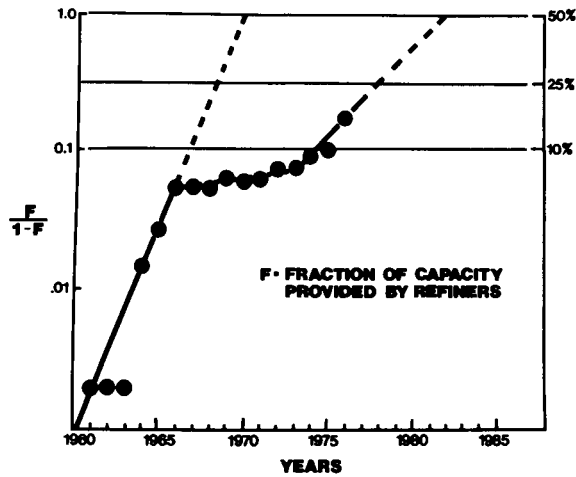
Figure 6.   Capacity substitution–RMP and TMP vs. total
Canadian mechanical pulp

refiner groundwood in modern high speed newsprint machines did not appear to be proving out and quality problems with low cost fiber, sawdust, were increasing. This latter problem was due to the trend to narrow kerf saws to reduce wood residue in lumber production.

Then in the early 70's, a "second generation" refiner mechanical pulping process was commercialized, based on many years of research and development work in Sweden, Canada and the U.S. [4,5,6]. This is now known as the "Thermomechanical Pulping Process". This process is carried out in disc refiners using chips preheated to about 135°C, a temperature which allows further softening, but is still low enough to avoid darkening of the lignin matrix. There now seems little doubt that thermomechanical pulp is capable of eliminating the chemical pulp in newsprint entirely in the spruce/balsam areas, and of reducing it to below 15% in the Pacific coast areas. This has led to the sharp upturn of the replacement curve, which predicts that 50% Canadian mechanical pulp production will be made by the refiner mechanical pulping process by 1983 (Figure 6). The possibility of using the very high yield pulp as a kraft pulp replacement in other products -- perhaps as a new market pulp, could accelerate the growth of refiner mechanical pulp capacity.

In view of the enormous cost, as discussed later, of building new chemical pulp facilities, the replacement of chemical pulp by thermomechanical pulp in newsprint may result in the release of substantial amounts of chemical (and particularly kraft pulp) capacity for market pulp. It is without question the cheapest way to obtain additional kraft pulp capacity, and is completely consistent with a cost minimizing strategy.

Twin Wire Formers

The fourdrinier paper machine held an unchallenged position in the paper industry from the middle of the 19th century until the early 60's. But research work on table roll drainage in the 50's was already undermining its virtual monopoly [7]. On the fourdrinier paper machine, water is removed from the pulp suspension on the wire by suction. This suction is provided by the separation of the surface of the table rolls from the wire (more recently by hydrofoils), and of course by the suction boxes and the suction couch roll.

The problem with water removal by suction alone is that the maximum pressure differential is, of course, one atmosphere. It was predicted that drainage at the

table rolls or foils of a paper machine would reach
this maximum at a machine speed of about 2800 feet per
minute, a speed that was being approached by newsprint
machines at the time. Thus further increases in
machine productivity, using the Fourdrinier design,
could only be attained by making the machines wider,
longer or both.

Each of these measures adds substantially to
capital cost and space requirements, and introduces
other mechanical difficulties. The time was therefore
ripe for a new approach.

The answer to the problem was to remove the water
by compressing the pulp suspension between two wires.
Confidence in the feasibility of this was reinforced
by the successful development of the twin wire board
machine (Inverform) by St. Anne's board mills [8] in
Bristol, England in the 50's. At the time of the
first Inverform installation in North America [9],
development work was well underway on twin wire formers
for newsprint. A major research effort at the Pulp
and Paper Research Institute of Canada led to the
development of the Papriformer [10].

The growth rate of twin wire newsprint machines is
shown in Figure 7 [11]. The most recent extrapolative
forecast suggests that 50% of Canada's newsprint capa-
city could have twin wire formers by 1982.

Continuous Digester

Since 1968 there has been a noticeable change in
the technology used for additional Canadian chemical
pulp capacity. Also at about the same time the
Canadian kraft pulp capacity started to show a reduced
rate of growth (Figure 8) [1]. From 1969 the share of
added capacity has been divided almost equally between
the continuous and batch digesters. During the pre-
vious 10 year period the added capacity strongly
favored the continuous digester (Figure 9).

The change in technology may be due to a number of
factors. In the mid 50's when the continuous digester
began to come into its prime it provided a ready solu-
tion for high steam consumption in batch digesters and
it produced a kraft pulp with slightly better strength
and better uniformity. The continuous digester had
other added advantages for the large scale installations
in the 60's -- it was more economical on space and
along with integral diffusion washing systems it became
more attractive for capital investment. During these
years, government incentives for building were strong
and forecasts of impending long fiber shortages were
widely believed.
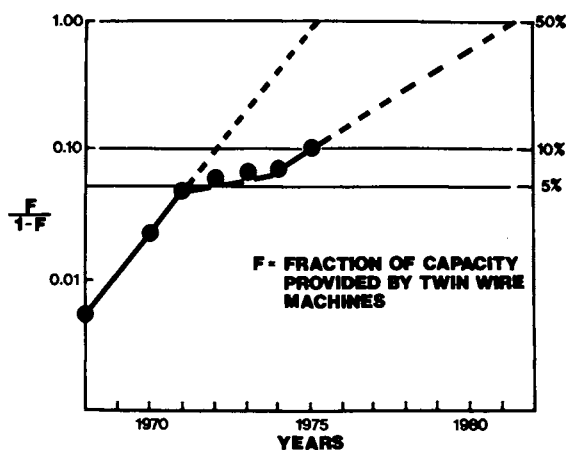
Figure 7. Capacity substitution–twin wire vs. total Canadian newsprint
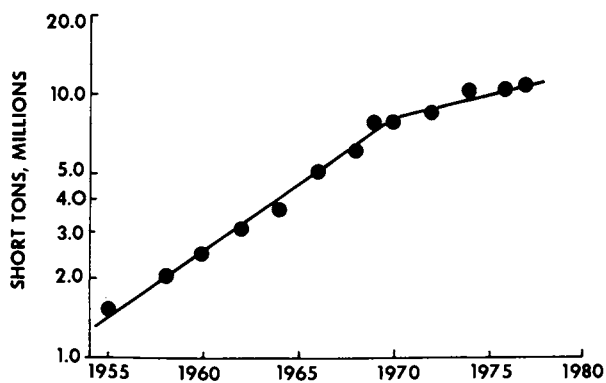
Figure 8. Canadian capacity of Kraft pulp, 1955–1977

A feature of the continuous digester has been that
the fines content of the chip feed must be kept at a
low level or plugging and heating circulation problems
will be encountered. The batch digester on the other
hand can accept significantly larger amounts of fines
and variable sized chips and still produce an accept-
able pulp quality. In the late 60's there began a
trend toward total utilization of the available sawmill
chips. In eastern Canada there was a trend to the
installation of stud mills adjacent to a pulp mill.
Both of these situations have led to a deterioration
in the quality of chips fed to the pulping process and
thus development has been directed back to the batch
digester to determine ways of reducing the steam con-
sumption in a period of rapidly escalating energy costs
and also to improve and make more uniform the quality
of the pulp.

Significant improvements were made in the late
60's and early 70's in the development of computer
control systems for batch digesters [12]. These
systems have been successful in optimizing the schedul-
ing of steam consumption and have also made significant
improvements in the uniformity of pulp quality.

During recent years there has also been a growing
desire for flexibility of operation in a pulp mill.
When a batch digester shuts down for maintenance, only
part of the pulp mill productive capacity is removed,
and frequently the on-line digesters can be sped up for
short periods of time at slight additional operating
cost but minimum effect of quality. Furthermore, the
major part of the added continuous digester capacity
since 1969 has been from four very large installations.
The added capacity from batch digesters has come from
a large number of incremental capacity increases across
Canada. The continuous digester is sensitive to
economy of scale, and today is probably suitable only
for expansions of 450 tons per day or more.

The growth rate pattern (Figure 9) for continuous
digesters demonstrates the danger of making purely
extrapolative forecasts.

Future Technology

The Pulp and Paper Research Institute of Canada
recently conducted a Delphi study for the Canadian pulp
and paper industry [13]. In this study the problem of
capital availability was basically foremost, although
the forecast for the growth rate of kraft mills demon-
strates an inconsistency. This problem of capital
availability is not specific to the pulp and paper

industry, neither is it specific to Canada, but it is probably the most important input to the pulp and paper industry's future strategies during the coming decade.

Capital availability represents a serious obstacle concerning the expansion of the kraft pulp industry -- for two reasons, economy of scale and inflation. The effect of economy of scale on the capital cost of bleached kraft mills is illustrated in Figure 10 [14]. Figure 11 shows the manifestation of this in terms of the capacities of the largest continuous digesters that have been installed during the last 20 years [15]. The effect of inflation is demonstrated by the actual cost of kraft mills built in Canada (Figure 12). The capital costs have been adjusted proportionately to bring them to a common level of 900 tons per day. This rate of increase is also apparent for most other capital components of the industry. Depreciation is based on actual rather than replacement costs, so that the difficulty being experienced by companies in generating the funds required for reinvestment is readily understood.

All this, of course, would not be too serious for the growth of the industry if it were capable of raising prices to whatever level was required to attract investment. It is meaningless to speak of such price increases in times of recession and over-supply. But even in the context of fiber shortages, as may well develop within a few years, the prospects for expansion along traditional lines are not encouraging. The need for the production of energy, food and shelter will probably receive higher national priorities than will fiber. Furthermore, there are potential substitutes for many paper grades, that can cause a reduction in consumption in the developed countries, such as microfilm and interactive TV that can move into traditional paper markets as the economics dictate. Thus abrupt price increases will result in market elasticity, the first signs of which are already beginning to show.

Can technology come to the rescue? Undoubtedly it can but the following should be considered. Assuming that it takes a minimum of 10 to 15 years to replace an established technology such as kraft pulping, then the laboratory work for a new small scale, low capital pulping process should now be well advanced in the laboratory if we are to see any significant change by, say 1985. No such technological revolution in chemical pulping is apparent today. Soda-oxygen pulping, which is advanced technologically today, is one important route towards the elimination of sulfurous air pollution, but is unlikely to present major opportunities for cost reduction.
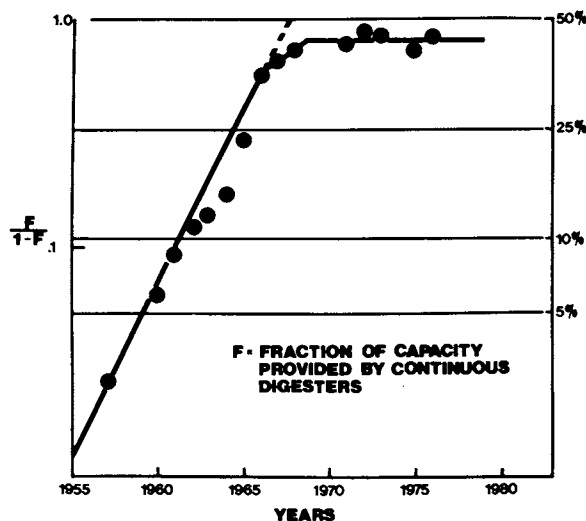
Figure 9. Capacity substitution–continuous digesters vs. total Canadian chemical pulp
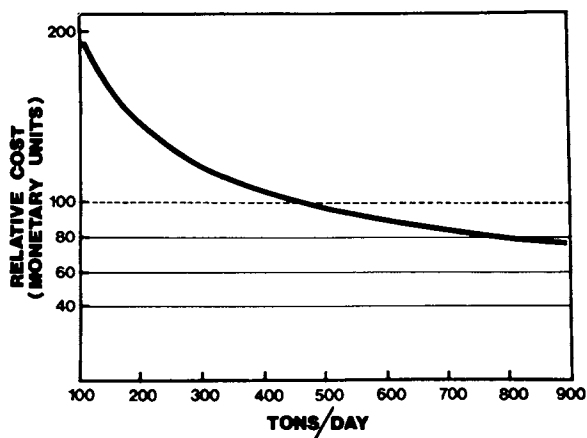
Figure 10. Variation of capital cost with size—bleached Kraft mill
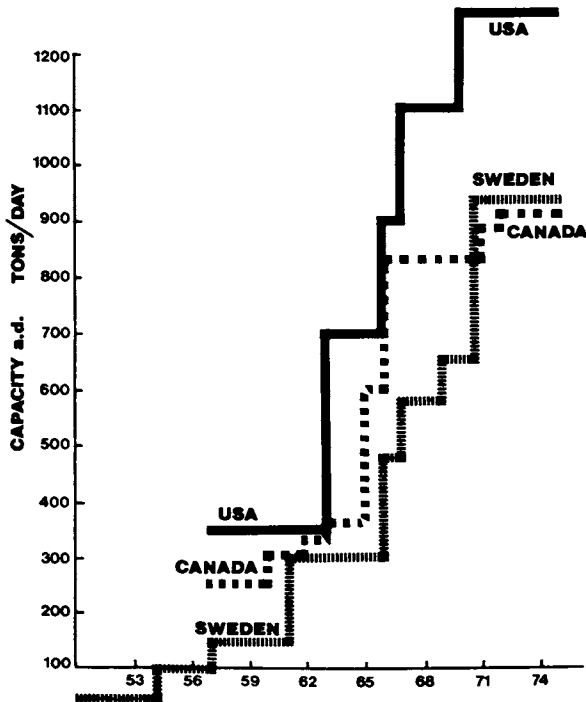
Figure 11.   Capacity of largest continuous digester

	CASE A 1967	CASE B 1972	CASE C 1977
CAPITAL COST/ ANNUAL TON	$268	$328	$698
TOTAL CAPITAL COST ($MM)*	80	98	209

*ASSUMING 300,000 TONS/YR. NOMINAL CAPACITY

Figure 12.   Escalation of capital cost—bleached Kraft pulp mills

The use of mechanical pulps wherever practical can be predicted. While the mechanical pulping processes are substantially less capital intensive, they also require a substantial external energy supply, unlike the chemical pulping process which uses the extracted lignin as a major source of energy. The capital required for this external energy must be taken into account in the overall picture.

In the sphere of papermaking, dry forming [16], in which the fibrous web is laid using air suspension rather than water, does hold promise for reduced capital cost, and is sufficiently advanced into the prototype stage, to have a potential impact by 1985. It merits careful watching, although it presents at best only a small step towards the solution of the overall capital problem. It does hold out the prospect of eventually locating paper mills close to the market, and hence close to the source of secondary fiber.

A further factor which will impede the development of radically new technology is the shortage of R&D strength in our industry. This problem is also not specific to Canada, and arises partly out of the huge technical effort that is required to meet progressively tightening environmental standards. It is roughly estimated that 30% of the technical manpower that was available for new product and process research in the early 60's is now absorbed into work directly related to pollution abatement.

To summarize, then:

The Canadian pulp and paper industry is highly oriented towards the manufacture of commodities, principally pulp and newsprint. This situation is likely to continue. The rapid growth of the Canadian pulp and paper industry during the 50's and 60's will not be maintained, because of capital rather than wood limitation.

No solution, in the short term, appears likely to the very high capital requirement of chemical pulpmills.

Technological change over the next decade will be largely in the direction of increased productivity and efficiency with some incremental growth. Thermomechanical pulping facilities and twin wire machines will continue to replace grinders and fourdrinier paper machines.

The emphasis for R&D in the Canadian pulp and paper industry is likely to be on greatly improving the efficiency of existing capital plants, making them easier to control, more versatile concerning wood quality and species, and adapting them to stringent environmental standards. The industry's behavior towards technology is expected to continue to be cost minimizing for some time.

Abstract

The rate of introduction of three significant technologies, refiner mechanical pulping, twin wire formers, and continuous pulping are analyzed in terms of the Canadian pulp and paper industry's strategy and behavior. Future technological growth is discussed and related to the Canadian environment, particularly capital resources. The next decade should see thermomechanical pulping and twin wire formers dominate the technological scene for the Canadian pulp and paper industry.

Key Words: thermomechanical pulping, twin wire, continuous digester, kraft pulping, newsprint, market pulp, refiner mechanical pulp.

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Recent Technical Developments in the Finnish Pulp and Paper Industry

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The turning-point in the development which brought about
a change in Finland's economy from one based upon agriculture
to one based upon industrial production came about one hundred
years ago. One of the reasons for this was the discovery at that
time that the traditional raw materials for papermaking, linen
and rags, could be replaced by wood fibres. The exploitation of
this new source of raw material opened up new opportunities for
utilisation of the extensive forest resources of Finland, not just
for the traditional export of timber, but also for the production
of more highly priced fibre products. The evolution which
started a century ago has made Finland one of the leading na-
tions in the field of pulp and paper.

Of course, the growth of this industry has not been steady
and smooth, but has been influenced by the dramatic historical
and economic events of the past hundred years. Spectacular
growth has been experienced during the years following the last
war, a period marked by a doubling, on the average of the
production of pulp, paper and board every ten years. Currently,
the production of chemical pulp amounts to 4.5 million tons.
The corresponding figures for paper and paper board are nearly
5.5 million tons. In respect to paperboard, growth has been
even faster than the average for the entire industry; it is now
over 10 times as great as that in 1950. A glance at the statis-
tics makes it apparent that the export value of all forest pro-
ducts, including timber and other products from the mechanical
woodworking industries, amounts to about 50 per cent of our
total foreign trade. This makes it clearly evident how greatly
Finland depends upon utilisation of the forests. In the past, this
figure was even higher, and we need not look back more than
about 20 years to discover that over 70 % of exports consisted
of wood products. At the same time as the relative share of
wood based exports in the foreign trade has diminished by reason

of a correspondingly vigorous growth in the exports of the metal
industry, important changes have also occurred within the
woodworking industry as concern the volume and value of exports
from the different sectors of the industry. The export of pulp-
wood has to a great extent ceased, to be replaced by import,
which has during some years amounted to as much as 10 per
cent of the raw material utilised by our industry. A recent
trend in the export figures indicates that the steadily growing
paper industry needs an increasing amount of the pulp produced
in Finland; as a consequences the peak in pulp exports was
attained in 1970. In regard to the export of mechanical pulp,
the turning point was reached much earlier; today, the export
of groundwood pulp, is extremely small, notwithstanding the
annual production of more than 2 million tons. However this
does not imply a future reduction in the manufacture of chemi-
cal market pulp. Construction work currently in progress will
by the end of this year add some 100 000 tons of bleached sul-
phate pulp, and in 1977 a further amount of 250 000 tons to the
capacity.

Despite an extensive reforestation programme, shortage
of raw material will constitute a limiting factor to the growth
of the fibre-producing industry. Of course, this situation is
not unique to Finland, and the solutions to the problems which
present themselves by reason of the raw material shortage are
familiar to most countries that produce pulp, paper and board.
For extension of the available resources, three ways seem
open:
- more extensive utilisation of the forests
- pulping to a higher yield, and
- technical utilisation of the nonfibrous components of
  the wood.

More extensive utilisation of wood raw material from the
forests is achievable in a number of different ways. Studies
carried out in Finland have been focused upon whole-tree utiliz-
ation, the use of stumps from both mineral soil and swamps,
and the pulping of fast growing hardwoods produced by means
of short-rotation cycle cultivation. Development work in rela-
tion to harvesting machinery is well under way, and stump
harvesters and whole-tree harvesters are now producing chips
on a commercial scale. In parallel with surveys of the avail-
ability of residual wood resources, and the development of
harvesting equipment, pulping investigations have been carried
out for characterisation of the raw material derived from the
various sources. In general, experience points to sulphate

pulping being the only pulping process that is applicable in
practice. The pulps produced are of slightly lower yield and
have slightly inferior strength properties than those obtained
from the tree trunk. An interesting development for Finland,
with its large areas of swamp, is that the swamps in addition
to fuel peat yield raw material for the pulp industry. Stumps
and fallen tree trunks buried in the swamps for up to 3000
years can be separated and collected to an amount of roughly
3 kg per cubic metre of peat. With the increased use of peat
for fuel, it has been calculated that by 1980 about 200 000 m^3
solid measure of stumps will be available. In contrast to stumps
obtained from mineral soil, bog stumps are free from bark,
sand and stones. One interesting feature of the sulphate-pulping
of stumps is that the lower yield is compensated by a consider-
ably higher yield of tall oil, or about 200 kg/ton of pulp.

Whole-tree chips from thinnings have been successfully
pulped by application of the sulphate process. The pulp can be
added, even to such a demanding paper quality as sack paper,
without exercising any influence upon the physical properties
of the sheet. Short rotation hardwoods yield the lowest strength
pulp, which is to be expected with a view to the short fibre
length of young hardwood trees.

The second way which enables extension of the available
resources of raw material is connected with the production of
pulp at a higher yield. In Finland today, the dominating interest
is centered upon the production of mechanical pulp. This ques-
tion is inseparable from the question of optimisation of the use
of the wood raw-material for different paper and board qual-
ities, to which can be added the aspects introduced by the pre-
sent trend towards reduced grammage. The main focus is on
thermomechanical pulp, an interest evidenced both by consider-
able investments in research into this pulp quality and its manu-
facturing process, and by the new installations announced,
which will by the end of 1977 supply more than 300 000 tons of
thermomechanical pulp for printing grades. At present two
thermomechanical pulping lines are in operation in Finland,
each of them with a capacity of about 50-70 tons/day. One in-
stallation in Kyro is based upon the Defibrator process; the
product is used as part of the furnish for wallpaper base. The
other line in operation, is from many standpoints the most in-
teresting installation in the area of mechanical pulping in Fin-
land today. The refiner, a Jylhä-finer, has been developed by
the Jylhävaara works of the United Paper Mills, and is installed
in this company's Kaipola Mill. This equipment has been sub-
jected to extensive trial runs, of which the aim has been   a

single-furnish newsprint sheet. This was found possible not only for a standard grammage, but also for light weight papers of 45, and even 40 g/m². The combined effect of the omission of chemical pulp and the reduced grammage is a diminution in the wood consumption amounting to about 40 per cent based upon printing area.

Even if commercial installations of refiners for thermo-mechanical pulping are in continuous production, and new installations are being made not only in Finland but all over the world, the process is still regarded as being under development; it is hoped that continued research, both into the fundamentals of fibre separation and into purely practical studies of the process variables, will be of benefit both in improved economy, and in the versatility of the fibre raw material obtained. It is hoped that this will eventually facilitate the use of mechanical pulp, even for qualities of paper which have so far been produced only from lower-yield pulps. In Sweden, a research project concerned with thermomechanical pulping is long advanced, and in Finland a project was started in our Institute this year. For this purpose, there is available a pilot-plant installation, based upon a 1000 kW double discrefiner, which can be operated both under atmospheric and elevated pressure. The chip-feeding system, developed and patented by the Institute, has been designed in particular to avoid blow-back phenomena. A not insignificant part of the work is being directed towards quantification of the load imposed upon the environment by the process.

It might seem from what has been said that refiner mechanical pulp, and thermomechanical pulp in particular completely dominate the thinking in Finland. It is therefore important to point out that during 1975 the largest paper machine for LWC-base paper in the world was started up at Kaukas based entirely upon stone groundwood obtained from a brand new, conventional groundwood mill, with four Tampella grinders.

A survey of development within the pulping sector would be incomplete if no mention was made of two projects for the changeover from sulphite- to sulphate-pulping. The Kymi Company, at its Kuusankoski mill, will discontinue the production of bleached sulphite pulp in 1977 when a new continuous sulphate line, with a capacity of 160 000 tons a year, will start production. In this mill, the first Kamyr displacement bleaching plant will be installed, following several years of successful pilot-plant trials. A similar changeover from sulphite to sulphate pulp production is in progress at Veitsiluoto. Towards the end of 1977, the old sulphite mill will be replaced by a sulphate

mill; the Kamyr digester will have a capacity of from 250 000 to 300 000 tons per annum, dependent upon whether softwood or hardwood pulp is being produced. When account is taken of these two changes from sulphite to sulphate pulp production, along with the previously noted addition to market pulp capacity, entirely concerned with sulphate pulp, and with the closing of two small sulphite mills included in the calculations; a very marked shift is observable in the ratio between sulphate- and sulphite-pulp production in Finland. After two years, sulphite pulp will amount to less than 25 % of the total chemical pulp produced.

The Finnish Paper Industry has concentrated upon the production of bulk qualities, mainly in the printing and packaging lines. Growth in the industry has also occurred within these sectors, as is observable from the size distribution of the paper machines, with most of the new installations falling within the upper wire width range.

Most of the machines installed have been built in Finland. A typical example is provided by the new machine at Kaukas; it has a wire width of 8100 mm, and a maximum speed of 1100 m/min, it was built by Valmet Oy, and it produces base paper for LWC coating grades. The coating is effected on a Wärtsilä off-machine blade coater. With this capacity of 130 000 tons of coated wood-containing LWC-grades, it is claimed that the Kaukas installation is the largest of its kind in the world. Another world record-holder is the condenser tissue-machine of Tervakoski, constructed by A. Ahlström Company's Karhula works, and which was started up last year. The wire width is 5000 mm, and the maximum speed 400 m/min, with a grammage range of 10-30 g/m^2.

The family of twin-wire machines also includes a Finnish development, the Sym-Former by Valmet. The name "Sym-Former" is derived from the word "symmetrical", and indicates that drainage occurs symmetrically toward both sides of the sheet. However, with a view to safeguarding good retention, the initial part of the drainage takes place on a Fourdrinier type wire; only after a certain time is the direction of drainage reverted by the action of the double wire and its drainage elements. The symmetrical drainage concept has also been followed up by Valmet, in the form of a Sym-press, of which the second version has been installed on the Kaukas machine.

One other new development is the high consistency headbox, originally invented in Sweden at the Swedish Wood Research Institute, but now further developed by the A. Ahlström

Company. This headbox, developed under the name of Form-
Flow, has been tried at the company's Kauttua paper mill on a
machine, with a grammage range from 65 to 250 g/m^2, and a
speed of 200 m/min. The principle of the Form Flow headbox
is the achievement of vigorous microturbulence in the pulp sus-
pension, which is pumped to the headbox. Since the consistency
is as high as 2 to 4 % it follows, that the volume of back water
amounts to no more than 10 to 20 % of that of a normal paper
machine. This also leads to savings in chests, pumps, and
wire length. Experience gained with the Kauttua machine has
been very promising; the paper has a good formation, and a
high Z-direction strength.

As was stated at the beginning, three ways are open for
the extension of available wood resources; two of them provide
opportunities for the augmentation of pulp and paper production.
The third way is aimed at utilisation of the nonfibrous compo-
nents of the wood, and is accordingly more concerned with the
economics of the integrated process, and with environmental
questions. This area contains a number of developments worth
reporting. In utilisation of the hemicelluloses and other fer-
mentable compounds in sulphite waste liquor for protein produc-
tion, two commercial installations, both with a capacity of
10 000 tons per annum, have gone into operation. Metsäliiton
Selluloosa in Äänekoski, produces fodder yeast from birch
sulphite waste liquor by application of the Attisholz process
with Torula yeast. The second one, at United Paper Mills,
Jämsänkoski mill site, is based upon the Pekilo process de-
veloped at the Finnish Pulp and Paper Research Institute, and
marketed by the Tampella company. In the Pekilo process,
acetic acid, hexoses, pentoses and aldonic acids of the spent
sulphite waste liquor are fermented, and give rise to the Pekilo
mycelium. The fibrous multicell structure of the mycelium
enables isolation of the Pekilo-protein by simple filtration. For
this reason the requirement of wash-water is very small, with
the consequence that the separation and washing of the product
does not impose a load upon the environment.

Whereas protein production is based upon the carbo-
hydrates of the spent sulphite liquor, the lignin compounds can
serve as a raw material for adhesives manufacture. In itself,
this is nothing new, and spent liquors have been used for this
purpose together with fenol formaldehyde resins. Nonetheless,
a new type of lignin adhesive has been developed at the Finnish
Pulp and Paper Research Institute. In this adhesive, lignin de-
rivatives of high molecular weight are copolymerised with fenol

formaldehyde resin. This adhesive, known commercially as
"Karatex", has been tested for plywood and particle board
gluing, both in the laboratory and in full scale trials, at three
Finnish plywood mills and one particle board mill. The results
have offered a great deal of promise, and two Finnish companies
have acquired the manufacturing rights. Lignosulphonates, with
a molecular weight distribution adequate for "Karatex" adhesive,
can easily be manufactured by an economically-acceptable pro-
cedure from softwood spent sulphite liquor, by means of ultra-
filtration.

     With respect to the utilisation of byproducts from the
sulphate industry, one interesting development is apparent. The
increased use of birch in sulphate pulping has resulted in de-
terioration in quality of the talloil. The mixed oil cannot be used
direct for further refining. A procedure evolved at Åbo Aka-
demi enables improvement in the quality to the level of ordinary
talloil by extraction of the neutral matter. This method of crude
soap refining has passed the pilot plant stage, and the first pro-
duction unit is now in course of construction at the Kaukas
sulphate-pulp mill. The technical development work, and the
economic surveys, have been carried out by the Finnish firm
Linotekno, and patent applications have been filed in Finland
and a number of other countries.

     In the field of utilisation of dissolving pulp for viscose
fibre production an invention made some years ago is at present
undergoing final mill trials. The SINI-viscose process accord-
ing to which a repeated mercerisation with a less concentrated
steeping liquor and a pressing is carried out immediately before
the xanthation in order to decrease the caustic content of the
alkali cellulose, has as a consequence a 20 - 30 per cent reduc-
tion in the consumption of the process chemicals, carbon di-
sulphide, sodium hydroxide and sulphuric acid, as compared
with the present process. Mill trials carried out in two staple
fibre and one cellophane mill have confirmed the results and
shown that the quality of the products remains the same or even
improves somewhat. It seems that the SINI-process which
requires investments, which are fairly small compared with
the advantages gained by reduced chemical costs and improved
environmental conditions, during the next few years will be
taken into use in several mills.

     In this report concerned with the trends in the pulp and
paper industry, the main interest has been devoted to produc-
tion processes, and the products obtained, but it is quite
obvious that the Finnish industry, just as the industry in other

countries, is confronted by the requirements of a cleaner
environment. No attempt can be made here to present details
of the measures that have been adopted, or to record the mil-
lions of Finnmarks invested for the prevention of water and air
pollution. It is sufficient to say that Finnish papermakers and
scientists are devoting a great deal of time to these problems.
One aspect of this is discernible in the interest in research
relating to sulphurless pulping or bleaching, with part of the
bleaching chemicals being replaced by oxygen.

There is one point in relation to environmental research
I would like to mention. An extremely interesting biological
method has been developed for the purification of condensates
from the sulphate mill by the Enso-Gutzeit Company. The
difference between this method and earlier unsuccessful
attempts at the application of biological treatment, lies in the
discovery of optimal conditions for one particular sulphur-
bacterial strain, which not only withstands, but in fact demands
an environment of toxic sulphur compounds. The treatment
plant comprise two different filter units, one a liquid and the
other a gas filter; in each case, the filtering material is a bed
prepared from softwood bark by a special method. The conden-
sates pass through the filter bed against an air stream. The
filtered water can be conducted into the water course, whereas
the air stream passes through a second filter bed, from where
it can be led direct into the atmosphere. The running costs of
the method are decisively less than those involved in competi-
tive methods, such as stripping, since energy is required for
the pumping of liquids and gases only, but not at all for heating
or steam generation.

Conclusions

An attempt to summarise trends in the Finnish pulp and
paper industry could perhaps take the following form.

1) A previous, very rapid increase in the production
volume, has been superseded by more modest growth.

2) A shift in the production schedule towards products
of a higher degree of conversion.

3) Confidence in new mechanical pulping systems, and a
trend towards increases in the percentage of mechanical pulp in
different paper qualities.

4) Attempts to utilise the entire biomass of trees for
fibrous and nonfibrous products.

Finally, although this has not been expressly stated in my pres-
entation, there is a very strong wish, based upon our negative
trade balance, that domestic raw materials, additives and ma-
chinery be used to the greatest extent possible. And of course
this is coupled with a wish to sell to paper makers throughout
the world equipment and "know how" which has been acquired
within all sectors of our own industry.

Past and Present Challenges of Japanese Pulp and Paper Industry

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The purpose of this paper is two-fold as indicated by its title; to review how the Japanese pulp and paper industry developed during the past 100 years and how this industry is now struggling to overcome environmental problems and resource shortages.

Growth of pulp and paper industry
     The pulp-wood cost has been more than half of pulp making cost.   Therefore, the availability of low cost pulp-wood has occupied the most important position in pulp and paper industry.   This is a reason why the history of pulping technology was also the history overcoming the shortage of pulp-wood at each period of the growth.
     Table 1 shows the economical situation of pulp and paper industry in Japan.   This figure is rather old statistics. Pulp and paper industry ranks 12th, and wood and wood products industry ranks 14th.   Therefore total sales of both industries, so-called forest products industry ranks 7th.
     There are different opinions in Japan how to divide the growth stages including the changes of pulp raw material and pulping technology.   For convenience, the growth during the past 100 years is divided into next five stages; First stage 1872~1930, Second stage 1931~1944, Third stage 1946~1955, Fourth stage 1956~1969 and Fifth stage 1970~present.

     First stage 1872~1930   Table 2 shows main items occurred in the First stage.   It was about 100 years ago that the first machine made paper was produced in Japan, that is, in 1874.   At that time, raw material was mainly cotton rag.   The industry kept growing steadily ever since.   Sulfite pulp was produced in 1889, ground wood in 1890 and kraft pulp in 1925.

Table 1. Economic situation of pulp and paper industry in Japan (1972)

Industry	Sales			Employee		
	Order	Dollars[*1]	%	Order	Number[*2]	%
Transport. machine & implement	1	29.70	13.3	3	844	10.0
Electr. machine & implement	2	26.41	11.8	1	1,179	14.0
Food	3	24.29	10.8	5	718	8.5
Iron & Steel	4	21.10	9.4	7	488	5.8
General machine & implement	5	19.78	8.8	2	889	10.6
Chemical	6	19.39	8.8	8	439	5.2
Fiber & Textile	7	10.85	4.8	4	736	8.7
Non ferrous metals	8	9.56	4.3	15	194	2.3
Metal products	9	9.51	4.2	6	499	5.9
Ceramic	10	8.33	3.7	9	415	4.9
Petroleum & Coal	11	7.61	3.4	19	38	0.5
Pulp & Paper	12	7.61	3.4	13	242	2.9
Publication & Printing	13	5.37	2.4	10	318	3.8
Wood & Wood products	14	5.20	2.3	12	248	2.9
Others		19.11	8.6		1,166	14.0
Total		223.72	100.0		8,413	100.0

*1 : Billion, *2 : 1,000

Table 2 First stage(1872~1930) of the growth of Japanese pulp & paper industry

1) 1872 Establishment of first paper company
2) 1874 Production of machine made paper
3) 1878 Production of rice straw pulp
4) 1880 Foundation of Japan Paper Association
5) 1889 Production of sulfite pulp
6) 1890 Production of groundwood
7) 1905 Use of electric power in paper mill
8) 1912 Publication of Japanese book "Paper Technology"
9) 1925 Production of kraft pulp

Table 3 shows pulp raw material and pulp production in
1903.   It is worth noting that wood pulp production
was only 26.2% of total pulp in 1903.

In the first half of this stage, Japanese engineer
improved pulp and paper production after the model of
imported technology under the guidance of foreign engi-
neers.   However, in the 1920's, the domestic and
foreign technique were mastered enough and the spirit
of independence also appeared.   Pulp-wood in the first
stage was mainly fir, hemlock and spruce.

Second stage 1931~1945   Table 4 summarizes main
items in the second stage.   In 1931, first dissolving
sulfite pulp was produced by the use of three stage
bleaching, that is by chlorine, sodium hydroxide and
hypochlorite sequence.   This year was also of first
use of chlorine in pulp bleaching.   Since then, pine
and beech were used as new pulp-wood, and reed and
chaffs were also used as the additional supplies.

In 1938, alcohol production from sulfite spent
liquor started.   It can be said that various technical
developments were risen in the second stage.   Pulp
production in 1941 was 1,277,000 tons and maximum
before the Second World War.   There were big pulp and
paper mills not only in Hokkaido, but also in Korea and
Sahalin.   Therefore, pulp and paper industry got a big
shock due to the end of the war.   Pulp production was
only about 200,000 tons in 1946.

Third stage 1946~1955   Table 5 shows the outline
of this stage.   In Third stage, a lot of wood species
were used as pulp-wood; pine, larch, sugi (Cryptomeria),
cypress in addition to fir, hemlock and spruce.   And
in the hardwood species, poplar, alder, oak, lime,
birch and so on were used besides beech.

First Kamyr continuous digester was operated in
1952.   Since then, this type of digester has become
main one in kraft pulp production.   In 1953, pulp
production were 1,510,000 tons which were above the
maximum before the Second World War.   During this
stage, high yield pulping process, so-called semichemi-
cal and cold soda processes were adopted, and prehydro-
lysis kraft pulping began in 1953.

Fourth stage 1956~1969   Table 6 shows the outline
of Fourth stage.   In the latter of Third stage and the
first of Fourth stage, pine was used as pulp-wood in a
great quantity.   However, due to the shortage and cost
up of softwood, the industry must look for other woods
in the early 1960's.   Thus, the pulp-wood shortage was
overcome by using hardwoods, slender branches, small-

Table 3 Pulp raw material and production in 1903

Pulp	Production	
	t/year	%
Mitsumata & Kōzo (Japanese paper)	18.330	23.5
Straw	16.380	21.0
Rag	15.990	20.5
Wood(groundwood)	10,920	14.0
Wood (sulfite pulp)	9,516	12.2
Imported	6.864	8.8
Total	78,000	100

Table 4 Second stage(1931~1945) of the growth of Japanese   pulp & paper industry

1)1931 Production of dissolving sulfite pulp
2)1936 Production of Mg-base sulfite pulp from bagasse
3)1938 Production of sulfite pulp from reed
        Production of straw pulp by chlorine process. 20 t/d
        Alcohol production from sulfite spent liquor
4)1939 Production of dissolving sulfite pulp from pine
5)1940 Production of dissolving sulfite pulp from beech
        Production of dissolving sulfite pulp from chaffs,10t/d
6)1942 Production of dissolving sulfite pulp for Bemberg rayon

Table 5 Third stage(1946~1955) of the growth of Japanese   pulp & paper industry

1)1947 Foundation of Japan Tappi
2)1951 Production of high yield pulp by cold soda process
3)1952 Production of bleached kraft pulp from hardwood
        Operation of Kamyr continuous digester (third in the world)
4)1953 Production of dissolving kraft pulp
        Production of dissolving sulfite pulp for acetate rayon
        Production of neutral sulfite chemical pulp
    Wood species
    Softwood: fir, hemlock, spruce, larch, sugi (Cryptomeria), Japanease cypress
    Hardwood: beech, poplar, alder, oak, lime, birch

sized trees, waste woods at sawmills and so on.   It is
certain that the change from softwood to hardwood was
possible as a result of considerable improvement in
pulping technology.   As shown in Table 7, the use of
hardwood rose above the use of softwood in 1964.
     In 1964, exclusive carriers were constructed for
the purpose of importing chips from other countries.
At first, they sailed to the North America, and then
to Asian countries, Australia and Soviet Union.   As a
result, the percentages of Japanese dependence on fore-
ign pulp-wood jumped from 2.8% (461,000 m^3) in 1965 to
39.4% (14,052,000 m^3) in 1974.   Such a development is
shown in Table 8.   This table shows also that the
ratio of purchased chips crossed over a half of total
pulp-wood in 1965.   Table 9 shows the imported pulp-
wood statistics.   Japan is now mainly importing pulp-
wood from North America.
     Judging from a point of pulping technology, the
progress in the Fourth stage was more versatile than
that in the Third stage.   In 1957, kraft pulp pro-
duction rose above the sulfite pulp production, and
fodder yeast was produced from sulfite spent liquor.
It is worth noting that hardwood kraft liner was pro-
duced in 1959 and synthetic paper was produced in 1966.
Both were produced first in the world.

     Fifth stage 1970~present   This stage concerns the
present and future problems.   At present, the Japanese
pulp and paper industry is struggling to overcome the
future shortages of pulp-wood and environmental prob-
lems.   These two problems will be discussed in the
following parts.

Future shortage of pulp raw materials
     As metioned previously, about 40% of pulp-wood are
imported from other countries.   At present, there are
about 75 exclusive carriers importing chips.   As a
result, a lot of wood species are used as pulp-wood, as
shown in Table 10.   However, even with the increase
of imported pulp-wood, the pulp-wood shortage has
become obvious.   In other words, the Japanese pulp and
paper industry is no longer a self-sufficient industry
as it used to be.   Table 11 shows the newest estima-
tion of supply and demand of pulp and paper by Ministry
of International Trade and Industry (MITI).   Pulp
production will recover the level of 1973 in 1978 and
paper production will recover the level of 1973 in 1977.
MITI estimates that pulp and paper production in 1985
will be 14,800,000 tons for pulp and 29,000,000 tons
for paper and paper board.   In order to achieve the
target, the following three point should be solved from

Table 6 Fourth stage(1956~1969) of the growth of
Japanese   pulp & paper industry

1)1957	Kraft production>Sulfite production
	Production of fodder yeast from sulfite spent liquor
2)1959	Production of furfural as dissolving kraft pulp by products
	First production of hardwood kraft liner in the world
3)1960	Production of lignin rubber
4)1962	Production of polystyrene foam paper
5)1964	Production of refiner groundwood
	Construction of chip exclusive carrier
	Pulp wood: Hardwood>Softwood
6)1966	First production of polymer paper in the world
7)1968	Production of xylose as dissolving kraft pulp by-products

Table 7 Consumed pulpwood statistics
          $(1,000 \, m^3)$

Year	Softwood	Hardwood	Total
1960	7,861	4,481	12,342
62	7,674	6,516	14,190
64	7,894	8,538	16,432
66	8,132	10,352	18,482
68	9,348	12,698	22,046
70	12,018	16,325	28,343
72	13,550	17,258	30,808
73	15,131	17,783	32,914
74	15,912	17,163	33,075
75	14,096	14,553	28,649

Table 8 Supplied pulpwood statistics $(1,000 \, m^3)$

Year	Domestic		Imports		Total
	Roundwood	Chip	Roundwood	Chip	
1960	7,983	3,040	193	—	11,216
65	7,673	8,479	207	254	16,613
67	9,975	10,005	163	1,401	21,544
68	7,401	11,950	299	2,927	22,577
70	6,566	16,050	559	4,726	27,901
72	4,419	17,966	370	7,159	29,914
73	3,712	17,446	667	10,556	32,381
74	3,799	17,716	1,232	12,820	35,627
75	2,672	14,324	578	11,213	28,787

Table 9 Imported pulpwood statistics($1,000 \, m^3$)

Year	North America	Soviet Union	Oceania	Others	Total
1960	—	193	—	—	193
65	253	167	—	41	461
67	1,402	97	—	65	1,564
68	2,909	55	3	259	3,226
70	4,091	257	158	779	5,285
72	5,435	128	1,112	854	7,529
73	7,501	417	2,349	956	11,223
74	8,729	579	4,744		14,052
75	7,533	723	3,535		11,791

Table 10 Wood species as pulpwood

		Wood species
Softwood	Domestic wood	pine, fir, spruce, hemlock, sugi(Cryptomeria), cypress, larch, hiba(Thujopsis)
	Foreign wood	
	Soviet	spruce, fir, Scotch pine, larch
	U.S.A.	Douglas fir, hemlock, white fir, spruce, cedar
	Southern area	merkusii pine , radiata pine
Hardwood	Domestic wood	beech, birch, alder, oak, tabu(Machilus), shii(Shiia)
	Foreign wood	
	Soviet	white birch, elm, aspen, ash
	Southern area	mangrove, eucalyptus, lauan, gum(waste wood)

Table 11 Outlook of supply and demand of pulp and paper (Unit: $1,000 \, t$)

Items	1973	1974	1975	1976	1977	1978
Pulp						
Demand	11,475	10,781	10,445	10,661	11,131	13,448
Production	10,200	9,558	9,395	9,311	9,581	10,848
Capacity	11,461	11,868	12,472	12,460	12,779	—
Rate of operation,%	89.0	80.5	75.2	74.7	75.0	—
Paper						
Demand	16,954	14,246	14,564	15,523	16,227	20,752
Production	16,628	14,433	14,100	15,337	16,700	20,468
Capacity	16,498	17,935	19,967	20,058	20,740	—
Rate of operation,%	100.8	80.5	70.6	76.5	80.5	—

a long range view of pulp raw materials.

     Resource developments in other countries   Table 12
summarizes the resource development in other countries.
At present, Japan is pursuing a pattern which will
contribute more to the prosperity of the host count-
ries, in other words, the industry is trying to go into
tie-ups with the host countries to undertake plantation
and even pulp and paper production in these countries.
One of the successful cases of the economic cooperation
in the manner mentioned above is the project in Brazil.

     Waste paper   Table 13 shows the origin of waste
paper in Japan.   The share of waste paper was in 37~
41% of paper and paperboard production from 1969 to
1974.   The industry is also trying to make more use of
waste paper as pulp raw material.   For this purpose,
The Center for the Promotion of the Use of Waste Paper
has been established to facilitate the constant supply
of waste paper and to increase the share of waste
paper.   The chronic insufficiency of the waste paper
recovery system in Japan has long prevented the increa-
se of recovery rate.   At present, the industry wishes
to increase the share of waste paper used as raw mate-
rial to 45% by 1985.

     Non-woody plant fiber   The use of rice straw as
raw material was earlier than that of wood, that is in
1878.   The inclination of collection season, the in-
convenience of collection, transportation and storage,
low pulp yield and so on have prevented the increase of
straw pulp production.   Recently, all straw pulp mills
stopped the production of it in Japan, because the
effulent problems was further taken part.   However,
from a point of future shortage of pulp raw material,
rice straw should be used again.   In the case of rice
straw pulp production, a new pulping way must be found
out, because the ash content of rice straw (about 17%)
is more than that of wheat straw (about 8%).   Also,
new straw pulp mill would be better to operate in
small production capacity from a point of the possibi-
lity of easy collection.
     In Japan, we can estimate 12,000,000 t/year of
rice straw.   Supposing that the industry will use
3,000,000 t/year of rice straw and pulp yield is 40%,
about 1,200,000 t/year of straw pulp are to be produced.
Concerning pulp production from non-woody plant, one
company is now making the plantation of some herbs,
so-called pulp grass.

Pollution problems

The pulp and paper industry must meet the regulation of anti-pollution set by the government and the local authorities, although the government has permitted a transititional period during which the industry can improve the production system to meet the environmental standards.   The industry was requested to achieve BOD and COD 120 ppm and SS 150 ppm by June in 1976.   The standards set by the local authorities are even more strict.   A new paper mill established in 1974 has agreed upon 12 ppm of BOD with the local authorities.   This mill has been adopting the coagulation and active carbon treatments of effluents.

Pollution abatement in existing pulp and paper mills

The existing pulp and paper mills have improved the closed system of the process considerably.   Anyhow, as a commonsence, pollutants should be taken in the production processes.   It is also considered in what process the surplus materials should be discharged.

Decrease of water consumption

It is well-known that pulp and paper mills are struggling to save the water consumption.   This is achieved by increasing the use of recovered water and recycling water.

There is a non-effluent paper board mill which is using waste paper, although the water consumption is actually 2~3 m^3/t paperboard.   This mill announced that the increase of operation temperature cused by non-effluents operation has prevented the slime trouble. The material yield was about 90% several years ago, but at present increased to 96~97% after the improvement of the processes.   That is, the previous pollutants was to be taken in the products, and there is no difference from the former qualities of paperboard.   Although people says that this is possible only in a paperboard mill, there may be a few processes which could be applied in the production of convention paper.

Development of pollution free pulping

There are two processes which have been progressed by the use of pilot plant; PFP process by Japan Pulp and Paper Institute and HOPES process by Toyo Pulp Company.   Both processes have been financed by subsidy of the Government.   Another pulping process, so-called alkalimethanol pulping has been studying by us since 1974.

As shown in Figure 1, this process is from sodium hydroxide cooking of chips and defibration of cooked chips followed by the repeated treatments with chemicals such as chlorine, chlorine dioxide and sodium

hydroxide for a selective delignification.   For an
example, there is C-E-H-E-D-E-D sequence after pre-
cooking.   Pulp yield is 60~70% depending on the pulp-
ing conditions, and the spent liquor is wholly recover-
ed, concentrated and burnt to obtain smelt of sodium
chloride and sodium carbonate.   Sodium chloride is
subjected to electrolysis to produce chlorine and
sodium hydroxide.   Chlorine is used to produce chlo-
rine dioxide.
     The advantages of this process are in low tempera-
ture pulping under normal pressure, no offensive odor
like kraft process and free controlling of pulp yield
depending on the pulp qualities required. And the
pollution load is also quite small.   However, high
power consumption and corrosion of the recovery equip-
ment should be pointed out, as the disadvantages of
this process.   Paper tends to be low in opacity and
tearing strength, because pulp contains much hemi-
cellulose.
     Flow chart of the HOPES process will be shown in
Figure 2.   This process is from two stage pulping
which is from sodium hydroxide treatment at 160~170°C
and sodium hydroxide-oxygen treatment at 120~130°C
under oxygen pressure less than 10kg/cm^2.   A modified
Kamyr digester is to be adopted.   Spent liquor is
subjected to a wet combustion process to decompose
organic matters and to recover sodium carbonate.   Pulp
yield is said to be 2~3% higher than kraft pulp and
pulp strength equivalent to kraft pulp in breaking
length and burst strength and to sulfite pulp in tear
strength.   Toyo Pulp Company announce that they have a
fair prospect of industrialization and a 50 t/D plant
is now undr construction.
     Flow chart of alkali-methanol pulping process is
shown in Figure 3.   Wood chips are cooked with 40%
methanol in aqueous sodium hydroxide or sodium carbo-
nate at the maximum temperature of 160~180°C.   The
advantages are in about 3~5% higher pulp yield than
kraft pulp and in equivalent pulp strength to kraft
pulp.   The development of this process depends on
methanol price.   It is worth noting that a part of
methanol comes from wood constituents.

     Environmental protection situation   The pulp and
paper industry has to meet anti-pollution standards
set by the government.   It is assumed that the govern-
ment will shift its control system from BOD and COD to
TOD and TOC, and also from ppm base to total load base
of pollutants.   Furthermore, the local authorities set
the regulation for the offensive odor of kraft mill.
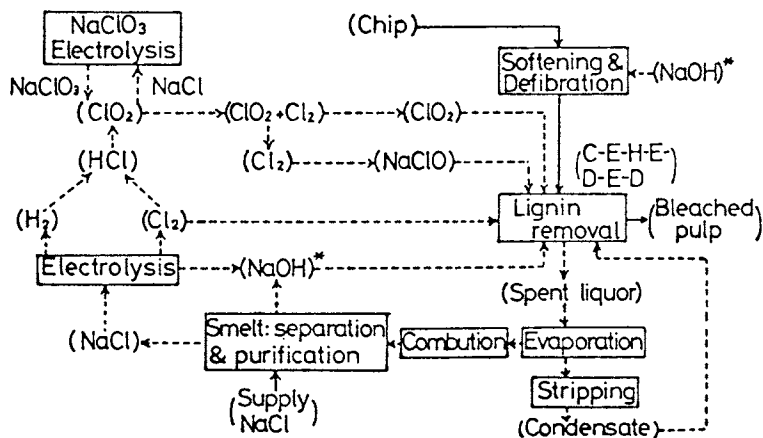
Figure 1. PFP flow chart by Japan Pulp and Paper Research Institute process
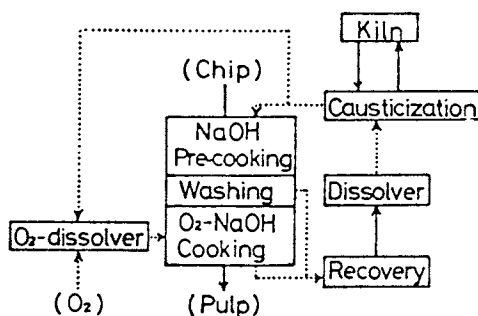
Figure 2. HOPES flow chart by Toyo Pulp Co.
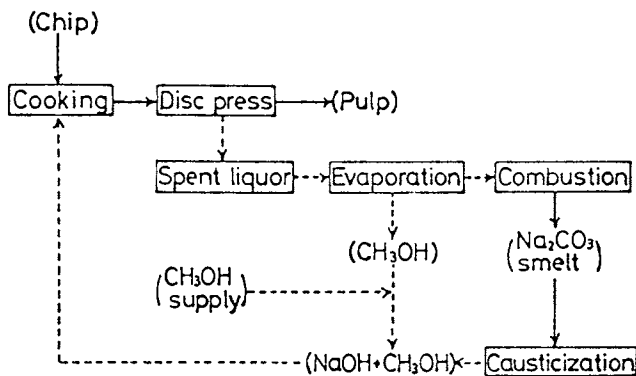
Figure 3. Alkali methanol pulping flow chart

Table 12 Resource development in other countries

Company	Location	Business (1,000 m³)
Daishowa Wood Prod.	Malaysia	Gum waste wood chips, 600m³/y
Sarawak Wood Chip Co.	Malaysia	Mangrove chip, 150
Sharikat Bakau Sabah Sdn. Bhd.	Malaysia	Mangrove chip, 150
P. T. Zedsko Indonesia	Indonesia	Wood and chip, 64(wood)
P. T. Triomas Forestry Development	Indonesia	Wood, 120
Harris Daishowa Pty. Ltd.	Australia	Eucalyptus chip, 900
Nelson Pine Forest Ltd.	New Zealand	Pine and beech chips, 400
Jant Pty Ltd	New Guinea	Sawing and chip, 150(chip)
Oji Malaysia Plant. Sendrian Bhd.	Malaysia	Plantation
Empreendimentos Florestais S.A.	Brazil	Plantation and chip, 3000(chip)

Table 13 Origin of waste paper(1,000 t)

Year	Mech. pulp	Unbld. chem. pulp	Bld. chem. pulp	Total
1966	1,556	1,353	281	3,190
68	1,521	1,743	342	3,606
70	1,958	2,185	553	4,696
72	2,127	2,367	669	5,163
73	2,528	3,087	720	6,335
74	2,238	2,967	661	5,866

Table 14 Investment amount of anti-pollution equipments in Japanese pulp & paper industry

Equipment	Amount, million $			Ratio, %		
	1974	1975	1976*	1974	1975	1976*
Air pollution	56	50	45	31.3	28.6	30.0
Water pollution	95	108	67	53.1	61.7	44.7
Noise, shake	4	4	29	2.2	2.3	19.3
Diposal treatm.	19	9	7	10.6	5.1	4.7
Others	5	4	2	2.8	2.3	1.3
Total	179	175	150	100	100	100

67 million $ (1972)   137 million $ (1973)

* Estimate

Over the past four years from 1972 to 1976, the total amounts invested in the equipments for anti-pollution reached about 710 million dollars in the pulp and paper industry. This can be said actually heavy investments. Most of the investments have been paid to set the equipments of anti-water and anti-air pollution as shown in Table 14. The environmental regulation will be more intensified year by year and the industry will be required to make the additional investments of anti-pollution technology devices and the development of new technologies.

Conclusion
Summarizing the development process of the Japanese pulp and paper industry, it can be concluded that there has been a lot of new technologies which supported the development of pulp raw material, the expansion of pulp and paper production, and the improvement of pulp and paper qualities. Especially, this industry has developed the technology to utilize hardwood as pulp raw material, and is now promoting very much its anti-pollution technology.
At present, the most important problem for this industry is the scarcity of land available in Japan for its expansion of production facilities. Building new mills is nearly impossible except the coastal zone of Hokkaido, the northern part of Japan. Therefore, more emphasis will be laid on the import of pulp and paper in the future. This is only possible by keeping good relationships with countries which have the potential of suppling pulp and paper to Japan. It is certain that the international co-operation is necessary to develop the pulp and paper industry in each country.

9

Recent Developments in the Swedish Pulp and Paper Industry

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     The pulp and paper industries in different coun-
tries, especially those in the industrialized world,
are tied together in many ways. To some extent they
compete with each other through their products. An
important factor in their technical development is
that machine and instrument suppliers of reasonable
size are always looking for markets all over the world,
so that technical novelties spread rapidly and effi-
ciently. Research specialists in different fields also
form a truly international brotherhood exchanging
views and discussing their problems at symposia, during
congresses and through personal visits.
     The important problem areas are the same all over
the world. Nevertheless the actual direction from
which a problem is attacked may differ between coun-
tries. The raw material situation, for example, varies
from the availability of large, still untapped forestry
resources to a pulp and paper industry, substantially
based on imported wood.
     Finland, Norway, and Sweden, the three Scandina-
vian pulp and paper producing countries, all have sim-
ilar climates and geological histories. As a conse-
quence our forests contain the same botanical species;
one type of spruce, one type of pine (in the foresee-
able future there will be two types of pine available
in our forests) and also birch. The technical prob-
lems associated with the processing of wood to pulp and
paper and the problems involved in marketing these
products are therefore very similar in these three
countries.
     A few statistics will indicate how the Swedish

forest products industries rate in the world and in the
internal economy of our country.

In Sweden the production of market pulp increased
2.3 times between 1950 and 1974, whereas in the same
period paper production increased no less than 4.7
times. In other words, there was a steady trend to-
wards greater integration of pulp mills with paper
mills. This tendency is still strong.

Sweden's position in the world as a paper produc-
ing region is modest. Sweden is much more important
in the world pulp trade, covering about 50% of the de-
mand from Scandinavia and North America together. The
steady and dominant market for Sweden is Western
Europe which consumes 85% of our pulp and paper export.

It has become common practice to compare the per
capita consumption of paper and paper products in dif-
ferent countries and to use this figure as a measure
of the economical health of a country. This measure
is open to criticism like all other measures of the
standard of living. It may be of interest to compare
also the per capita export of market pulp plus paper.
This figure can be used as a quantitative measure of
the national importance of the forest products indus-
try.

I shall now briefly consider the importance of
the whole of the forest products industry to the na-
tional economy. In 1973 the industry accounted for
24% of the value of all exports. This percentage has
steadily decreased since the 1950's in spite of a con-
siderable rise in production. The foreign exchange
earned during 1974 by the forest products industry
paid our total oil bill and in addition covered the
food deficit and still left some money for vacationing
abroad.

Five problem areas are clearly evident: capital
cost of extending capacity and modernizing existing
plants; labor productivity; wood supply; energy con-
sumption; environmental problems, especially water
and air. You will note that neither quality nor mar-
keting problems are listed above. With a steady 85%
of the export market in Western Europe, which is a
deficit area as far as the fibre supply is concerned,
we should not need to worry about the market. Of
course we are then silently but confidently assuming

that our industry will continue to be able to produce
the goods at internationally acceptable prices. I
shall now discuss these problem areas to some extent
and I shall give a few examples of technical activities
of different kinds within them.

    Capital Costs. The rapidly rising capital costs
are a headache well known not only to pulp and paper
manufacturers everywhere but also to the heavy chemi-
cal industry and other industries as well. The
chances are, however, that in the pulp and paper field
something substantial can be done about it. Much of
the processing essentially means handling large quan-
tities of water containing an amount of fiber which in
some operations is below 1 %. Dry forming of current
paper grades, aside from special products, is a defin-
itely interesting but still far away solution. A-
waiting this final solution - if it ever comes - a de-
velopment from the Swedish Forest Products Research
Laboratory is of interest. It will enable the amount
of water handled in the formation of paper on the ma-
chine to be diminished by a factor of between 5 and 10.

    The basic principle of this high consistency sheet
forming method is demonstrated. The fibre suspension
enters a cross machine distributor from which a number
of cylindrical holes lead into the actual forming zone.
This consists of one sharp bend and a number of smooth
bends. The energy consuming microturbulence created
by the first bend is high enough to break down the
fibre flocs. A very low channel height, of the order
of 1 to 2 mm, prevents any serious reflocculation dur-
ing the flow through the later part of the forming
section and the decay channel. Here the fibres form a
network of considerable mechanical strength, providing
the fibre consistency is sufficiently high. Expressed
in another way, the fibres form a single floc - the
future paper sheet. This limits the lowest consisten-
cy of up to 5% has been used successfully, and even
this will not be an upper limit. The limit is gener-
ally set by the pulp feeding system, including pumps,
storage tanks etc. The sheet is thus formed in the
head-box instead of on the wire as in the conventional
method. Following small-scale trials a 900 mm wide
flow-box was built and placed on top of the wire of
our experimental paper machine, just before the dandy

roll. It was fed directly from the machine chest.

After extensive trials on our experimental ma-
chine, a 2.6 m wide flow-box for industrial use has
been constructed and built by our licence holder, A
Ahlström Oy of Finland. It has been installed on a
fine paper machine in one of their milles in Finland.
On February 19, 1975, it was started up for the first
time, and within 5 minutes paper was being reeled up.
The formation of the paper is comparable with that ob-
tained on conventional paper machines.

Subsequent runs on the fine paper machine have
shown that the high consistency head-box is very easy
to operate. The relatively high pressure drop in the
head-box contributes to an extremely uniform cross
direction profile. It has also been established that
the pressing and drying is improved. The solids con-
tent after the press section rose from 40% with con-
ventional forming to 44% when a 135 g/m^2 grade was run.

The felted sheet structure also affects the me-
chanical properties of the sheet. The strength in the
z-direction, i.e. perpendicular to the plane of the
sheet, is generally increased by a factor of two. As
a result of this increased resistance to delamination,
the compression strength in the plane of a high con-
sistency sheet is higher than that of a conventional
sheet. This is explained by the fact that failure in
compression is caused by delamination. On the other
hand a reduction in breaking length amounting to 30%
has been measured. This reduction will be decreased
as a result of a further development of the formers to
obtain an even better formation.

It has been shown, using a new high consistency
handsheet former, that the loss is breaking length due
to the felted sheet structure need not exceed 10%.
Sheet thickness is increased compared with that of
conventional sheets. This makes the centre ply of
board products an ideal application. The 2.6 m wide
industrial head-box has also been successfully used in
that application. High consistency forming can also
be applied to several other types of paper, including
corrugating medium and liner and considerable savings
are expected both in investment and in operating costs.

The channel in the head-box is very narrow. It
therefore became necessary to develop a high

consistency screen capable of removing particles which
would otherwise block the channel. The screen is re-
quired to work at consistencies up to 5%, preferably
even higher. Such a screen is also desirable after an
in-line refining stage following a continuous kraft
digester, as well as in the screen room. A high con-
sistency barrier screen has now been developed, also
at our institute. The laboratory prototype has been
running well at 5% consistency. The screen is being
further developed for fine screening purposes in coop-
eration with Sunds AB, Sweden.

  Labor Productivity. The desire to increase the
labor productivity is not new. Considerable gains
have been achieved in forestry as well as in the for-
est products industries. The number of man hours re-
quired per m^3 of pulpwood ready for transportation de-
creased in the years. The Swedish forests are to 50%
in private ownership, the rest being divided in equal
parts between the government and local municipalities
on the one hand and the forest products industry on
the other.

  Productivity in the pulp and paper industry has
increased according to a similar pattern, mainly
through application of the principle of economy of
scale. The rapidly increasing use of computers first
as a processing aid and lately also in production
planning has, of course, also been an important factor.

  Among recent technical developments I should like
here to mention a new analytical technique which in
fact has a relevance to the productivity problem area.
When liquors of different kinds used in or obtained
from different pulping processes are analysed, the
usual procedure is to add something which reacts with
one of the components, the amount of product formed
being measured physically by a suitable method. More
often than not heat is evolved in the reaction. Every-
body knows that the thermometer is one of our oldest
and most reliable precision instruments. Why not
measure the temperature increase instead?

  With this simple reasoning as background a Swed-
ish company, MoDoCell AB in northern Sweden has to-
gether with an instrument company developed a contin-
uous calorimetric analyser (not colorimetric). The
reaction conditions are neither isothermal nor

adiabatic and the method can best be described as a
steady-state flow calorimeter. The temperature of the
surrounding water bath must be kept constant within
$\pm 0.001°$ C. It does not matter if the water bath
changes its temperature very slowly.

The method has been used for a number of analyt-
ical problems such as the determination of effective
alkali in black liquor, of chlorate in chlorine di-
oxide production, of residual chlorine in the chlorine
bleaching of pulp. A full description will be given
at the TAPPI bleaching conference in 1976.

<u>Wood Supply</u>. Definitely the most pressing prob-
lem today for the Swedish forest products industry as
a whole is the problem of ensuring the availability of
wood raw material. When we talk loosely about shortage
of wood this must be understood in a correct way. For
the greater part of this century our capital of wood
has increased. From the 1920's until today our re-
sources have increased by almost 40%. This means that
we now have forest reserves - a growing and renewable
resource - which are almost certainly larger than at
any time in our history. Our present difficulties
should be discussed from this starting point.

Firstly, an accelerated expansion of our forest
products industry in the last 10-20 years has now
caught up with the annual production of wood in the
forests and it is a matter of debate whether or not it
has even slightly exceeded it. Secondly, there is un-
fortunately a statistical distribution of the age of
the trees which in a few decades will lead to a tem-
porary decrease in the amount of wood suitable for
cutting. Remember that the age of the trees when a
forest is cleared is usually somewhere between 70 and
100 years.

Strong initiatives have been taken in seeking
remedies; for example, increased fertilization in the
forests and more efficient use of the trees - includ-
ing the tops, branches, stumps, and roots. This meth-
od of extending our raw material supply did not appear
to be economically feasible some years ago but the
situation was substantially improved by the price in-
creases for pulp and paper in 1973-74.

<u>Energy Consumption</u>. Sweden is very dependent on
imported oil. We have no oil, practically no coal and

the hydroelectric power cannot be increased very much.
Energy prices have always been high and as a result
the pulp and paper processing industry was even before
the oil crisis well rationalized with regard to energy
consumption.

Still, of course, the sudden price increase of
oil makes it desirable to save energy through contin-
ued streamlining of the processes wherever possible.
Since 1975 the political situation enters into the
picture in a unique way. In the spring of 1975, the
Swedish Parliament adopted as governmental policy that
the total energy consumption in our country would not
be allowed to increase by an average more than 2% per
annum until 1985. Towards the end of this century
zero-growth is foreseen. This policy is subject to re-
evaluation in the Parliament in 1978. However, it is
expected that the energy consumption of the industry
would be allowed to increase by up to 6% per annum
balanced by an increase of less than 2% on the part of
other users.

The energy cost contributes only 6% to the sales
value of the products; still the total energy con-
sumption is about 40% of that for the industry as a
whole. On the other hand pulp and paper makers also
produce large amounts of energy especially through the
burning of waste liquors from digesters. About half
of the steam required and one third of the electric
power needed is generated within the plants. The end
result is that about 20% of the energy consumed must
be bought from outside sources. This still brings the
pulp and paper industry together with the steel indus-
try into the top position as energy consumers. Both
industries are therefore under pressure from the Gov-
ernment to do whatever is possible to decrease their
energy consumption.

Our branch organization, the Swedish Pulp and
Paper Manufacturers Association (corresponding approx-
imately to the American Paper Institute) has an active
energy committee working on problems of mutual interest
and has also got some funds from the industry at their
disposal for R and D. The Government on its side is
now releasing considerable funds for R and D on energy
problems and has indicated that the pulp and paper in-
dustry will be in a favoured position to receive

grants for collective research in the energy area. As previously mentioned, our industry is already well rationalized in energy matters and no revolutionary savings are likely to occur. Rather, a large number of small improvements will be possible. One interest- ing study has been made by the Swedish Steam User's Association contracted by the branch organization. For a number of plants, the minimum energy consumption has been calculated for each link in the processing chain, assuming that the best technique available to- day is used throughout the plant.

On the energy production side the use of bark to replace part of the oil in steam production is in- creasing rapidly. From the national economy point of view the desirability of an increased production of electrical back-pressure power is clearly seen. The practical realization has turned out to be a very com- plicated problem where the whole price structure of electric power in Sweden must be taken into considera- tion.

Environmental Problems. A few years ago it be- came apparent that the Swedish pulp and paper industry had to make very big investments in equipment and processes changes for water and air pollution abate- ment. The Swedish Pulp and Paper Manufacturers Assoc- iation therefore took the initiative in starting an extensive, joint research project, the SSVL environ- mental care project. This consisted firstly of a sur- vey of the best available techniques, and secondly of a number of research and development projects designed to serve as a guide for investment in environmental care. The SSVL project was carried out between 1970 and 1973 with a total budget of about 7 million US dollars. (SSVL - abbreviation in Swedish of Forest Industries' Water and Air Pollution Research Foundation.)

The SSVL project was divided into eight subproj- ects. I shall say a few words about two of them: the accidental discharges and the closure of the water systems in paper mills.

Accidental Discharges. According to the data collected, accidental temporary discharges account for between 20 and 50% of the total discharge of chemicals by the pulp mills (excluding the bleaching plants) and

for between 30 and 50% of the discharge of fibres.

They can be divided into three main groups according to their cause: failure of apparatus (for example, the tearing of a filter cloth); the human factor (for example, a forgotten valve); regulator errors (for example, overflow due to process departments being out of phase).

Temporary discharges are often of short duration (about 10 minutes). Extremely brief discharges can therefore be discovered only by continuous measurement and supervision of the effluents or by very frequent sampling. The sodium content in the effluent from a kraft mill was determined in samples taken at 15 minute intervals over a three-month period. Very large variations were found even between two successive samples.

The closer the measurements are made to the source of the discharge the greater will be the difference between temporary and continuous discharges, and the easier it will be to determine what proportion the former constitute of the total. From values obtained, it can be estimated that the temporary discharges are responsible for an annual loss amounting to 80,000 t per year of fibres in the Swedish pulp industry and to 100,000 t of Na_2SO_4 per year in kraft mills.

Temporary and accidental discharges therefore constitute an important item for consideration when a company intends to invest money in measures to reduce pollution. This is an area where economic and environmental interests coincide.

Closing Paper Mills. The mean water consumption and fibre loss in Swedish paper mills in 1971, and a theoretical situation assuming the best technology available in 1973 -- that is to say, what could be achieved through the general application of existing knowledge and equipment -- were considered. This is, of course, not economically feasible in the case of older machines since it would necessitate radical modifications. It is always a goal towards which the industry can aim and -- no doubt -- also a goal towards which the offical authorities want us to work. What is shown here is a theoretical goal as seen in 1973. Where we are actually today is just now being evaluated.

We have definite evidence how the water pollution
situation in Sweden is improving. The total BOD load
is decreasing at an accelerated rate but the pulp and
paper industry is still the dominating pollutant as
far as BOD is concerned. If the values from 1972 are
extrapolated, the improvement is closely following the
prediction, in fact we are at the moment lying a trifle
below the prognosis. The difference is hardly statis-
tically significant, though. The quality of the water
in our largest lake, Vänern (the surface is about one
fifth of lake Erie) has steadily decreased since the
beginning of this century due to lignin effluent from
surrounding pulp plants. The situation is now defi-
nitely improving.

Before concluding, I will say a few words about
collective research in Sweden. First, it should be
explained that we have in our country no anti-trust
law of US type. All companies within a branch are
welcome to join forces in R and D and in programs for
technical development generally speaking. Chances are
good that the Swedish government will also contribute
financially to such projects.

The existence of the Swedish Forest Products Lab-
oratory is based on this policy of cooperation between
the government and all industries within a branch. We
are employing about 330 people and have an annual bud-
get close to 9 million dollars.

Another example of a joint industrial undertaking
is the SSVL project already referred to. Much of the
real work was done at different industries and during
a great amount of sub-group meetings where experts
from different plants met, compared notes from their
own practical experiences, and discussed what could be
done to improve the environmental situation on specific
points. The SSVL environmental care project has been
considered a success. Today several projects are ac-
tive which are more or less modelled after the SSVL
project. I will mention three of them.

A direct follow up of the SSVL environmental care
project is Nordmiljö 80 (a direct translation would be
Northern environment 1980). This is a joint Scandina-
vian undertaking with Finland, Norway and Sweden as
partners and a total budget of around 2.5 Mdollars
(11 MSw crowns), to be spent in three years. It is

run in cooperation with the environmental protection
authorities in the three countries. The aim is to find
appropriate methods for environmental supervision with-
in the pulp and paper industries. The prevention of
the accidental discharges is one important point with-
in the project.

Our forestry and forest products industries have
joined forces in the PHU-project, i.e. whole tree
utilization project, running for three years at a
total cost of around 3 Mdollars. The driving force
behind this project is of course our raw material sup-
ply situation. It is necessary that we evaluate all
possible ways to increase the use of the biomass which
nature is producing for us in the forests.

The third example is the T-pulp project, survey-
ing the manufacturing methods and especially uses for
all types of paper of thermomechanical pulp. It is
also running three years and has a total budget of
slightly more than 3 Mdollars.

All these projects are run with fairly detailed
and fixed time schedules. Also, three years is a very
short time to make something technically valuable
starting from research. They are therefore no true
research projects in the restricted sense of the word,
rather the emphasis is on the development side. As an
illustration it can be mentioned that although the
Swedish Forest Products Research Laboratory is admin-
istrating the T-pulp project, our own research projects
on mechanical pulp are deliberately put outside the
project. Of course the results from these projects
are continuously put at the disposal of the T-pulp
project.

Summing Up. This has perhaps been a too kalei-
doscopic presentation of the Swedish forest products
industry. What lies before us are all the difficult
and important problems connected with a completely new
raw material supply situation. In addition to this we
have the never ending demands from the environmental-
ists. All this is well balanced by our firm belief
that Western Europe is a steady and natural market for
our export products also in the foreseeable future.

100 Years of Cellulose Fiber Finishing Research and Development in Switzerland

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This paper contains a historical review of 100 years of basic and applied cellulose research in Switzerland and a discussion of recent, partly unpublished results concerning the crosslinking of cellulose fibers obtained in academic and industrial research laboratories in Switzerland. An investigation of the mechanism of catalysis of crosslinking by metal salts is reported.

1) History of Cellulose Research in Switzerland

Cellulose research in Switzerland has always concentrated principally on cellulose fibers, particularly cotton fabrics. In addition, however, our present understanding of the concept of macromolecules in general and the submicroscopic arrangement of cellulose molecules in cell walls owes much to investigations made in Switzerland.

The title of this paper "100 years of cellulose research and development in Switzerland" is not absolutely correct - strictly speaking it should be 99 years.

The reason for this is that in 1877 Carl Nägeli and Simon Schwendener, two Swiss professors of botany published the second edition of their book "Das Mikroskop, Theorie und Praxis" (The Microscope, Theory and Practical Application) [1] in which they use for the first time the word micelles, i.e. ordered particles of submicroscopic dimensions. They postulated that water may enter between these particles and by means of this concept they explained swelling and other properties. Their idea was not accepted generally, however, for many years until X-ray structure determinations in the Twenties demonstrated that their hypothesis was, at least in principle, correct.

It is important to note that the word micelle

197

was created in 1877; the concept, however, is older,
but it was also developed by one of the authors, name-
ly Carl Nägeli. In the book mentioned the definition
of a micelle is given on page 424:
  "Die Molecüle gruppiren sich zu kleinen, jedoch
  mikroskopisch nicht wahrnehmbaren Krystallen,
  die wir Micellen* nennen wollen."

  (The molecules group themselves in small, micros-
  copically undetectable crystals, which we will
  call micelles).

     From the point of view of the history of science
the footnote attached to the word "Micellen" is even
more interesting:
  *"Wir haben früher die fraglichen Gruppen klein-
  ster Theilchen als "Molecüle" bezeichnet. Seit-
  dem jedoch dieser Ausdruck in der Chemie eine
  ganz andere und voraussichtlich bleibende Bedeu-
  tung erhalten hat, führt die genannte Bezeich-
  nung nothwendig zu Missverständnissen, deren Be-
  seitigung am besten durch Aenderung des Namens
  geschieht."

     In this footnote the authors refer to the fact
that Nägeli, in his book "Die Stärkekörner" (The
starch grains), published in Zurich in 1858 [2] called
these particles not micelles, but molecules. He changed
the nomenclature in 1877 because then the term mole-
cule became to mean what it does today.
     In 1858, Nägeli wrote [ref. 2, p. 332] that atoms
are either elements or compounds, i.e. simple or "com-
bined" atoms. He defined starch as an atom consisting
of 12 carbon atoms, 10 hydrogen atoms and 10 oxygen
atoms. This is of course in contradiction to our pre-
sent, more precise definition of an atom. Later, in
the same book, he uses the expression "molecule" for
the submicroscopic unit which, in 1877, he and Schwen-
dener renamed micelle.
     It is obvious from the elementary ratio 12:10:10
for carbon, hydrogen and oxygen that in 1858 the cor-
rect atomic masses were not known, however, this prob-
lem will not be discussed here.
     For our present lecture it is important to note
that the macromolecular nature of cellulose, starch
and synthetic products was first realized only in the
Twenties by Hermann Staudinger, at that time Professor
of General and Analytic Chemistry at the Swiss Federal
Institute of Technology (ETH) in Zurich. The concept
of macromolecules was developed by Staudinger in Zu-
rich in spite of the scepticism and disbelief of the
whole scientific world. The first paper in which Stau-
dinger described the macromolecular nature of so-called

colloidal compounds was published in 1920 [3]. In the
Ph.D. thesis of K. Frey [4] made under Staudinger's
supervision [5] the macromolecular nature of cellulose
was demonstrated.

Staudinger's pioneering work on macromolecules
was honored by the Nobel Prize in 1952[1].

After Staudinger's pioneering work the conforma-
tion, i.e. the arrangement in the three dimensional
space of chain-like and globular molecules, was still
an unresolved problem.

Here we have to distinguish between the arrange-
ment of such molecules in solution and in the solid
state.

In 1934, Werner Kuhn, a Swiss chemist working at
the Institute of Technology in Karlsruhe in Germany
developed the concept of dissolved chain molecules hav-
ing a statistically coiled structure [6]. On this ba-
sis he was able to solve quantitatively the problem of
rubber elasticity [7] and, in the Forties, when he was
Professor of Physical Chemistry at the University of
Basle in Switzerland, he and Hans Kuhn were able to
explain the correlation of the length of chain mole-
cules with the viscosity and the flow birefringence of
their solutions [8].

For cellulose technology and fiber research in
particular the arrangement of molecules in the solid
state is very important. Part of our present knowledge
in this field originated in Switzerland. In spite of
the fact that Nägeli's concept of micelles was very
hypothetical and crude at the time of its discovery,
it is astonishingly that he postulated the principle
of an idea which can be recognized in the results of
more recent research on the submicroscopic structure
of plant cell walls, i.e. native cellulose. Here the
pioneering work of Frey-Wyssling and Mühlethaler, two
biologists at the Swiss Federal Institute of Technolo-
gy in Zurich, concerning the electron microscopy re-
ceived world-wide recognition: In 1948, they were able
to get, for the first time, electron microscopic pic-
tures of microfibrils in cellulose with a diameter of
200 to 300 Å [9].

At that time it was generally assumed that micro-
fibrils were the smallest submicroscopic units above
the molecular level. It was therefore a sensation when
Mühlethaler discovered in 1960 [10, 11] the elementary
fibrils, i.e. units with a diameter of 30 Å, contain-

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[1] It may be mentioned here that no less than 6 che-
mists and 3 physisists who were professors at the
ETH have received Nobel Prizes, the last being Pro-
fessor V. Prelog in 1975.

ing about 42 cellulose chains only. A combined chemi-
cal and electron-microscopic investigation by Muggli,
Elias and Mühlethaler [12, 13] demonstrated later that
the molecules in these elementary fibrills are not fol-
ded as in many macromolecules obtained from melts or
solutions in the laboratory.

Nägeli's term "micelle" disappeared from the no-
menclature of submicroscopic units of cellulose. It
reappeared, however, in the physical chemistry of
aqueous solutions of partly hydrophobic compounds, e.g.
solutions of soaps and synthetic detergents. It was
introduced there by van Bemmelen [14], McBain [15] and
others [16].

2) History of "Swiss Cotton" Research and Development

Let us review now briefly some industrial deve-
lopments in the finishing of cellulosic fibers in tex-
tile mills in Switzerland! The term "Swiss cotton" has
become a standard expression in spite of the fact that
there is not a single bale of cotton grown in Switzer-
land. The term refers to lightweight cotton fabrics of
very high quality standards with special finishing ef-
fects. Where did it originate?

In 1841 in England, John Mercer discovered that
the lustre and other properties of cotton can be
changed by a treatment with caustic soda[2]. It took,
however, almost half a century until industrial merce-
risation was introduced in England by Thomas and Pre-
vost. Swiss textile mills started to produce merceri-
zed yarn at the end of the century. Very soon two
Swiss firms, Heberlein & Co. AG in Wattwil and AG Ci-
lander in Herisau realized that treatments with other
chemicals resulted in very interesting and permanent
changes in the cotton fabric: A treatment with relati-
vely concentrated sulfuric acid had a partchmentizing
effect and, when combined with mercerization, yielded
transparent fabrics of a unique lustre [18]. The pro-
duct was called Organdy. Later a variety of other
treatments with nitric acid and with zinc and other
salts resulted in new effects which were welcomed by
the fashion industry [19].

Another method of approach was to crosslink the
cellulose fibers. Originally developed for regenerated
cellulose fibers at the beginning of the century as a
treatment with formaldehyde, crosslinking first gained
some importance in the Twenties, when Tootal Broad-
hurst Ltd. in England used resins of the phenol-form-

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[2] Details of the history of mercerisation have been
described by Döhle [17].

aldehyde type [20, 21]. Later, urea-formaldehydes were found to be superior. It was not until the mid-Thirties, however, that an essential break-through took place in this field when more permanent effects were obtained by the pad-dry-cure process. This process was discovered simultaneously and independently by C. Bener at Raduner textile mill in Switzerland [22] and by L. A. Lantz and A. L. Morrison at Calico Printers in England [23]. Processes of this type had their first boom period in the later Forties and early Fifties when the fashion trends of the time demanded threedimensional effects on fabrics such as Everglaze.

Their real importance became evident, however, when they were applied to all types of easy-care cotton fabrics; this is, on a world-wide basis, by far the most important development in finishing pure cotton, rayon and cotton/polyester blends in the last twenty years.

In spite of the enormous amount of research and development work put into this field all over the world it is astonishing that there are still improvements possible which reach the production stage. Two relatively recent examples from Switzerland are the MS (microstretch) process of Raduner [24] in which lightweight fabrics are stretched across the fabric in regions of less than 0.5 cm by a combination of special rolls before the crosslinking proper takes place.

The other new development is the so-called MA process of Triatex International in Zurich [25]. By dipping fabrics with crosslinking solutions containing suitable surfactants it is possible to get an even pick-up of only about 35 to 40 % (w/w).

In order to investigate the basic principles of this process, a special microscopic technique which utilizes fluorescent compounds as staining reagents was developed in our Department [26, 27]. It demonstrated that the usual pad-dry-cure technique has the disadvantage that in fabrics containing 80 to 90 % (w/w) of the finishing liquor diffusion of the finishing chemicals to the surface takes place when water diffuses out of the fiber and fabric in the drying stage. We made, however, the interesting observation that this diffusion of crosslinking chemicals dissolved in water becomes neglegible as soon as the fibers contain less than about 35 % water. The critical phase is therefore the removal of the first half of the usual 80 % pick-up of the finishing liquor. Removal of the remaining 35 % water is, however, not critical.

The MA process avoids this diffusion by applying only 30 to 40 % liquor from the beginning. In principle we found, however, that either by extremely slow drying of a fabric padded in the normal way, i.e. with

about 80 to 90 % pick-up or by freeze drying a diffusion of the chemicals to the surface can be almost completely avoided. Unfortunately these processes are, however, not economical.

The observation that by extremely slow drying no or very little diffusion of the finishing chemicals takes place is understandable on the basis of the fundamental law of diffusion of molecules, i.e. the Stokes-Einstein equation (1). This equation states that

$$D = \frac{kT}{6 \pi \eta r_0} \qquad r_0 = prop \sqrt[3]{M} \qquad (1)$$

the diffusion coefficient - which measures the rate of diffusion - is proportional to Boltzmann's constant k and the absolute temperature T and inversely proportional to the viscosity of the medium (η) and the radius r_0 of the particle, assuming the particle to be a sphere. The radius of such a particle, on the other hand, is proportional to the cube root of the molecular mass M. The diffusion is therefore relatively little dependent on the size of the diffusing molecules. In practise differences in the diffusion rate of small particles such as water molecules and larger particles such as crosslinking reagents will therefore be more noticeable when the overall diffusion is slow.

3) The Origin of Yarn Texturizing

Processes for texturizing yarns of thermoplastic fibers have become very important in the last twenty years. One should not forget, however, that the original invention of texturized yarns was made with rayon fibers. The principle was described in a patent [28] in 1932 by the Heberlein company: It was demonstrated that wool-like yarn can be obtained by overtwisting, moistening and drying in the overtwisted state and removing the overtwist afterwards. As this treatment was not permanent at all, the moistening was later [29] combined with a formaldehyde treatment during overtwisting. The yarn was stabilized in this strained state. The principle of falsetwisting, i.e. a combination of two yarns with s- and z-twist was also developed at this time. During the Second World War a considerable production of such wool-like fibers took place in Switzerland when genuine wool was not available in sufficient quantities.

The permanency of the false-twist effect was, however, not completely sufficient and the abrasion strength of these texturized rayon fibers was not satisfactory. Fortunately, however, the thermoplastic

polyamide fibers became available and Heberlein disco-
vered that, with these fibers, the false-twist process
could be realized by a simple thermal treatment; no
chemical reaction was necessary. It is well known that
this invention initiated the world-wide success of
texturized yarn, the first product being Heberlein's
Helanca.

4) Recent Investigations of the Properties of Cross-linked Fabrics

In the following part of this paper the mechanism
of reactions in crosslinking and their relation to tex-
tile mechanical properties will be discussed in more
detail. The purpose of this report will be to demon-
strate that a careful investigation of the chemical re-
actions themselves can be helpful in optimizing the
properties of finished fabrics, consisting partly or
completely of cellulose fibers.
It may be remembered that, in spite of the fact
that formaldehyde treatments of cellulose fibers have
been made for 70 years and with urea-formaldehyde re-
sins for 40 years, it was still debated in the early
Sixties if a chemical reaction between cellulose and
the chemical applied to it takes place at all. J. T.
Marsh, one of the pioneers in the technology of this
field, had doubts about the problem until 1962 [21].
The first clear evidence was given by Abend,
Stamm and Zollinger [30] in 1966 for cellulose cross-
linked with divinyl sulfone: Cotton and rayon fibers
treated with divinyl sulfone gave, after acid treat-
ments, degradation products which contained two glu-
cose units at the two ends of mono- and dimeric sul-
fone derivatives.
For cellulose treated with crosslinking reagents
which are not stable to degradation in strongly acidic
media, a permethylation technique was developed by
means of which it was possible to determine even the
relative reactivity of the three hydroxyl groups on an
anhydroglucose unit of cellulose [31].
Most of our research in the late Sixties and early
Seventies was carried out with formaldehyde. There are
several factors which indicate that formaldehyde might
be an ideal, commercial crosslinking agent for cotton
finishing: 1 mole of formaldehyde is 14 to 30 times
cheaper than 1 mole of the various cyclic ethylene
ureas; cellulose formals have an excellent stability
towards hydrolysis in washing operations; they do not
retain chlorine and show no signs of yellowing when
ironed. There are mills in Europe which use formalde-
hyde, although cotton crosslinking with formaldehyde
is said to have the disadvantage of extensive strength

losses and low reproducibility.

    We decided therefore to compare the resilience/
strength loss relationship of formaldehyde crosslinked
fabrics relative to fabrics crosslinked with dimethyl-
olethylene urea (DMEU). The latter was taken as repre-
sentative of highly reactive cyclic N-dimethylol urea
compounds.

    For this purpose we crosslinked a standard cotton
poplin in pad-dry-cure processes with formaldehyde and
with DMEU, varying the reaction time, temperature and
the concentrations of the crosslinking reagent and the
catalyst ($MgCl_2$). Basically, we compared the dry crease
recovery angles (a measure of resiliency) of all
samples with the tensile strength.

    In addition we determined the degree of polymeri-
sation (DP) of crosslinked cotton (after removal of
the crosslinks) in order to separate the total loss in
tensile strength into the so-called permanent damage
[32] which is due to the decrease in DP of cellulose
caused by hydrolysis during curing, and the temporary
strength loss which is caused by the stiffening of the
macromolecular network by the crosslinks. Careful re-
moval of the crosslinks nullifies this strength loss.

    For cotton crosslinked with N-methylol compounds
this division of the total tensile strength loss into
temporary and permanent damage has been made several
times in the past, as it is relatively easy to remove
such crosslinks by mild acid treatments. For cellulose
formals, however, this has not been made without da-
maging the polymer itself. However, Lewin and Weinstein
[33] found that the determination of the DP of trinit-
rocellulose can also be applied to cellulose formals:
In cotton crosslinked with formaldehyde the oxymethy-
lene bridges are removed on nitration without hydroly-
tic degradation of the cellulose chain.

    Several series of pad-dry-cure application on a
100 % cotton poplin[3] varying catalyst and crosslinker
concentration and temperature yielded the results
which are summarized in Figure 1.

    One recognizes that the crease recovery/tensile
strength relationship of DMEU applications are signi-
ficantly better than those with formaldehyde: A 7.0 %
loss in tensile strength is observed per 20^0 (W + F)
increase in crease recovery angle. Crosslinking with
formaldehyde gives a poorer relationship. The formal-
dehyde curve can be described by an initial loss of
16 % in tensile strength and by an additional 7.5 %
loss per 20^0 (W + F) increase in dry crease recovery
angle. Compared to DMEU applications, formaldehyde has

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[3] Details are described elsewhere [34 – 37].
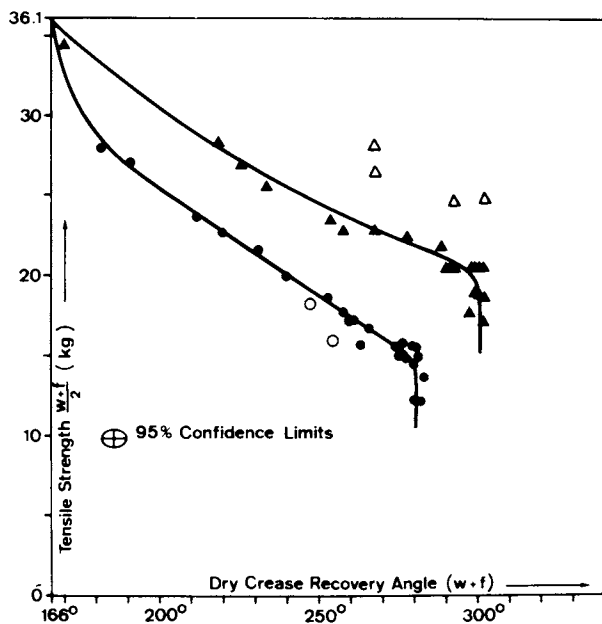
Figure 1. Dry crease recovery angle/tensile strength rela-
tionship for cotton poplin crosslinked with formaldehyde
(● and ○) and with DMEU (▲ and △). ○ and △: Pad-
ding solution containing more than 20% w/v of formalde-
hyde and DMEU, respectively.

the disadvantage of this initial loss and a slightly
greater loss per 20° increase in crease recovery angle.
    The upper limits of dry crease recovery angles
for DMEU and formaldehyde (300° and 280°, respectively)
agree with those reported in the literature [38]. A
better crease recovery angle/tensile strength relation
is obtained if padding solutions with more than 20 %
DMEU are used. With formaldehyde, however, no such in-
fluence can be observed.
    What are the fundamental causes of the poorer
crease recovery angle/tensile strength relation of
formaldehyde crosslinked cotton?
    This question can be answered if the tensile
strength loss is separated into permanent and tempora-
ry loss. In Figure 2 the total (direct determination)
and permanent (from DP measurements) tensile strength
losses of DMEU- and formaldehyde crosslinked samples
are plotted against dry crease recovery angle. From a
comparison of the DMEU and formaldehyde curves it is
quite obvious that the permanent loss is much greater
in the latter case.
    If we analyse, on the other hand, the tensile
strength loss data for the temporary damage fraction,
it can be demonstrated [34, 35] that in this respect
formaldehyde is no worse than DMEU-treated cotton.
    In terms of practical application the range with
dry crease recovery angles higher than 250° is the most
important. In this range the results show that for
DMEU treatments of the total tensile strength loss of
7 % per 20° (W + F) increase in dry crease recovery
angle only 0.5 % is due to the permanent damage. For
formaldehyde treatments, of the total loss of 10.5 %,
6.3 % are due to the permanent damage.
    The higher permanent strength loss obtained with
formaldehyde is due to the fact that formaldehyde is
about 8 times less reactive than DMEU. Formaldehyde
treatments need about 8 times more catalyst ($MgCl_2$)
than those with DMEU in order to obtain the same resi-
liency. The higher catalyst concentration is the cause
of the higher permanent loss in formaldehyde treat-
ments.
    Our results demonstrate therefore that under very
mild crosslinking conditions the fabric is per se al-
most not damaged by DMEU. After a large number of
washings such a fabric will therefore have about the
same tensile strength as a fabric which was not cross-
linked. Observations which support this conclusion
have been made by Du Bois [39].
    Therefore it is worthwile to investigate further
if mild treatments improve the resilience/damage ratio.
The application of some new catalysts with higher ac-
tivities appeared to us to be particularly interesting

in this context, as they can be used at lower curing temperatures. Most of these catalysts are mixtures of metal salts with organic acids such as tartaric acid and citric acid [40, 41]. Another type consists of mixtures of magnesium salts and tetrafluoroborate [42].

The application of these highly active catalysts in crosslinking with formaldehyde at temperatures between 80°C and 125°C gave a very small, barely significant improvement in the resilience/mechanical strength relationship relative to experiments with conventional catalysts at 160°C [34-37]. Yet for the application of DMEU at lower temperatures the use of highly active catalysts significantly improves the relationship between crease recovery and tensile strength. In Figure 3 the experiments with $MgCl_2$/tartaric acid at 85°C and 105°C are compared with the results of experiments with $MgCl_2$ alone at 130 to 160°C (solid line).

The improvement is due, as shown elsewhere [34, 35], to a decrease in the temporary damage, i.e. the damage which is caused by the stiffening of the molecular network by crosslinks. Type, length or location of crosslinks with DMEU are therefore favorably influenced by a decrease in temperature. In addition curing at lower temperatures is advantageous from the point of view of conservation of energy.

In the case of formaldehyde, however, the permanent damage which, as Figure 2 shows, is a significant part of the total damage, is about the same over the whole temperature range of 85°C to 160°C.

As these results with formaldehyde indicate that a decrease in temperature does not change the ratio of rates of crosslinking and cellulose hydrolysis, we decided to measure the temperature dependence of these rates directly. In an optimal crosslinking process, the ratio between the rate of crosslinking, r_{cx} and the rate of hydrolysis, r_H, should be as large as possible.

Both reactions are very complex in the sense that several physical processes (swelling of cellulose, diffusion of catalysts and chemicals into the fibre, adsorption in the fiber) are combined with chemical processes (methylol and formal formation, protonation and dissociation of glucosidic bonds between anhydroglucose units) [43, 44]. Furthermore, one must consider that crosslinking is reversible, but hydrolysis is not; the rate ratio r_{cx}/r_H decreases therefore with increasing time.

The temperature dependence of a chemical reaction is usually expressed by the activation energy relationship. This equation is used here but we should like to emphasize that the values for E_a are, strictly speaking, only _apparent_ activation energies as they
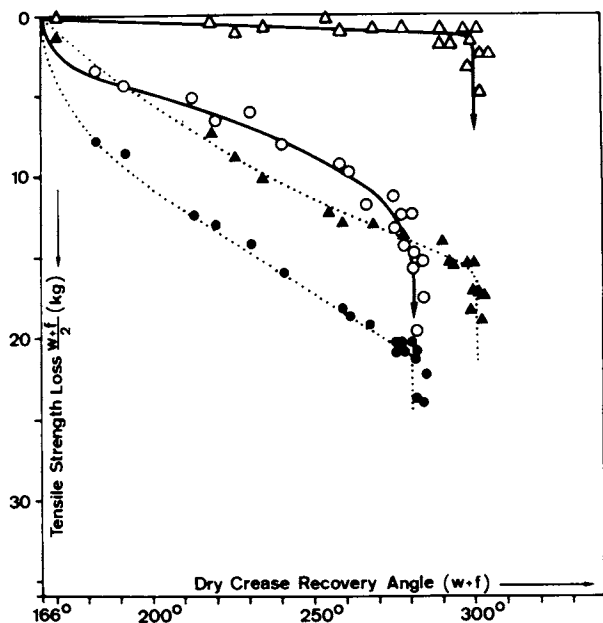
Figure 2. *Influence of total loss (····; ▲, ●) and perma-*
nent loss (△; ○) in tensile strength in crosslinking with for-
maldehyde (●, ○) and with DMEU (▲, △)
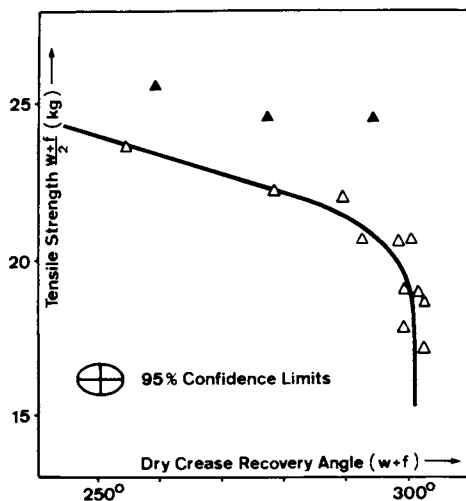
Figure 3. *Dry crease recovery angle*
and tensile strength for crosslinking with
DMEU using MgCl₂ at 80–160°C (△,
solid line) and MgCl₂/tartaric acid at
85°C and 105°C (▲)

refer to overall rate constants, i.e. rate constants
which include terms for physical and chemical steps
such as adsorption equilibrium which are also tempera-
ture dependent. (A true activation energy in molecular
terms is one which is restricted strictly to <u>one</u> iso-
lated step on the reaction path).

$$k = A \ e^{-\dfrac{E_a}{RT}} \qquad\qquad (2)$$

E_a = Activation energy
A = Preexponential factor
R = Gas constant
T = Absolute temperature

Literature data for the activation energy of
crosslinking with formaldehyde and for the heteroge-
neous hydrolysis of cellulose vary greatly.
It was therefore important to have a reaction sys-
tem where the conditions could be carefully controlled.
In particular, all parameters except time and tempera-
ture must be constant in all experiments.
The method used was as follows: Samples of cotton
fabric were crosslinked in an aqueous solution of form-
aldehyde, acidified with HCl to pH 1.30, ionic strength
(KCl) I = 0.10 at 67.4°C, 77.6°C and 87.0°C. Indivi-
dual samples were taken out at various times and
washed. The cellulose formal group content and the de-
gree of polymerisation of the samples was determined
and used for the calculation of the overall[4] rate con-
stants k'_{cx} and k'_H. The system and the kinetic equations
used are described elsewhere [34].
The evaluation of the kinetic data yielded the
following apparent activation energies (with 95 % con-
fidence limits):

E_a(crosslinking) = 110.8 ± 5.2 kJ/mol
                (26.5 ± 1.2 kcal/mol)

E_a(hydrolysis)   = 125.1 ± 9.3 kJ/mol
                (29.9 ± 2.2 kcal/mol)

The ratio of rate constants k'_{cx} : k'_H is 0.044 at
67.4°C, but 0.033 at 87.0°C. A low reaction tempera-
ture should therefore improve the crease recovery
angle/tensile strength relationship. It can be calcu-
lated from the difference E_a(hydrolysis) − E_a(cross-

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[4] k'_{cx} and k'_H are called overall rate constants be-
    cause, in contrast to k_{cx} and k_H, they refer not to
    the chemical rate proper, but to the complex rate of
    diffusion, sorption and reaction.

linking) = 14.3 kJ/mol, however, that the temperature must be lowered from 160°C to 95°C to increase the ratio $k'_{CX} : k'_H$ by a factor of 2. Such a factor is too small to be really significant.

5) The Mechanism of Metal Ion Catalysis in the Cross-linking of Cotton

As mentioned before, crosslinking of cellulose is a complex process consisting of physical processes and at least two chemical reactions, namely the reaction of the crosslinking reagents with a hydroxyl group of one cellulose chain and, second, the crosslinking proper, i.e. the reaction with another cellulose chain. In the following we will concentrate on the rate-determining part of crosslinking with formaldehyde in the pad-dry-cure process using $MgCl_2$ and $MgCl_2$/tartaric acid mixtures as catalysts.

Crosslinking of cellulose with formaldehyde consists essentially of two chemical reaction steps, namely the formation of the hemiacetal (or O-methylol, equation 3) and the crosslinking proper, i.e. the formation of the formal (or oxymethylene bridge, equation 4).

$$Cell-OH + CH_2O \rightleftarrows Cell-OCH_2OH \qquad (3)$$

$$Cell-OCH_2OH + Cell'-OH \rightleftarrows Cell-OCH_2-O-Cell' + H_2O \qquad (4)$$
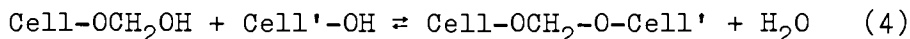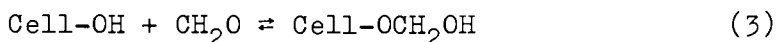
Many investigations have shown that the formation and hydrolysis of acetals is subject to specific acid catalysis. This can be accounted for by the mechanism (equations 5-8) postulated by Barker and Vail [45].

$$Cell-OCH_2OH + H^+ \xrightleftharpoons{fast} Cell-OCH_2\overset{+}{O}H_2 \qquad (5)$$

$$Cell-OCH_2\overset{+}{O}H_2 \xrightleftharpoons{slow} [Cell-O\overset{+}{C}H_2 \leftrightarrow Cell-\overset{+}{O}=CH_2] + H_2O \qquad (6)$$

$$Cell-O\overset{+}{C}H_2 + Cell'-OH \xrightleftharpoons{fast} Cell-(\overset{+}{O}H)CH_2-O-Cell' \qquad (7)$$

$$Cell-(\overset{+}{O}H)CH_2-O-Cell' \xrightleftharpoons{fast} Cell-OCH_2-O-Cell' + H^+ \qquad (8)$$
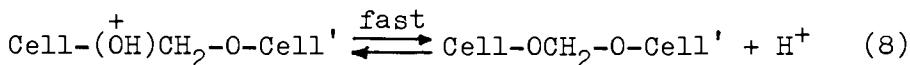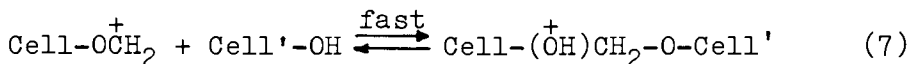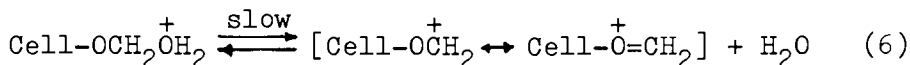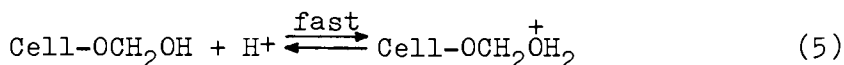
Concerning catalysis by metal salts, no clear experimental evidence for or against the existence of specific metal ion complexes as effective catalysts has been presented previously, although a specific metal ion catalysis has been postulated. It was argued

[46] that the thermal decomposition of MgCl$_2$ into
Mg(OH)Cl + HCl (where HCl is the catalyst) occurs only
at temperatures higher than 181°C and that the equilib-
rium lies on the side of the hydroxides and oxides on-
ly at temperatures higher than 800°C. On the other
hand, however, a relationship between the catalytic ac-
tivity of metal ions and their Lewis activity was as-
sumed [47].

For mixed catalysts of the MgCl$_2$/tartaric acid
type, Pierce et al. [40] and Ravikrishnan [41] assume
that complexes formed between the metal ion and the or-
ganic acid are the catalysts proper. Both emphasize,
however, that the mechanism of catalysis is still un-
known.

For our investigation [37] we chose a kinetic ap-
proach. We measured the rate of crosslinking in the
presence of various potential catalytic species, alone
and in combinations, assuming that, in the latter case,
the observed rate is the sum of the individual rates.

Equation 9 describes the crosslinking reaction in
the presence of MgCl$_2$, whereby the term $k_{Mg^{2+}}[Mg^{2+}]$
represents all Mg^{2+} containing species which catalyse

$$k^{obs}_{MgCl_2} = k_{H_3O^+}[H_3O^+] + k_{Mg^{2+}}[Mg^{2+}] \qquad (9)$$

the reaction. Specific metal ion or metal complex ca-
talysis only occurs if the second term is considerably
larger than the term $k_{H_3O^+}[H_3O^+]$.

In order to investigate this question experimen-
tally one has to take into account that pH-measure-
ments on the fabric under curing conditions, i.e. with
a very low water content are impossible. On the other
hand it seemed reasonable to assume that the presence
of a buffer would allow hydroxonium ion concentration
in the fabric to be kept almost constant during curing
even if, by metal complex formation or other reasons,
hydroxonium ions are formed. In addition, we took into
account the possibility that ionic strength might be
an important factor in crosslinking. Therefore experi-
ments with 0.050 M KCl were carried out at the same
time as experiments with 0.025 M MgCl$_2$ (ionic strength
in both cases: I = 0.050).

The kinetic results in Table I show that the rate
of formaldehyde crosslinking with MgCl$_2$ is at least
fifty times greater than that of the system with KCl.
The mere presence of Mg^{2+} ions, however, is not a suf-
ficient condition for catalysis: In the presence of a
buffer which keeps the pH at about 5, the rate of
crosslinking in the presence of Mg^{2+} ions is not sig-
nificantly higher than that with K$^+$ ions and a buffer.
Thus, it is obvious that the process is governed by the

Table I. Observed rate constants k_{obs} of crosslinking cotton with formaldehyde (pad-dry-cure at 160°C)

Padding liquor	Buffer in padding liquor	pH of the padding liquor	pH on the fabric during curing	k_{obs}
6.5 % CH_2O/0.025 $\underline{M}$ $MgCl_2$	-	5.1	?	370 x 10^{-5} sec^{-1}
6.5 % CH_2O/0.050 $\underline{M}$ KCl	-	5.1	?	7.3 x 10^{-5} sec^{-1}
6.5 % CH_2O/0.100 $\underline{M}$ $MgCl_2$	0.5 $\underline{M}$ HProp +0.5 $\underline{M}$ KProp	4.6	~5	3.5 x 10^{-5} sec^{-1}
6.5 % CH_2O/0.200 $\underline{M}$ KCl	0.5 $\underline{M}$ HProp +0.5 $\underline{M}$ KProp	4.7	~5	2.6 x 10^{-5} sec^{-1}

HProp, KProp = Propionic acid, potassium propionate

proton concentration. This means that a specific acid catalysis occurs in the case of $MgCl_2$.

It is interesting to discuss briefly potential reasons for this increase in hydroxonium ion concentration in highly concentrated crosslinking systems containing $MgCl_2$.

The magnesium aquo ion $Mg[H_2O]_x^{2+}$ is a very weak acid ($pK_a = 9.8$ at $100^\circ C$ [48]) and is therefore not an effective catalyst. Thermal decomposition of $MgCl_2$ is not probable either, as it has been observed only above $181^\circ C$ [49]. Complex formation with cellulose, however, and, if used, with N-methylol crosslinking agents, may raise the acidity during curing. Complexes of zinc ions with polyhydroxyl compounds are known [50]. This effect may be enhanced with bleached or damaged cotton where carboxylic groups are present.

This type of catalysis is also the cause of the increased reactivity of $MgCl_2$/tartaric acid mixtures in crosslinking: In a manner similar to that described above for the systems containing $MgCl_2$ alone, we determined the individual rate constants for the various species present in such systems [34, 36]. These rate constants are shown in the kinetic equation (10).

$$k_{mixture}^{obs} = k_{H_2O}[H_2O] + k_{H_3O^+}[H_3O^+] + k_{Mg^{2+}}[Mg^{2+}]$$

$$+ k_{H_2Tart}[H_2Tart] + k_{MgTart}[MgTart] \qquad (10)$$

The kinetic experiments showed that the following sequence of catalytic activity occurs:

$$k_{HCl}^{obs} : k_{MgCl_2/H_2Tart}^{obs} : k_{H_2Tart}^{obs} : k_{MgCl_2}^{obs} : k_{MgTart}^{obs}$$

$$>2400 : \qquad 670 \qquad : \quad 9.8 \quad : \quad 5.5 \quad : \quad 1.0$$

HCl is, at a given molar concentration, by far the most effective catalyst in crosslinking with formaldehyde by the pad-dry-cure process.

HCl is at least
2400 times more reactive than magnesium tartrate
 430 times more reactive than magnesium chloride
 240 times more reactive than tartaric acid and
 3.6 times more reactive than the mixture $MgCl_2$/H_2Tart

One can also conclude that the observed catalytic activity of the mixture of $MgCl_2$ and tartaric acid is 44 times greater than the sum of the catalytic activities of the two components. This factor is a measure of the "synergetic effect of mixed catalysts" previous-

ly discussed by the discoverers of these catalysts
[40, 41].

Our investigation demonstrates therefore that ca-
talysis by hydroxonium ion accounts for 74 (or more)
percent of the total in the catalysis of crosslinking
with formaldehyde using mixed metal salt catalysts.

We also studied the complex equilibria which are
responsible for the high hydroxonium ion concentration
in mixtures of $MgCl_2$ and tartaric acid. pH-values of
solutions of tartaric acid, of mixtures of $MgCl_2$ and
tartaric acid in a molar ratio 1:1, and of hydrochlo-
ric acid were measured up to a concentration of 5.0 M
and compared with values calculated assuming that all
nine particles are present in the system: Mg^{2+}, Cl^-,
H_2Tart, $HTart^-$, $Tart^{2-}$, $MgHTart^+$, $MgTart$, H^+ and OH^-.[5]

The experimental pH-values did indeed decrease
strongly with increasing concentration and coincided
fairly well with the calculated values based on the
type of complex formation shown in equations (11)-(12).

$$Mg^{2+} + H_2Tart \rightleftharpoons MgHTart^+ + H^+ \qquad (11)$$

$$MgHTart^+ \rightleftharpoons MgTart + H^+ \qquad (12)$$
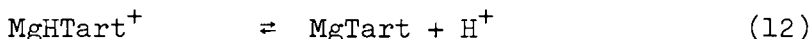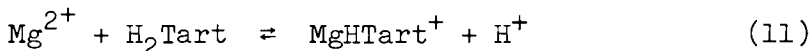
These data support our conclusions that, first,
direct catalysis by the magnesium ion or its complexes
is negligible relative to hydroxonium ion catalysis,
and second, that magnesium ions and their complexes
with carboxylic acids have an indirect catalytic ef-
fect by increasing the hydroxonium ion concentration.
This concentration increased when the concentration of
the metal salt/carboxylic acid system was increased,
but to an extent greater than expected from a linear
relationship. This is exactly the process which takes
place in curing: Here a decrease in the water content
of the dry fabric to the so-called bone-dry fabric
takes place. This is equivalent to an increase in the
concentration of $MgCl_2$, tartaric acid and their com-
plexes in the little water which is still present and
therefore curing leads to a drastic increase in the
hydroxonium ion concentration.

Would it not be easier to get this high hydroxo-
nium ion concentration by simply adding greater amounts
of hydrochloric acid to the padding liquor instead of
$MgCl_2$ and tartaric acid? It is true that the activity
required for the crosslinking reaction could be ob-
tained; simultaneously, however, the rate of hydroly-
sis, the cause of the permanent damage, would be in-

Complex equilibrium constants for this system are
known [51].

creased. The ratio $k'_{CX} : k'_H$ discussed in the third sec-
tion of this paper would be influenced unfavorably be-
cause, as mentioned before, this ratio decreases with
time as crosslinking is a reversible reaction, but the
hydrolysis of cellulose is irversible. In crosslinking
with hydrochloric acid alone the high hydroxonium ion
concentration is present before and after curing, i.e.
for a long time. This is not the case with $MgCl_2$ or
$MgCl_2$/tartaric acid mixtures which are only highly
acidic in the extremely concentrated solutions present
in curing. After curing the fabric will adsorb mois-
ture again and thus the acidity will decrease. With
these metal ion catalysts it will decrease to an ex-
tent greater than expected from a linear relation with
the moisture content; with HCl, however, the decrease
is linear.

   What is the reason for the fact that tartaric
acid or citric acid are much better cocatalysts than
unsubstituted carboxylic acids such as acetic acid or
dicarboxylic acids such as succinic acid? The metal
ion complexes with carboxylic acids and dicarboxylic
acids are more stable if the acids contain hydroxylic
groups in a position alpha to the carboxylic group(s).
The complex equilibria are shifted to the side of the
complex (and therefore more hydroxonium ions are
formed) if a chelate complex such as 1 is formed. The
stabilisation of metal complexes by chelate formation
was investigated on a quantitative basis for the first
time by Schwarzenbach at the University of Zurich [52]:
He found that complex equilibrium constants increase
by factors of up to 10^6 on chelate formation. He called
this factor the chelate effect. We conclude that this
effect is the essential basis of the activity of the
cocatalysts in crosslinking discovered by Pierce and
Frick [40], and by Ravikrishnan et al. [41].

$$\text{(13)}$$
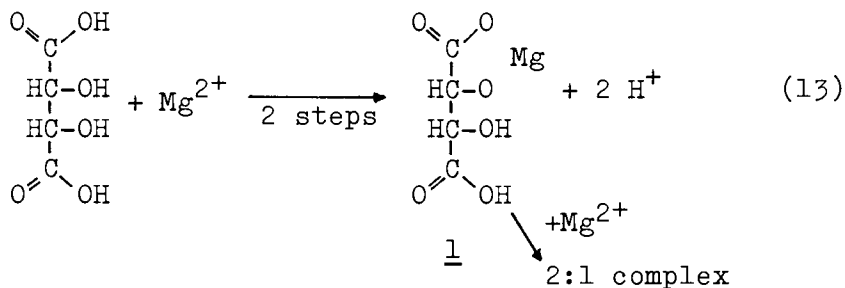
6) Concluding Remarks

In summary, we have described first some basic
investigations of macromolecules carried out in the
second part of the 19th and the first half of the 20th
century which became the basis of applied research on
light-weight fabrics called "Swiss cotton" (second
section) and which influenced also the invention of
texturized yarn, discussed in the third section. The
fourth section refers also to applied research, namely
to the optimization research in crosslinking cotton
fabrics. The last section contains results of basic
research, namely on the mechanism of catalysis in
crosslinking; explanations are given for the empirical
observations made in investigations of the optimiza-
tion of the crosslinking process.

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Recent Canadian Developments in Fiber Science

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Although it undoubtedly doesn't come close to matching the level of activity in the USA, textile research and development in Canada probably does approximate in scope the American endeavours in the same area. In other words although there is a very large difference in scale of R&D between our two countries, consumers expect the same varieties of products and so a similar array of textile technologies is called for. In many instances, such technologies cannot be based uniquely on Canadian science; there isn't enough of it. It is frequently both desirable and possible to import appropriate technologies and, in numerous instances, American technology is used.

Nevertheless, it is obvious that scientific and innovative advancements are not restricted by national boundaries and a brief account of some Canadian developments in textile and fiber science may be of interest. I propose to describe five different kinds of R&D activities; these examples have been selected arbitrarily although not necessarily at random. It is hoped that this spectrum of "case histories" will represent the scope of Canadian activities. This is of course, an account of people rather than of laboratories or institutions.

I Novel Yarn Manufacture

No description of Canadian achievements in textiles R&D would be complete without reference to the major advances introduced by the Bobtex Corporation of Montreal. Most of you will have heard Dr. Andrew Bobkowicz (or one of his colleagues) describe his company's Integrated Composite Spinning System (Figure 1) in more detail than can be accommodated in

this lecture. Figure 2 illustrates the processing
concept, and Figure 3 shows a model of a three compo-
nent ICS yarn.

Of the many potential advantages for this yarn
making system, a few relating to versatility and
efficiency are as follows: (i) a wide range of ICS
yarn compositions; (ii) yarn engineering to meet
specific end use applications; (iii) high production
speeds; (iv) lower yarn material costs. The flexi-
bility of the concept and the machinery is reflected
in the following compositional options: Fibers - 30
to 60%; Thermoplastic polymer - 20 to 50%; Carrier
filament(s) - 10 to 60%.

This Bobtex breakthrough, of which the Canadian
scientific and technological community is very proud,
is a typical "overnight" success. It is based on
many years of difficult, expensive, fundamental
research and it has relied upon the complete dedica-
tion as well as the innovative genius of its inventors
in order to reach the marketplace. The impact of ICS
yarn manufacturing technology is only just beginning
to be apparent, following the ITMA '75 demonstration
and the concomitant announcement of the non-exclusive
license arrangement under which the Leesona Corpo-
ration (Textile Machinery Division) is able to manu-
facture and sell the Bobtex ICS equipment on a
worldwide basis.

II   Triacetate Polypropylene Carpet Fibers

A second example of Canadian industrial R&D in
textile and fiber science is the development at
Celanese Canada Ltd. of cellulose triacetate and
polypropylene carpet yarns. While the use of this
example considerably stretches the meaning of the
word "recent" in the title of this talk, it also
represents a multi-million dollar business based on
patents and processes which were unique to Canada
at the time.

While it is by no means a technically acceptable
description of the research performed at the Celanese
Canada laboratories, the essence of what was accom-
plished is indicated in the next three Figures:
Figure 4 refers to the Palmer-Larue process; Figure 5
refers to polypropylene coloration and extrusion;
Figure 6 lists the further processing procedures as
well as the end product of the entire R&D effort. As
far as I know, these polypropylene/cellulose triace-
tate pile yarn carpets are still unique to Canada.
I know from personal experience that these carpets

The world's first integrated

composite spinning system

To combine continuous filament properties

with polymer resin economics and staple

fiber outer texture and aesthetics into

a new type of composite spun yarn.

Figure 1. Bobtex ICS process

ICS YARN PACKAGE
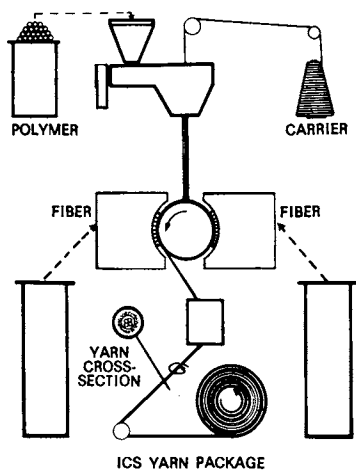
Figure 2. ICS process diagram

CARRIER

POLYMER

STAPLE FIBER
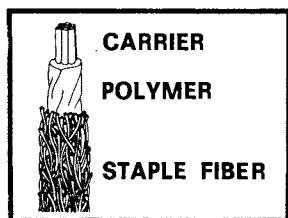
Figure 3. Model of a three-component ICS yarn

- Development of the Palmer-Larue process for
    the melt-spinning of cellulose triacetate
    fibers
- Development of a continuous color-spin-draw-
    crimp process (>100 man years of R & D)
- More than 100,000,000 lbs. of melt spun
    triacetate carpet fibers produced.

Figure 4.   Celanese triacetate R & D

- Coloration of the fibers by blending
    pigments with polypropylene in powder
    form
- Design and development of melt extruders
    using apparatus in which the polymer
    remains in a molten state for less than
    one minute.

Figure 5.   Celanese polypropylene R & D

represent as good a carpet value as one can buy.
     In connection with my earlier reference to person
-accomplishments, I wish to draw your attention to the
following item. The same scientist who headed the
Celanese research team in the 1950's and early 60's
has subsequently directed the development of an enti-
rely different type of carpet yarn in the laboratories
of a different company. In this latter instance the
new carpet yarn is four-ply and consists of three
different levels of dyeability of nylon yarns together
with a conducting monofilament of nylon to impart
antistatic properties. Needless to say, the concept
is not a Canadian invention, but the novel technology
which was developed in Canada was both patentable and
saleable.
     As I leave the industrial side of this R&D
survey, I would like to note that both examples I have
described resulted in the presentation of the Canadian
Textile Science Award, to Emilian and Andrew Bobkowicz
and to Dr. Walter Palmer in 1971 and 1973, respecti-
vely. Thus, while my selection of examples was
arbitrary, it was by no means done randomly.

III   Fluorochemical Fabric Finishes

     This example comes from a military materials
laboratory in which much of the research relates to
improved methods for providing protection for mili-
tary personnel. The investigation, under the direc-
tion of Dr. John McAndless, involved a study of liquid
repellent finishes, on the fabric materials used in
military clothing, to provide protection against
wetting by rain and other liquids such as oils, fuels
and chemical agents.
     Certain fluorine-containing polymers are unique
in their ability to repel both water and oily fluids,
and common fluorochemical repellents include polymers
of fluoroalkyl acrylate (and methacrylate) esters as
shown in Figure 7. The ability of fluorochemicals
to protect fabrics from being wetted by low surface
tension oily liquids results from the inherent low
surface energy of perfluoromethyl (CF_3) groups which
form the outermost layer of the fluorinated surface.
     The surface conditions necessary for producing
effective liquid repellency are shown in Figure 8.
The required packing of CF_3 groups is usually achie-
ved by employing polymeric compounds containing
straight chain, fully fluorinated substituents having
a minimum of 8 carbon units in length, with the
substituents oriented perpendicular to the fabric

- Combination of all the unit operations
  into one continuous process including
  spinning, drawing, crimping, cutting,
  and baling.
- Use of polypropylene fibers in blends
  with triacetate fibers to produce a
  low static, dense, hard twist carpet
  of good wear resistance and appearance
  retention.

Figure 6. Celanese carpet yarns
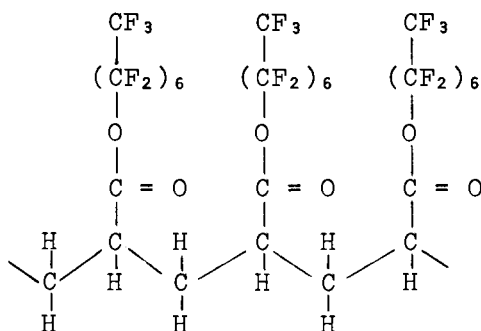
Figure 7. Fluorochemicals

1. FLUOROCHEMICAL EVENLY DISTRIBUTED OVER FIBERS

2. PROPER ORIENTATION OF FLUORINATED GROUPS

3. CLOSE PACKING OF FLUORINATED GROUPS

Figure 8. Surface conditions for producing effective liquid repellency

surface. This is indicated in Figure 9.

Since fluorinated polymers are very expensive, however, they are often extended with conventional water repellent compounds and other adjuncts in finishing formulations. The properties and problems with Quarpel treatments are shown in Figure 10. This situation is typical of a variety of both commercial and experimental finishes.

A study was undertaken at the Defence Research Establishment Ottawa (DREO) in order to establish a mechanism which could account for the loss of oil repellency which occurs when Quarpel-treated fabrics and fabrics treated with certain fluorochemical/ adjunct finishes are subjected to wearing. A second aim of the work was to determine whether repellent properties, once lost, could be recovered by any practical means.

A series of finishes was applied to cotton/nylon fabrics using conventional pad/dry/cure techniques. The finishes included Quarpel and fluoropolymers from 3M, Dupont and Ciba-Geigy combined with poly (alkyl methacrylate) esters. The fluoropolymers all possessed straight-chain fluorinated substituents of 8 carbon atoms in length. The alkyl substituents on the adjunct polymer molecules ranged in length from one to eighteen carbon atoms.

Fabrics treated with these finishes were sub-jected to accelerated wear using an experimental wearing machine developed at DREO. Of the many data obtained for different finish combinations on fabrics tested on the wearing machine, Figure 11 shows some typical ones. It is noteworthy that slower loss of oil repellency occurs if the length of the alkyl substituents on the adjunct is about the same as the length of the fluorinated substituent of the fluoro-chemical. It is also significant that too much adjunct causes a more rapid loss of oil repellency on wearing.

What is especially interesting, however, is the fact that, after 20 hours on the wearing machine and subsequent heating in a forced air oven for 5 minutes at 150°C, all fabrics showed a substantial recovery of oil repellent properties. In some cases a recovery very close to initial values occurred.

A possible explanation for all these observations is as follows. Disorientation of substituents at the surface of the finish (during wear) exposes non-repellent alkyl or methylene groups. This problem is exacerbated when the adjunct molecule substituents are much different in length (much shorter <u>or</u> much

CF$_3$ CF$_3$ CF$_3$ CF$_3$ CF$_3$ CF$_3$

POLYMER 'BACKBONE'

FIBER
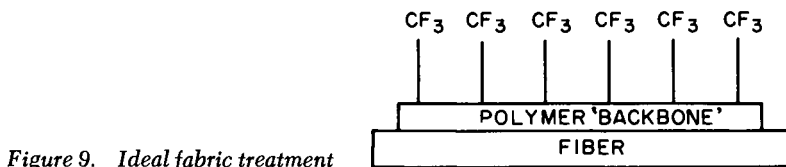
Figure 9.   Ideal fabric treatment

1. CONTAIN A FLUOROCHEMICAL AND A
    DURABLE WATER REPELLENT ADJUNCT.

2. INITIALLY, QUARPEL TREATMENTS CONFER
    EXCELLENT WATER-AND OIL-REPELLENCY TO
    FABRICS.

3. ON LAUNDERING AND WEARING, QUARPEL-TREATED
    FABRICS MAY RAPIDLY LOSE OIL REPELLENCY
    UNDER CERTAIN CONDITIONS.

Figure 10.   Quarpel treatments
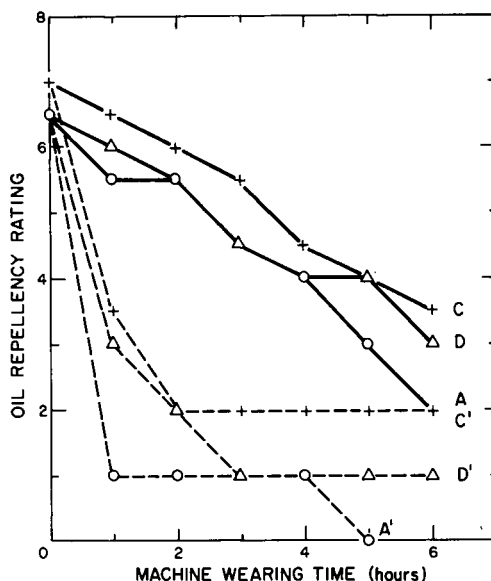
Figure 11.   Oil repellency (modified AATCC 118-1966) of worn fabrics with finishes containing as adjuncts (A) poly(methyl methacrylate), (C) poly(ethylexyl methacrylate), and (D) poly(octyl methacrylate). (———) Fluorochemical/adjunct is 1/1; (– – – –) fluorochemical/adjunct is 1/5.

longer) than the fluorinated substituents on the
fluorochemical molecules. Partial (or considerable)
recovery of repellent properties upon reheating the
fabrics is accounted for by the thermally-induced
orientation of finish components within the fabric
structure, at or just below the worn surface.

IV A Rapid Method for Studying Acoustic Behavior

As my fourth example, I have selected some
research from the laboratories of Prof. Keith Slater
at the University of Guelph. He and his students
have devised a new swept-frequency technique for the
rapid, inexpensive assessment of the approximate
acoustic performance of a material in the laboratory
or in a field situation.
Figure 12 shows a block diagram which illustrates
the method. The advantages derive from the use of a
swept-frequency sound source (instead of a fixed band
of noise) and a point to point integrator. By means
of the acoustic profile obtained in this way, one
can readily derive the measurement of the sound
transmitted or reflected by a given structure. Of
special relevance in the textile business, is the
determination of the reduction in sound owing to the
introduction of a textile product, e.g., a carpet.
The rapidity and inherent portability of the swept-
frequency procedure allows for the facile acoustic
"tuning" of a room, theatre, or other enclosure.
Since numerous operations in the textile
manufacturing areas are inherently noisy, it is useful
to be able to take Slater's equipment into various
parts of a mill in order to: (a) measure the severity
of the noise problems; and (b) evaluate rapidly the
efficiency of various corrective procedures. Finally,
this particular acoustic-behaviour method is being
evaluated as a technique for rating the comfort of
clothing. The comfort and/or protection afforded by
wearing apparel is very difficult to measure objecti-
vely but is known to depend in a complex way on a
variety of fabric parameters. Some of these same
parameters determine the acoustic behavior of fabrics.
Initial attempts to relate acoustic absorption to
fabric parameters and thence to comfort criteria
seem promising.

V Infrared Spectra of Monofilaments

My final example refers to a recent research
project from the Textile Chemistry group at the

National Research Council in Ottawa. A new method
has been developed for recording the infrared (IR)
spectrum of a short length (< 2 cm) of a single mono-
filament.

The use of wide slit settings (on the spectro-
meter) for a sample mounted precisely in the active
area of the IR beam allows the recording of the
spectra of single filaments. Virtually any grating
IR machine can be used although it is preferable if
the automatic slit program can be overridden.

A very simple sample-mounting device (Figure 13)
employs steel plates with accurately machined edges
to grip the fiber. The plates are themselves held
in position by a magnetic rubber sheet and the fiber
ends are taped to this sheet. The fiber can be
accurately positioned in the IR beam by manipulating
the magnetic rubber sheet on the steel mounting plate.

Two applications which cannot be achieved by
conventional non-destructive IR sampling techniques
can be used to illustrate the single fiber technique.
(I) Figure 14 shows the difference in IR absorption
by a polypropylene monofilament when it is aligned
parallel and perpendicular to the direction of prior
UV irradiation. Both spectra were recorded on the
same 1 cm zone of the fiber.
(II) Figure 15 shows the variations in optical density
along a 10 cm length of polypropylene monofilament
which had been irradiated in a Xe-arc Weather-Ometer
for 200 hours. The optical density of the OH and CO
bands varies markedly along the particular filament
length selected. This variation might result from
fluctuations in UV sensitive impurities along the
fiber.

While there are limitations to the diameter of
filaments that may be used singly, the method has a
wide potential applicability in textile and fiber
science. Recently a refinement has been developed
whereby the IR spectrum of very much smaller diameter
(e.g., < 1 tex) filaments can be obtained. Four to
six such filaments, arranged side by side in a simple
holder, can be used for purposes of identification or
characterization, for example, where the total weight
of fiber required is only a few micrograms.
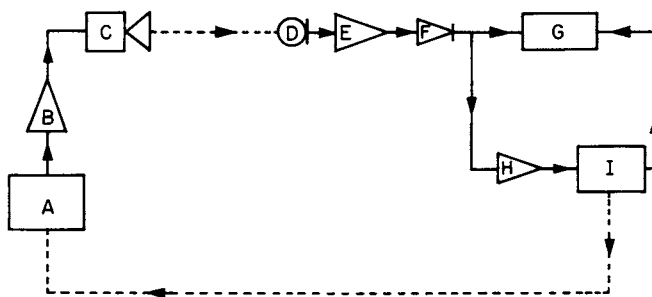
Figure 12. Block circuit diagram for the swept-frequency acoustic technique. (A) Sweep generator; (B) amplifier; (C) loudspeaker; (D) microphone; (E) amplifier; (F) rectifier; (G) recorder; (H) amplifier; (I) point-to-point integrator.
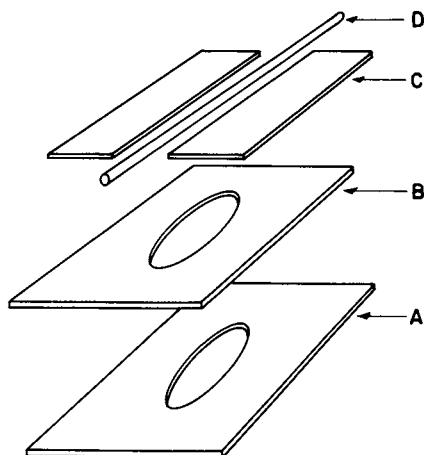
Figure 13. Monofilament holder—expanded view. (A) Mounting plate; (B) magnetic rubber sheet; (C) fiber constraining plates; (D) fiber.
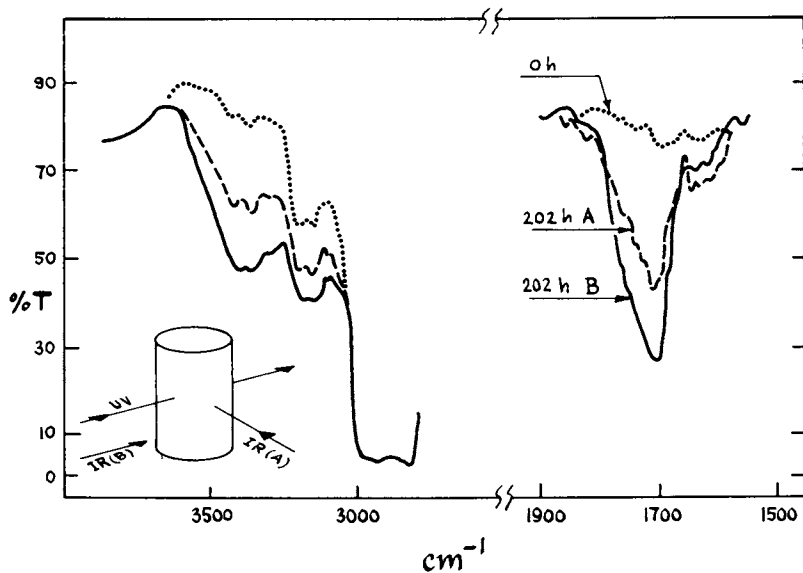
Figure 14. IR spectra of the same 1-cm length of a polypropylene monofila-
ment after 202 hr exposure in a xenon arc Weather-Ometer. (A) Perpendicular
to uv; (B) parallel to uv.
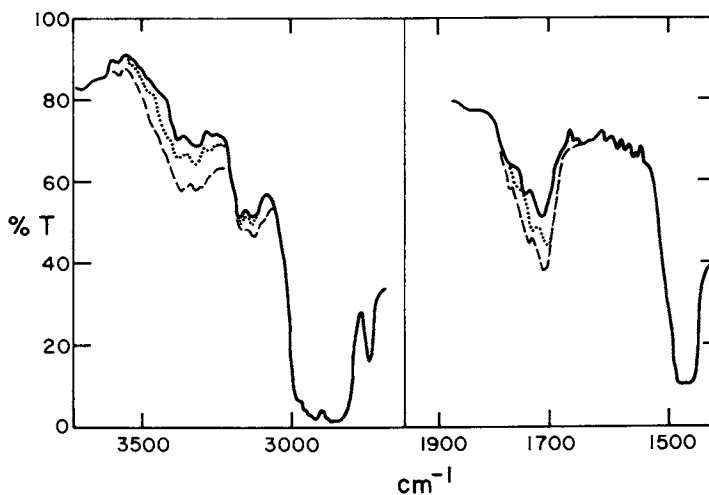
Figure 15. IR spectrum of a single polypropylene filament in different
zones along a 10-cm length, after uv irradiation

Acknowledgements

12

New Aspects of Textile Research

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1 - Introduction.

The main purposes of the textile research is to explain
the properties of the fibers in relation with their structure
to be able to foresee or to modify them as wished.
So in early times (1928) the practical behaviour of wool
was supposed to be governed by the -S-S linkages (1,2) that
is the chemical primary structure.
But, although the textile fibers are of very different
chemical nature and of very varied primary structure, their
behaviours may be considered as of same bearing.
This fact suggests, that the behaviour or the properties
are rather in connexion with the structures of higher order.
In this way the secondary and tertiary structures have been
studied by X-Rays diffraction and soon people went in quest
of correlations between crystallinity and properties (3).
With the development of electronmicroscopy the fine
morphological structure has also been revealed and also some
morphological structure and properties relationships have been
deduced (4).
Also the fibrillar architecture of the fibers has been well
studied : in wool (5,6) the protofibrillar and the microfibril-
lar structure can be distinguished ; in the case of cellulosic
fibers, the different fibrillar structures (fine or coarse well
heli-coidally oriented or not) are specifical for cotton,
polynosic, modal and normal viscose fibers (7) ; with the
help of microscopical peeling techniques it has been shown (8)
that synthetic fibers have also a very developped fibrillar
structure. On the other hand, the lamellar structure also has
been demonstrated (9,10) and correlated to the fibrillar struc-
ture (11).
These different morphological parts (fibrils and lamellae)
lye in a not continue phase (sometimes called "matrix" for wool
i.e.), or free. This means that between high cohesive solid parts
there are voids, holes and pores in the multiphase system of a
fiber.

We can speak about the actual texture of fiber.
The texture is different if the fiber is in more or less
wet state, under stress or not, in the presence of reagent or
not, that is : in the different practical conditions of use
of fibers during dyeing, finishing, dressing etc... in presence
of water or organic solvent and under given applied mechanical
strains. So it seems necessary to us to look at the importance
of actual texture in relation to the properties of textile
fibers.

2 - Texture Of Fibers.

   2 - 1. Approach.   The texture of fibers has been studied
early in connexion with sorption of water and alcohols.
SPEAKMAN (12) considered that the sorbates enter the fiber
through pores which are of about the same size as the length of
molecules of homologous series of alcohols which are sorbed
by the fiber : so he found i.e. that the wool fiber cannot sorb
n-butanol or larger molecules. BRADBURY (13) has shown that
even larger molecules (n-hexanol) may be sorbed by wool fiber,
but the saturation sorption values needs as longer time as
the sorbed molecules are larger : even after 30 weeks the satu-
ration sorption of n-hexanol at 80°C is not yet reached.
BRADBURY concluded that the pore size distribution of a fiber
changes with time : some pores of various sizes are present
initially in its structure, others being produced by movements
of atoms and atomgroups.
   These movements may be the result of both thermal fluc-
tuations and interactions with sorbate, solvent or reagent
molecules.
   The resulting change of texture may be permanent if the
conditions change. But with constant conditions the equilibrium
needs sometimes very long delays : CHABERT (14) has shown, that
even after 485 days, both : the absorption and the desorption
of water for viscose held in rigorously maintained conditions
of relative humidity and temperature are not yet in a steady
state.
   Because of this relative unstability, it (13) has been con-
sidered that texture - in terms of pores and holes and voids -
is not significant.
   But the change of texture (as like many other characteris-
tics) is a matter of kinetics and of sensitivity of measurements.
If the ideal steady constant state is difficult to be reached,
nevertheless a quasi-steady-state can be considered.
   It is also a fact, that in the practical conditions of use,
the time given for physical chemical reactions is only about
one to several hours. What happens after many weeks or years
may be of interest for fundamental research but does not dimi-
nish the importance of what happens in the required time of
applied physical chemical strains.

    2 - 2. Investigations of Texture : Methods. The classical
BET Surface aera determination gives a picture of accessible
surface, and therefore of porosity. But this technique has been
completed by many other methods of investigation.

    a) Mercury Porosity (15). Following WASHBURN'S LAW, the
quantity of mercury entering the pores depends on the applied
pressure p and on the radii r of pores :

    p = 26 cos θ/r (σ = superficial energy of Hg and θ = the
                        contact angle).

    This technique with the application of high pressure may
distroy the actual texture of fiber to be measured.

    b) Solute Exclusion (16, 17, 18, 19, 20). It is an inverse
gel permeation chromatography with calibrated monodispersed
inert (to the fibers) molecules and macromolecules ; the
variations of concentration before and after contact in given
conditions of temperature and time, give an estimation of the
pores size distribution.

    c) Electron Microscopy. SOTTON (21) described a technique
of treatment of fibers with H_2S, followed by an immersion in
$AgNO_3$ solution : the precipitation of Ag_2S reveals the porous
structure of fibers. MEIMOUN, PARISOT, HAGEGE, CATOIRE
(22, 23) included dienic monomers in the accessible parts of
fibers and after polymerisation through radiations, fixed OsO_4,
to reveal the pores.

    d) For the unaccessible voids and holes in the fiber, the
central scattering of X-rays (24, 25, 26, 27) following the
POROD'S LAW (28) enables to evaluate their sizes.
    The following table summarizes the possibilities of investi-
gation.

                              TABLE 1

POROSITY :	
BET-Ads. : Kr, N_2, etc....	: From 3 nm to 300 nm
Hg-pressure	: from 1 nm...
Solute exclusion :	
glucose	: from 0,8 nm...
raffinose	: from 1,2 nm...
.	
dextrans	: ... up to 160 nm
Electonmicroscopy	: from 1 nm...
(Classical microscopy	: from 1000 nm...)
INACCESSIBLE VOIDS :	
Central scattering of X-Rays	: from 0,2 nm to 50 nm

The practical physical chemical conditions of reactions during dyeing, finishing, dressing... are made in the presence of solvent (water or organic solvents), that is in the more or less swollen state of the fibers.

The best approaches of these practical conditions are fulfilled in the solute exclusion technique. That is the reason why we paid more attention to this technique.

The unsteady, changeable texture is directed by the possibility of movement of atoms and atomgroups, and even of morphological parts. Let us consider the structure and interaction situation of the fibers, which is responsible of the possibility of movement.

3 - Structure and Interactions in the Fiber.

3 - 1. Approach. Fibers are half crystalline and it is well known (29) that there are very high ordered regions (with high cohesion) neighboured with low ordered regions (with weak cohesion).

Low ordered region means the existence of free volumes of more or less magnitude.

For high ordered regions, only perfect crystalline parts may reach the maximal cohesion and also the maximal breakingstrength : that is the case of "whiskers" fibers or nearly for very fine stretched glas fibers (30). The presence of faults and holes in greater crystals originates dislocation and possibility of slippage.

In the general case of fibers the different morphological parts show different ranges of cohesion intensities :

In the crystalline parts, the stacks of macromolecules or macromolecule segments show in the privilegeous orientation of molecules a longitudinal cohesion given by covalence, and a lateral cohesion through what we can say : secondary bonds or interactions (H-bonds, Van der Waals forces, ionic-attractions and interactions).

In the so called "amorphous" regions, the same kinds of cohesion by covalence and by secondary interactions exist, but the stacks are not dense and the individual orientation of macromolecule segments may change considerably from one to another.

In the crystalline parts, the high lateral cohesion is given by a very close banded lying and numerous secondary interactions of nearly the same intensity. In the amorphous regions the secondary interactions are distributed in space and in intensities to give an irregular network with different bonding intensities.

3 - 2. The Interaction and the "Perturbators". Let us
recall for example the case of H-bond : we have the general
form :

$$R - X - H \;\; + \;\; Y - R_1 \xrightleftharpoons{k_o} \;\; R - X...H...Y - R_1 \qquad (E_1)$$

with distances d_{xy}, d_{RR_1} on the left and d'_{xy}, d'_{RR_1} on the right.
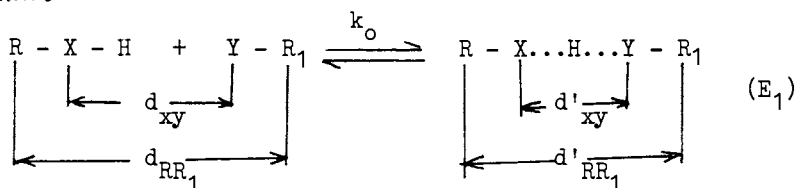
The H-bond interaction is an equilibrium situation ;
the equilibrium parameter k_o is governed by temperature and
by the distances d_{xy}, d'_{xy} (or d_{RR_1} , d'_{RR_1}).

Now, if a "perturbator" of the form $R_2 - Z - H$ or $R_3 - Q$
reaches the interaction region, competitive interactions may
arise as :

$$R_2 - Z - H + Y - R_1 \xrightleftharpoons{k_1} R_2 - Z...H...Y - R_1 \quad (E_2)$$

or

$$R - X - H + Q - R_3 \xrightleftharpoons{k_2} R - X...H...Q - R_3 \quad (E_3)$$
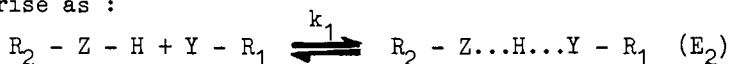
that means that the first equilibrium (E_1) is displaced to the
left.

Water or other plasticizers are such perturbators (as
R_2ZH, E_2) and they effect mainly the accessible non-crystalline
parts.

To summarize : temperature, stress (which changes the
distance), plasticizers are to be considered as "perturbators of
interactions". This situation is the same for all kinds of
secondary interactions.

3 - 3. The Interface between Crystalline and non Crystal-
line Regions. Now we have also to pay attention to the inter-
face between the non accessible strong crystalline part with
high cohesion (which is difficult to disturb) and the accessi-
ble weaker non-crystalline parts of perturbable cohesion. In
these frontier regions the cohesion is given by discrete
secondary bonds and some time, by covalence. It is possible to
distinguish frontier regions with relatively more covalence
bonds and with relatively less covalence bonds : the first
may be responsible of the fibrillar and lamellar structure as
supposed by PREVORSEK (31) and the second being responsible
of the lateral cohesion.

3 - 4. About Transitions. For almost perfect crystalls
the melting point is at a fixed temperature corresponding to
a very change from the solid state to the liquid state.

For polymers, it is well known that below a "glassy transition temperature", they are in the glassy state ; as lower the temperature as more rigid the polymeric body.

By rising the temperature some secondary bonds can be broken and the degree of freedom may sudden rise. For each class of intensity the breaking of secondary bonds brings a new jump of degree of freedom, and at each jumping corresponds a transition : as many modes in the polymodal distribution of secondary bond intensities as many transition temperatures.

Not only temperature is working as "perturbator" of secondary bonds, but also the combinated action of plastizer, stress and temperature may break some secondary bonds, so that new apparent transition temperatures appear in different environmental conditions :

- of relative humidity for hydrophilic fibers,
- of solvent vapor for hydrophobic-hydrophilic fibers,
- and of stress-strains for all fibers.

3 - 5. Some more about Holes. The use of fibers concerns their behaviour under the melting point, that is in the glassy and in the leathery states (32) mainly.

In the glassy state the degree of freedom is governed by oscillations, changes of valence-angle, more or less motion of side chains if any, but practically without total free rotation of C-C bonding.

In the viscoelastic state, the motion of segments of macromolecules in the non-crystalline regions is connected with oscillation and rotation, but the general orientation of the macromolecule remains : the more or less coiling-uncoiling motion is "microbrownian" or "peristaltic" (P. RYS) in contradistinction of the "macrobrownian" motion with displacement of the gravity center of the molecules (33).

The microbrownian motion originates the steady motion of free segments to reach the maximal entropy.

In contradistinction with the "oscillation-volumes" - see : FRENKEL (34) "Schwingungsausdehnungsvolumen" - there are real holes ; KANIG (35) thinks that there is a constant ratio between oscillation-volumes and the real holes, but as shown by KOVACS (36) this ratio may change. Concerning the relaxation free volumes and the real holes as little they may be, the situation can be described with a distribution or more or less stable holes.

By rising the temperature or the stress, or the plasticizer content (or all together), the microbrownian motion becomes macrobrownian in the places of new broken secondary bonds, so that the situation there, joins the situation of a viscous liquid : that is also the reason why the glassy transition temperature has been considered as a melting temperature of some parts in the amorphous region (37) which become like a viscous liquid.

The breaking of secondary interactions (H-bonds) when stress is applied, has been proved by BOURIOT (38) for different kinds of polyamide fibers (6-6, 6, 7, 11 & 12).

In the true liquid, the rate processes (39) govern the self diffusion of molecules in the liquid : that is a holes system with distributions of holes in space and size changing quickly with time.

Because of the presence of solid bonds and of relatively high energetic barrers in the fiber, in the case of viscoelastic behaviour, the changing of the distributions of holes in space and in size occurs in reduced manner. But this change can be risen by increasing the temperature, or under stress, or in presence of interaction perturbators : hot water in the case of hydrophilic fibers, carrier in the case of dyeing of more hydrophobic textiles.

3 - 6. Consequences. In a given environmental situation (temperature, water or solvent, applied stress etc...) the holes and pores distributions in space and in size tend to a nearly steady state, or to be considered as such in reasonable practical delay.

But the pores and holes govern the accessibility and therefore the kinetics of the physical chemical reactions.

The pores and holes distributions in space and size, depend mainly on the interaction situation in the non crystalline regions (interfaces and plain amorphous). This situation of cohesive forces (dispersion, induction and orientation) governs also the cohesion of the total fiber, that is also the technological properties. In other words, if our working hypothesis is correct, the most of the characteristics and properties depend mostly on the cohesion situation in the non-crystalline regions. The corresponding free volumes and the nearly steady size distribution of pores and holes could give a picture of the cohesion situation.

To verify these working hypothesis, different kinds of experiments have been made.

4 - Stress-Strain Behaviour.

The classical stress-strain curves show mainly two parts : the "Hookean region" with a relatively high modulus and the "viscoelastic region" with an elastic contribution of low modulus. Classicaly (40) the Hookean behaviour is attributed to the crystalline part, and the viscoelastic behaviour to the non-crystalline part. At first it has to be said, that it is amazing that the high cohesive crystalline part deforms before the less cohesive non-crystalline region ! (fig. 1).

That was the reason why, for wool i.e., we followed (41) the evolution of the high ordered regions with stretching up to 30 % with X-Rays :

In an effort to obtain quasi-equilibrium of the wool-water structure, we have stretched wool fibers at very low rates of extension (1,6 %/hour) in a constant atmosphere and followed the α - β transformations with a Philips P.W. 1048 texture goniometer, using a transmission technique with a counter measuring the meridional reflection at 5.14 Å and the 4.65 Å equatorial reflection : there is no change of the reflection positions. That means, that the distances between molecules segments in the high ordered parts do not vary, even for 30 % extension, that is far more than the Hookean deformation !

On the other hand, we have also shown (42) that the Hookean modulus of wool fibers changes significantly if wool is immerged in different solvents (water, perchlorethylene, methanol, isopropanol...) without penetration of the high ordered parts. This means that the Hookean deformation does not depend on the high ordered or crystalline part. (fig.2)

BOURIOT (38) investigated the evolution of the H-bonds with stretching different kinds of polyamide, by specifical shifts of the I.R. Spectrum : the same trend for all polyamides was found. With stretching, the number of free -NH- (not H-bonded) increases, and the intensities of the remaining bonded-NH decrease.

The phenomena is reversible inasmuch as the stretching itself is reversible.

These facts mean, that the Hookean deformation is mainly correlated to the lateral cohesion in the non-crystalline regions and probably in the interface, governed by the secondary bonds : if they are accessible to perturbators like solvents i.e., so the cohesion intensity changes and therefore : the Hookean modulus changes too.

In some cases the cohesion intensity may increase if initial perturbators are displaced : immerged in isopropanol the initially absorbed water of the wool is extracted and the cohesion rises ; also in the anhydrous state, the hydrophilic fibers show a higher Hookean modulus than in the standard atmosphere.

For natural cellulosic fibers with high degrees of crystallinity, the free volumes in the non-crystalline parts are of little sizes : by wetting the entering water contributed more to an increasing cohesion by creation of new interactions, than to a decreasing cohesion through perturbator's effects.

For artificial cellulosic fibers with lower degrees of crystallinity, the free volumes in the non-crystalline parts are of very larger sizes and the perturbator's effect is much higher than the effect of creating new bonding interaction ; the wet modulus is much lower than the dry (in standard atmosphere) modulus.

Overgoing the Hookean behaviour, a higher stretching leads to break some or many initial secondary bonds of the non-crystalline parts, but through the following better orientation of the freed segments of macromolecules, the stretching leads also to create new secondary bonding. As higher the stretching, as more such new bondings may be produced.

CHAMPETIER (43) described experiments made on Polyamide by means of the "repeated little Cycles" technique : For different stades of stretching the forces are periodically reduced and increased to obtain a local Hookean behaviour : the modulus considered as tangential modulus, increases in fact with the rate of stretching, corroboring our hypothesis. (fig. 3)

5 - Sorption under Stressing.

It is well known (13, 44) that for some textiles (wool i.e.) the sorption of water or solvents of the stress free fibers goes with a little reduction of volume.

We (41) have shown that between 0 and 8,6 % elongation the increase of regain at 20°C with the same R.H. corresponds to an increase of Water sorption. Even for the so called "boundwater" which represents the most of the absorbed water at 12 % R.H. (20°C) the regain of wool fibers increases from 3,804 % ± 0,016 % to 3,897 % ± 0,0116 % if the fibers are brought to an elongation of 8,6 %, that is a high significant increase of 0,093 % ± 0,032 % due to the strain.

That is consistent with the observation of the increasing of deuterium accessibility with elongation (45).

The heat of wetting increases also linearly with elongation after a significant minimum for an elongation of about 2 % - 3 % (41), which corresponds nearly to the real Hookean behaviour limit. For Polyester submitted at different rates of elongation FREYTAG and all (46, 47, 48) have also found a minimum of dye uptake for similar value : that also corresponds to the real Hookean behaviour upper limit. (fig. 4 & 5).

It seems that for the Hookean region, the cohesion mainly given by secondary bonds in the interface, is responsible of this cohesion elasticity with low deformation (elongation) in length and little contraction in width. After breakage of them, the accessibility increases, new sites are created and slippages occur with generating of larger holes and pores to the cost of the little ones. (fig. 6).

6 - Texture and Fatigue Behaviour.

Another possibility for investigation consists in following the change of texture through fatigue.

We developed (49) a statistical approach of fatigue behaviour based on the consideration of 3 different mechanisms of catastrophic rupture of fatigue. This theory implies that:(fig.7)
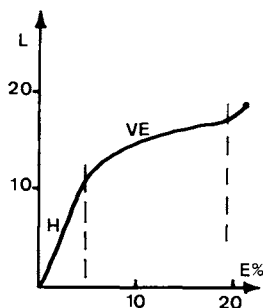
Figure 1. Normal viscose: stress–strain behavior. (H) Hookean region; (VE) visco-elastic region; (R) rupture.
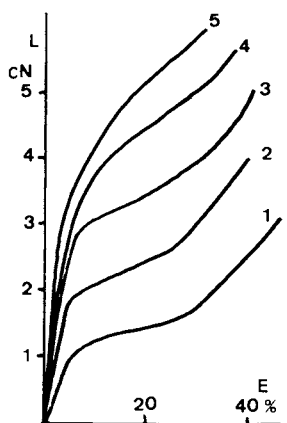
Figure 2. Wool: load (L)–strain (E = elongation) behavior in different environmental conditions. (1) In water; (2) in methanol; (3) in standard atmosphere; (4) in perchlorethylene; (5) in isopropanol. The Hookean modulus is significantly different (200–300 measurements for each case).
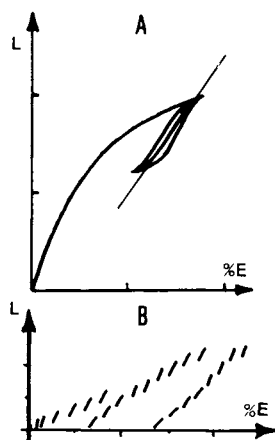
Figure 3. (A) "Little repeated cycles" [after Champetier (43)] to estimate the local (tangential) modulus. (B) Nylon fiber: 10 mm, stretched at 6 mm/mm: the evolution of the local modulus [after Champetier (43)].

Figure 4. Heat of wetting (W.H.) as a function of fiber wool elongation. The veritcal line of each experimental point indicates the maximal absolute error. (Regression: WH = 23.85 + 0.11 E correl. = 0.99)
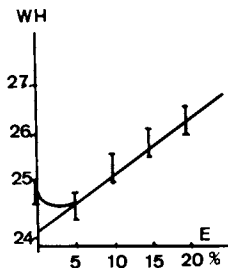
Figure 5. The relative difference of dye uptake (dyeing kinetic parameter) {$\Delta C/C$} (%) plotted as a function of the difference of elongation. C: ΔE (%) between a reference yarn wound with minimal tension (0.18 cN/dtex) and yarns wound with greater tension. This function shows a minimum between 0.5 and 3% ΔE.
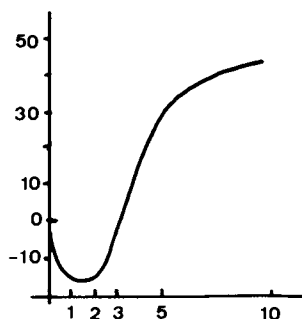
Figure 6. Through stretching (ΔE) the high cohesive HC (crystalline) regions remain inert, but in the "amorphous" region the hole distribution changes: the holes (h) become greater (h'). At the interfaces, the secondary bondings (H-bonds, Van der Waals forces, electroattraction . . .): b are stretched, and if the elongation becomes higher as the Hookean deformation, some of these secondary bondings at the interfaces break, allowing slippages of the now freed parts.
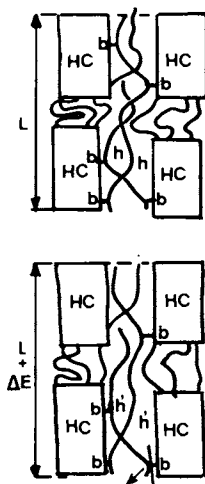
- a first mechanism is directed by the initially large
faults (mostly superficially : big pores), which follows a Grif-
fith's mechanism ; if the applied stress is high enough, the
catastrophic rupture occurs soo. : the probability of rupture
following the 1st mechanism decreases with time ;
    - the 2nd mechanism is directed by the progressive produc-
tion of larger holes and pores to the cost of the little ones ;
if a new larger hole or pore becomes large enough, the size
becomes critical and the Griffith's mechanism applies too ; here
the probability of catastrophic rupture may be independant from
time ;
    - the 3rd mechanism corresponds to the classical notion
of fatigue, that is the generalized dislocations in connexion
with the generalized breaking of secondary bondings and even
of some covalence bondings with the production of free radicals ;
the rupture in this case occurs only after a given "inhibition-
time", that is the time during which not enough bondings are
broken to reach dislocation ; but after this inhibition time
the probability of catastrophic rupture increases with time.
    For each mechanism it has been shown (49,50) that only
an exponential function can describe the statistics of fatigue
behaviour :

$$R(t) = 1 - F(t) = \exp \left(- \int_0^t h(t)dt\right)$$

where the Reliability function : $R(t)$ or "survival function"
is related to the "Failure Function" : $F(t)$ and to the instan-
taneous failure rate : $h(t)$.

$$\left(\text{Exp} - \int_0^t h(t)\, dt\right)$$ may be of a kind of generalized

Gamma (or Erlang) function or of a generalized Weibull function.
    Practically the generalized Weibull function gives satis-
fying results :

$$R_i(t) = \exp - \left(\frac{t-t_{oi}}{a}\right)^{b_i}$$

    where : t_{oi} is the inhibition time for the mechanism
number i,
    b_i is lower than 1 for the 1st mechanism, equal to 1
for the 2nd mechanism, and higher than 1 for the 3rd mecha-
nism.
    Considering the 3 different mechanisms and not the clas-
sical smoothed Weibull-line, it is generally possible to con-
firm the existence of the 3 mechanisms and also to confirm
our working hypothesis (fig. 8).
    If we are right, the change of pore size distribution
may be visualized i.e. with the help of the technique of
SOTTON (21).

Figure 7. Fatigue behavior. Survival function R(t) vs: time t. The 1st, 2nd, and 3rd mechanisms individually and together (1 + 2 + 3). In this last case, during Δt, only the 2nd mechanism plays; the first mechanism does not apply anymore, and the third mechanism has a long inhibition time t_o3.
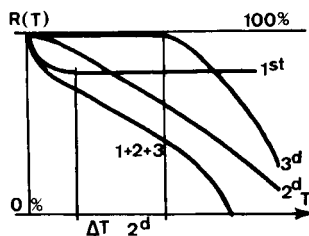
Figure 8. Weibull representations: experimental values and (a) the classical smoothed dotted line (CW = classical Weibull line); (b) the 3 full lines in connexion with the 3 mechanisms; (1) 1st and 2nd mechanisms; (2) 2nd mechanism alone; (3) 2nd and 3rd mechanisms.
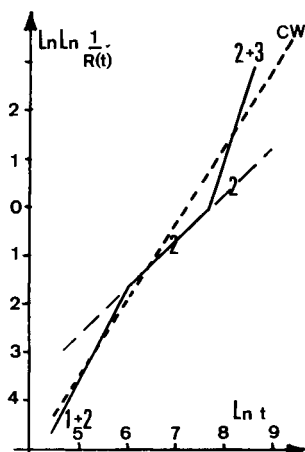
In fact, before the applying of repeated stretching on acrylic fibers (51) the picture of the porosity shows a lot of little pores ; after the applying repeated stretching, the number of larger pores has grown to the cost of the number of the initial little pores, with an increase of "order index" (after (24) : STATTON) from 65.7 % to 72.5 %
        In the same manner, solute exclusion technique has shown a shift of the pore size distribution in favor of the larger pores, also in the case of viscose fiber yarn fatigued by repeated stretching ("static load" = 1 cN/tex ; 2,5 % extension, 5000 extensions) :as follow :

before stretching :

Specific volumes up to 27 nm : 1,472 ml/g (CV : 3,6 %)
                  up to 0,8 nm : 0,686 ml/g (CV : 3,9 %)

after repeated stretching :

Specific volumes up to 27 nm:1,520 ml/g (CV : 3 %)
                  up to 0,8 nm:0,657 ml/g (CV : 3 %)

N.B. : The change of porosity can also be reached only through hydrothermal effects without applied stress (52) : up to 140°C the hydrothermal fatigue leads to the formation of larger pores with a new distribution of pore - sizes. Over 140°C the perturbator effect of water allows the mobility of molecules segments and morphological parts, and without stress, the structure change of the relaxed fiber leads to a distribution with finer pores.

7 - Dyeing and Pore Size Distributions.

        For example the results for two kinds of textiles are reported : wool and polyester.
        In the case of wool, it is well known that the practical aqueous dyeing needs to bring the water-fiber system over 50°C. In the case of polyester it is well known that the practical aqueous dyeing needs temperature over 120°C. Let us considerer the pore size distribution at different temperatures, and after 90 mn.

        7 - 1. Wool. a) At 20°C the pore size distribution of wool (42) (puffered at pH = 2) shows, that there is practically no pore greater than 1,2 nm (in diameter). With the rising of temperature and from about 50°C the pore sizes increase highly significantly and reach 5 nm (in diameter) at 90°C : the accessible volume increases from 0,42 ml/g at 20°C to 0,54 ml/g at 90°C, but with a decreasing of the volume of little pores (up to 1,2 nm) of about 30 % (fig. 9).
        The bigger pores facilitate the penetration of dyestuffs.

If before the application of the aqueous dyeing conditions (at 90°C during 90 mn) the wool was pretreated with liquid NH_3, the pore sizes distribution becomes enlarged and shifted to the higher pore sizes.

b) The effect of perchlorethylene (90 mn at boiling : 121°C) preceding the application of the aqueous dyeing conditions at (90°C during 90 mn), on the pore size distribution is revealed by the very pronounced shift of the distribution to the larger sizes.

c) The chlorination of wool (42) intensively shows similar effects : the accessible volume increases nearly 3 times and the pore sizes reach 10 nm ! This fact may also explain the ease to dye and to print wool after chlorination !

7 - 2. Polyester. a) It is well known, that the aqueous dyeing of polyester at the atmospheric pressure needs several hundred of hours. At temperature below 100°C the accessible pore volume is lower than 0.05 ml/g. With the increasing of the temperature, the accessible pore volume increases strongly between 120 and 135°C (fig. 10). The distribution depends on the setting conditions of the yarns (48).

b) The exudation of oligomers also seems to be in connexion with the volume of pores greater than 1,8 nm in diameter (that is the size of the cyclic trimer (54) (fig. 11)

c) The movements of porosity change, of oligomer exudation and of dyestuff pickup are very similar and suggest that they are closely related (fig. 12).

8 - Discussion and Conclusions.

It seems that the actual texture : porosity and holes distribution, plays an important role as in the mechanical properties as in the physico-chemical behaviour.

This actual texture is the picture of the actual cohesive situation, that is the distribution of the intensities of cohesive secondary bonding.

In the high ordered parts, the lateral cohesive bonding is maximal and therefore the bonding in these parts is very fast.

In the amorphous part, the cohesion is variable from place to place depending on distances of interaction sites, on applied stresses, on temperature and on perturbators effects.

In the interfaces the discrete covalent bondings play the role of anchorages and the discrete secondary bondings govern the Hookean behaviour ; if the Hookean elastic deformation is overshooted, some of the discrete secondary bondings are brocken and the deformation is connected with a now possible slippage and of some molecule segments or morphological parts leading to a new arrangement of the voids and of the orientation of molecules in the amorphous parts.
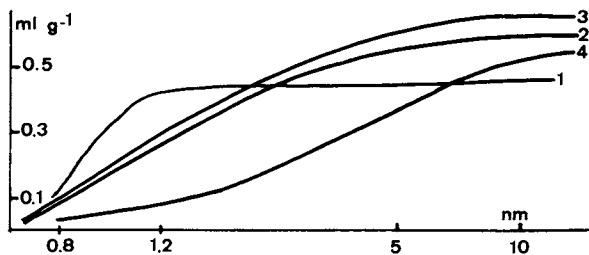
Figure 9. Wool fiber porosity. The accessible (pore) volumes (ml/g) vs. pore sizes (in nm). (1) In water 90 mn 20°C (pH 2); (2) in water 90 mn 90°C (pH 2); (3) in liq. NH₃, then in water 90 mn 90°C (pH 2); (4) in perchlorethylene at boiling (121°C, 90 mn) then in water 90 mn 90°C (pH 2). With temperature the number of little pores is reduced, but the total accessible volume increases, and greater pores are created.
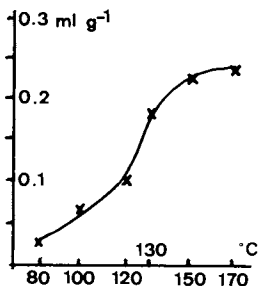
Figure 10. Polyester fiber porosity and temperature. The accessible volume increases highly with the temperature and is particularly pronounced between 120° and 135°C.

Figure 11. Polyester fiber porosity and the exudation of oligomers. The amount of surface oligomers seems to be correlated with the accessible volumes of pores greater than 1.8 nm in diameter.
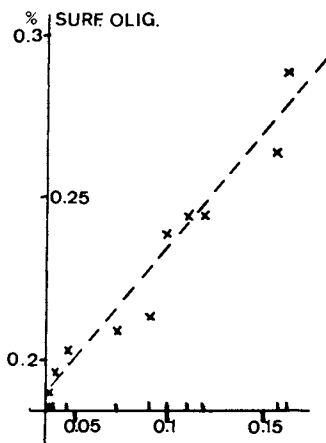
Figure 12. Polyester: in connection with the treatment temperature, the movements of porosity change, oligomer exudation, and dyestuff pickup are very similar.
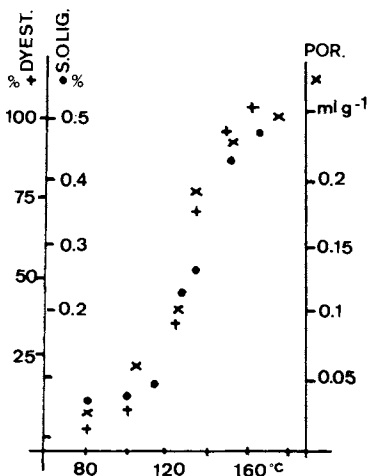
This new arrangement of voids in the sense of enlarging of holes and reducing the number of little holes corresponds to a new given more or less stable texture and porosity.

That is, that the actual porosity and texture estimate the actual interaction situation before or after a given treatment. It would be possible also to estimate this actual situation through other measurements i.e. : the solubility parameters or the variation of glassy-temperatures in different conditions.

A new approach in textile research may be possible through : the description of distributions of the intensities of secondary bondings, and therefore also the distributions of pore and hole sizes ;
and the description of shifting of these distributions in connexion with applied stresses with temperature and with the presence of interaction perturbators as water, solvents or other chemical products ;
and it has to reminded that this shifting, this change is a matter of kinetics.

That means, the evolution of the distributions has to be followed with time and considered in connexion with the practical conditions.

In other words, after having worked on the situation of the solid inert parts of the fiber, it seems also necessary to look after what happens between these solid inert parts in the fiber.

Abstracts :

The reactivity of fibers and their practical behaviour depend on their structure. Our new proposal is to consider the textile fiber as an heterogeneous multiphase system. The action of any kind of reagent depends on the accessibility and the mutual fiber-reagent affinity. Accessibility is governed by the actual porosity (total free volume and pore distribution) with also depends on interactions with the fiber (Van der Waals forces, H-bonds, electrocharges distributions) ... under given conditions. Porosity changes determinated by temperature, pH, solvent and stress action or modifications, are closely related to dyeing and mechanical behaviour.

The high ordered regions are physico-chemically inert in the conditions of the usual treatments. But the non ordered regions and their interfaces with the "crystals" completely determine practical behaviour.

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13

Recent Developments in the Research and Technology of Chemical Fibers in Japan

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It is difficult to summarize in a limited time the whole aspect of
the recent developments in the textile chemistry and industry in
Japan, so in this paper some recent topics will be introduced on
the new chemical fiber products in Japan.

A New Process of Polyester Production from Terephthalic Acid and Ethylene Oxide

At first, I would like to introduce a new process of polyester
production from terephthalic acid and ethylene oxide developed by
Toyobo Co.
In the early years the raw material used for the manufacturing
of polyethylene terephthalate(PET) was dimethyl terephthalate (DMT).
As the technology of producing highly purified terephthalic acid (
TPA) has advanced, TPA-based processes have become of increasing
commercial interest as new route for the manufacture of PET. Among
many TPA-based processes, only TPA-ethylene glycol(EG) process has
been widely commercialized. Many works have been done for TPA-ethy-
lene oxide (EO) process as another important route of direct ester-
ification. But this process had never commercialized. This was per-
haps due to the dificulties in controlling of highly reactive EO
and in proper selection of operating conditions.
Toyobo Co. started the research some ten years ago on the di-
rect esterification and polymerization in continuous process, and
established the technology after four years operation of a 0.5 ton
per day pilot plant. The first commercial plant with a capacity of
25000 tons per year came on stream at Iwakuni in May, 1973 and sin-
ce then the production has being successfully continued.
Figure 1 shows the outline on this process which comprises the
following four stages: esterification, precondensation, polyconden-
sation, and direct spinning. Fiber grade TPA and a recycle stream
of the solvent used as reaction medium and unreacted EO from solve-
nt recovery tower E are fed to esterification reactor D. EO and es-
terification catalyst are also fed to reactor D. The reaction is
carried out at high temperature and pressure, and is automatically

252

controlled so that the conversion of TPA to bis(2-hydroxyethyl)te-
rephthalate (BHET) is kept constant. The product stream from the
bottom of reactor D is fed to precondensation reactor G through
evaporator F. Polymerization catalyst and TiO₂ pigment are also
fed to reactor G. In the precondensation reactor G, the reaction
of BHET with TPA to form oligomer takes place at an elevated temp-
erature under atomospheric pressure. The oligomer or precondensate
is finally polymerized to a required intrinsic viscosity in poly-
condensation reactors H and J operating at elevated temperature
under vacuum. The product is fed either to direct spinning system
or to chip production units.

In this process the removal of diethylene glycol (DEG), by-
product in the esterification reaction, is impossible as the puri-
fication stage such as recrystallization is absent. Therefore, mu-
ch attention was paid to minimize the DEG content of the final po-
lymer by thoroughly selecting the operation conditions of the en-
tire process. The DEG content of the polymer is lower than that of
the polymer resulted from TPA-EG process. In consideration of the
polymer quality and production cost, the most suitable value of DE
G content in the polymer would be 1.8-2.4 mole % for textile use.

As the esterification is an exothermic and heterogeneous rea-
ction, care must be taken to insure a smooth reaction. The reaction
of TPA with gaseous EO is very slow. Therefore, the esterification
should be carried out with liquid EO under pressure. The reaction
is accererated by various basic compounds, among them tertiary am-
ines and quarternary ammonium compounds are the most suitable cata-
lyst for industrial use.

Another important factor in the esterification is reaction me-
dium. Although the rate of the reaction is very high in absent of
solvent, the control of the reaction is very difficult and the DEG
formation is remarkable. The addition of organic solvent generally
makes the reaction more controllable and decreases the DEG formati-
on. The tendency to reduce the reaction rate and the DEG formation
depends upon the kind and amount of solvent added, and therefore,
careful choice of solvent is important. Addition of solvent is also
advantageous in reducing vapor pressure of the reaction system and
also reducing explosion range of gaseous EO-air mixture.

Polycondensation stage in this process is essentially same as
that of DMT or TPA-EG process, but the special type of polyconden-
sation catalyst used in this process makes several times more re-
active than the conventional catalyst such as antimony oxide. It is
said that the polymer is more luminant than the polymers containing
antimony catalyst and contains less impurities derived from cataly-
st, and consequently has very high spinnability. It contains no es-
terinterchange catalyst and has high thermal and hydrolytic stabi-
lities.

High Modulus Vinylon (Vinal) Filament

It is known that the modulus of polyvinyl alcohol (PVA) crystal in the direction of molecular chain is larger than other polymers such as nylon, polypropylene, etc. Then it is presumed that PVA is a suitable polymer to give high modulus fiber. However, the tenacity and Young's modulus of conventional Vinal were not over than 9 g/d and 200 g/d respectively up to this time.

But recently Kuraray Co. and Unitika Co. succeeded to produce the new Vinal which has the tenacity of 12 g/d and Young's modulus of 250-300 g/d. It was found when some swelling agents were added to the coagulation bath for the wet spinning of PVA, the maximum drawability of the coagulated fiber was remarkably increased and high modulus Vinal fiber was obtained.

This new Vinal fiber has highly oriented para-crystalline structure and the molecular chains in amorphous region are also highly oriented. Therefore, high level of modulus and tenacity are preserved at high temperature. Creep is lower than 1 % at 100°C for 60 min. under the tension of 1 g/d. Figure 2, 3 and 4 show such experimental results. It was recognized in Japan and United States that the new Vinal filament showed the excellent results as radial tire cords.

Acrylonitrile Fiber Mix-Spun with Casein (Chinon)

After long research since 1956, Toyobo Co. developed a new chemical fiber named Chinon. Since I suppose it is already well-known on this fiber in the United States (1), I do not refer to this fiber so much in this paper.

Milk casein is dissolved into conc. aqueous solution of zinc chloride to which acrylonitrile monomer and catalyst are added and polymerized in the solution. In this solution a part of acrylonitrile is assumed to graft polymerized onto casein molecules. Then this solution is spun into dilute zinc chloride aqueous solution and the fiber thus obtained is stretched.

Generic name "promix" was given to such a fiber in Japan, because it was made by the mix-spinning with protein. The characteristics of Chinon is silk-like hand or silky touch and it can be dyed with acid dyes to deep shade.

Flame Retardant Polyester Fiber (Heim)

Now I will talk about some fibers of special properties. The first is the flame retardant polyester fiber called "Heim", developed by Toyobo Co. (2, 3).

Number of patents have been issued on flame retardant polyester. It has been disclosed in the patents that bromine and phosphorus are two important effective elements to make polyester flame retardant. Bromine is known to act as a radical scavenger to terminate the oxidation reaction in the flame. But as yet only little has been reported on the mechanism of the action of phosphorus on polyester.
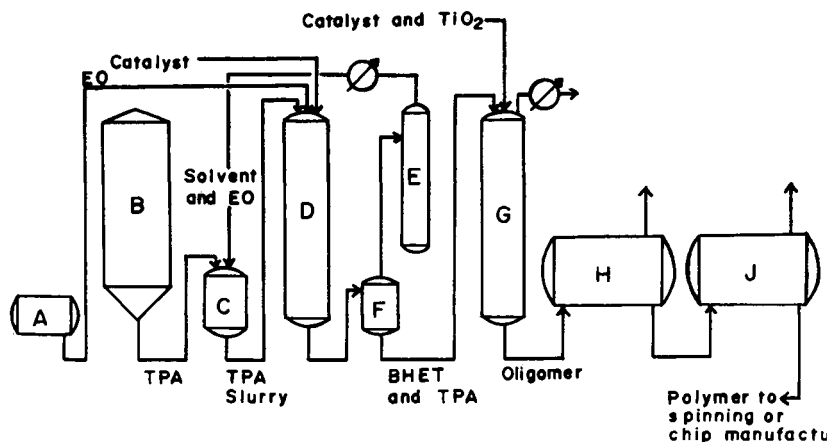
Figure 1.   *Toyobo direct esterification and polymerization process. (A) EO storage tank; (B) TPA storage silo; (C) mixing vessel; (D) esterification reactor; (E) solvent recovery tower; (F) evaporator; (G) pre-condensation reactor; (H) 1st polycondensation reactor; (J) 2nd polycondensation reactor.*
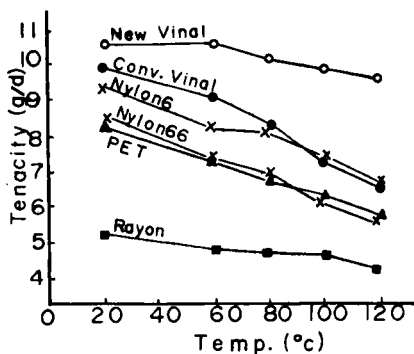
Figure 2.   *Tenacity of various fibers at high temperature*
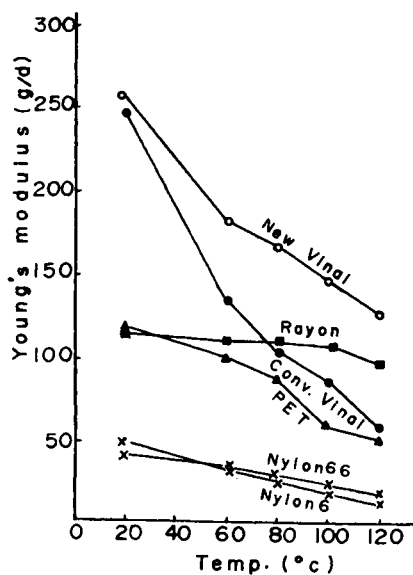
Figure 3. Young's modulus of various fibers at high temperature
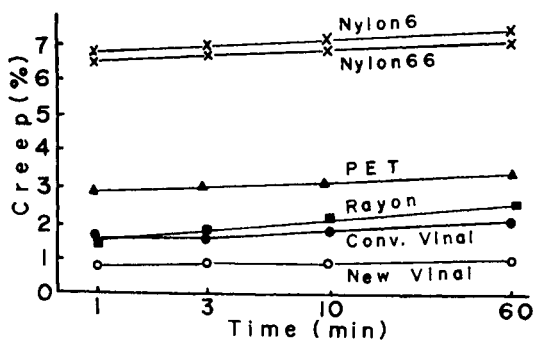
Figure 4. Creep of various fibers at 100°C under the tension of 1 g/d

Toyobo Co. succeeded to develop a flame retardant polyester fiber by applying polyphosphonate as the flame retardant modifier and has begun commercial production of the flame retardant polyester fiber named "Heim".

As a flame retardant additive, poly[phenyl(sulfon bis-4-phenyl)phosphonate] (abbreviated as GFP) was synthesized from bisphenol S and benzene phosphonic dichloride. Its molecular weight measured by vapor pressure osmometry was 12000.

Bisphenol S   Benzenephos-   Poly[phenyl(sulfon bis-
                       phonic dichlo-   4-phenyl)phosphonate]
                       ride   (GFP)
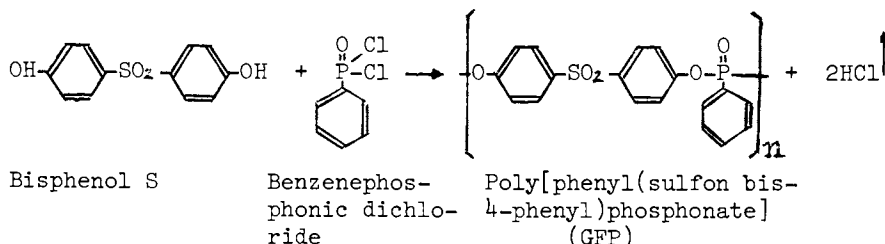
A certain ratio of polyethylene terephthalate (PET) and the flame retardant additive were blended and dried in a vacuum drier. Then the mixture was melt-extruded through a screw extruder, quenched in water and cutted into chips. These chips were then melt-spun and stretched by means of conventional melt spinning technics. Physical properties of Heim are almost identical to those of conventional polyester fiber as shown in Table I and II.

Table I. Physical Properties of Heim Filament Yarn (150 Deniers)

	Heim Type 448	Conventional Polyester
Tenacity (g/d)	4.2 – 4.7	4.8 – 5.0
Elongation (%)	25 – 28	25 – 26
Knot Tenacity (g/d)	3.2 – 3.7	3.8 – 4.0
Knot Elongation (%)	10 – 12	13 – 15
Shrinkage (%)		
in Boiling Water	8.0 – 10.0	8.0 – 9.0
in Air at 160°C	13.0 – 15.0	11.0 – 12.0
Initial Modulus (kg/mm^2)	1200	1200
Recovery at 3% Elongation (%)	100	100
Melting Point (°C)	252	264

Table II. Physical Properties of Heim Staple Fiber (1.5 Denier)

	Heim Type 441	Conventional Polyester
Tenacity (g/d)	4.0 – 4.5	5.5 – 6.0
Elongation (%)	32 – 37	25 – 30
Knot Tenacity (g/d)	3.5 – 4.0	4.5 – 5.0
Knot Elongation (%)	25 – 30	20 – 25
Shrinkage (%)		
in Boiling Water	0	0
in Air at 160°C	3 – 4	2

Heim is more easily dyed with disperse dyes than conventional polyester. Color fastness to light of disperse dyed Heim is approximately equal to that of conventional polyester fiber. Heim continuous yarn can be textured on the conventional false twisting machines. As to the flame retardancy of Heim, oxygen index (OI) increases as shown in Figure 5 monotonously with an increase of the phosphorus content.

In the case of fusible materials such as nylon and polyester, they will shrink or drip out from the flame when they are brought into a test flame, and it is difficult to decide quantitatively the flame retardancy. In this case the following test method called Basket method was deviced (Figure 6). 1 gram of powdered sample was placed in a basket made of wire net of 50 mesh. A flame from a microburner was put on to the bottom of the basket for 20 seconds and then was taken off. The residual flame time (RFT), the weight of the drip and the weight of the residual char were measured as the characteristics parameters. By this method simultaneous evaluation of flammability and the tendency to drip were possible.

In Figure 7 the residual flame time (RFT) is shown as a function of phosphorus and bromine content of the modified polyester. When phosphorus was added to polyester, the residual flame time increased a little at first, but reached to a maximum and then decreased rapidly. Addition of bromine compounds, on the other hand, leaded to a monotonous decrease in the residual flame time with the increase of bromine content. It is clear from these results that phosphorus is more effective than bromine on the weight base in lowering the flammability of polyester. In Table III are shown the test results obtained by Basket method. It is shown that the residual flame time is less and the residual fraction on the basket is remarkably larger for Heim than for ordinary polyester.

Table III. Results obtained by the Basket Method

Sample	Residual Fraction (%)			Residual Flame Time (sec)
	on Basket	off	Total	
Ord. Polyester	18	7	25	58
Heim	90	6	96	2

45° Inclined Coil Test (Figure 8) is the method adopted in Japan Industrial Standard (JIS) L 1091 D. The number of impingements of the flame needed to burn 9 cm of the sample in the 45° inclined coil was measured. Those fabrics which need more than 3 times of impingement to burn 9 cm of sample are recognized to be flame retardant materials for curtain by the Fire Defence Agency of Japan. Table IV shows the results on Heim of various colors and ordinary polyester. Heim passed the coil test, but ordinary polyester failed. As shown in Table V, the flame retardancy of Heim lace curtain is durable to various treatments.
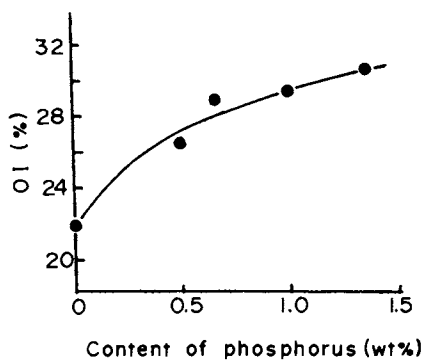
Figure 5. *Relation between oxygen index (OI) and the content of phosphorus of the PET/GFP blended yarn*
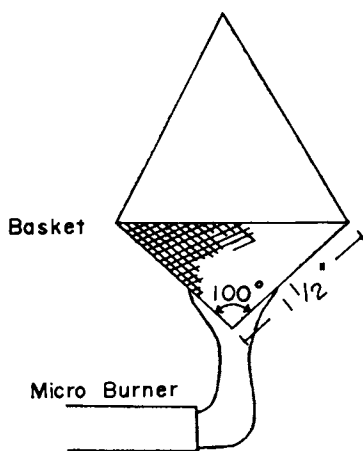
Figure 6. *Basket method for flammability test*

A : GFP

B : $O=P(O-\langle\bigcirc\rangle)_3$

C : (structure)

D : (structure)
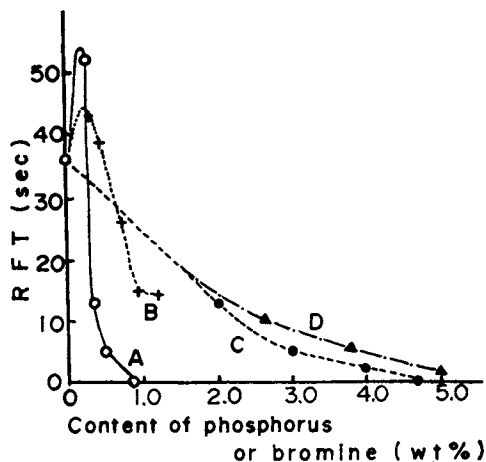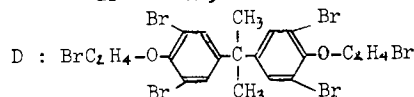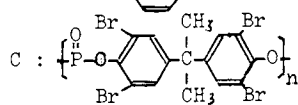
Figure 7. Change of residual flame time (RFT) with content of flame retardant elements
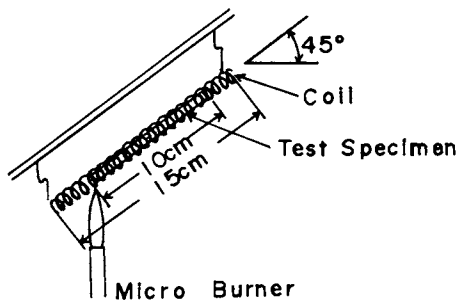
Figure 8. Apparatus used in 45° coil test based on the Fire Defence Law of Japan

Table IV. Flame Retardancy of Heim based on the Fire Defence Law of Japan

Sample	45°Plane Test (3 sec.Exposure)			Coil Test	Evaluation
	After Flame (sec)	After Glow (sec)	Char Area (cm²)	(times)	
Heim					
White	0	0	5.0	5	passed
Beige	0	0	5.0	5	"
Saxe	0	0	5.0	5	"
Cream	0	0	4.3	5	"
Black	0	0	5.4	5	"
Ord. Polyester					
White	0	0	7.8	1	failed
Acceptance Criterion	≤ 3	≤ 5	≤ 30	≥ 3	

Table V. Durability of Flame Retardancy of Heim Lace Curtain after Various Treatments

Sample	Condition of the Treatment	Coil Test (times)
As Knitted	176°F, (80°C), 20 min.	5
Scoured	176°F, (80°C), 20 min.	5
Bleached	Chlorite, Boil, 90 min.	5
Dyed	Carrier, Boil, 90 min.	5
	230°F, (110°C), 60 min.	5
Laundered	134°F, (60°C), 50 times	5
Dry Cleaned	87°F, (30°C), 50 times	5
Fade-O-meter	200 hrs.	5
Heated	248°F, (120°C), 48 hrs.	5

Electro-Conductive Fiber (Selmec)

After several years of extensive researches, Kuraray Co. successfully invented special electro-conductive fiber and developed a series of textile goods named Selmec, which had durable properties of high electroconductivity and static elimination (4,5).

The principle of making such a fiber is to give nickel plating on the surface of organic fiber by the process of nonelectrolytic plating. This principle is as same as that used to give metal plating on the surface of plastics. But in the case of fiber, the surface area per unit weight is remarkably large, so the velocity of metal plating reaction is so high that the plating bath become unstable and the production of commercial scale is impossible.

Kuraray Co. solved successfully this problem, obtaining very stable nonelectrolytic nickel-plating bath by adding to the bath a small quantity of guanidine, imidazoline or imidazole as stabilizer. Mercapto benzimidazole was very effective (6). Sodium citrate as chelating agent and sodium acetate as buffering agent were added to the plating bath (pH≒5) which contained nickel sulfate and sodium

phosphite (NaH_2PO_2). Any organic fiber can be used as basic fiber
material. The method suitable to commercial production was establi-
shed by spraying the plating solution over the skein of fiber ($\underline{7}$).

These nickel-plating fibers have tenacity, elongation, Young's
modulus, flexibility, and specific gravity as same as conventional
textile fibers as shown in Table VI. They have almost the same ele-
ctric resistance as carbon fiber. They have high electroconductivi-
ty, antistatic effect and shielding effect for electrostatic induc-
tion. Table VII shows the main usages of Selmec fibers

Table VI. Comparison of Physical Properties of Kuraray Electro-
           Conductive Fiber (K.C.F.) with other Conductive Fibers

	K.C.F.	Metallic Fiber (Stainless Steel)	Carbon Fiber
Strength (g/d)	3.0 – 6.0	2.7 – 4.5	1.0 – 1.5
Elongation (%)	15 – 25	1.0 – 2.0	0.6 – 2.0
Young's Modulus (g/d)	60 – 95	19000	4200 – 4500
Moisture Regain (%, 20°C, 65%RH)	2.0 – 3.5	0	–
Specific Gravity	1.5 – 1.9	7.9	1.5 – 2.0
Electric Resistance ($\mu\Omega$cm)	$1 – 6\times10^3$	72	$8 – 100\times10^2$

Table VII. Main Usages of Selmec Fibers

Form of Fiber	Main Usages
Filament Yarn	1. Electroconductive working suit 2. Shielding cloth for electromagnetic wave 3. Space heater, etc.
Spun Yarn	1. Static eliminator 2. Antishock glove 3. Antistatic blanket 4. Antistatic filter bag 5. Antistatic sewing thread 6. Antistatic working suit, etc.
Staple Fiber	1. Antistatic carpet 2. Other general materials for antistatical and static eliminating uses

For the purpose of comparison of static eliminating property
of Selmec with other electroconductive fibers, the discharge start-
ing voltage and discharging current wave of the testing fibers we-
re measured (Figure 9). When the sample were located by 5 cm above
the alminum plate (50 x 50 cm) charged at 10 kV. It was shown that
the discharge starting voltage and discharging pulse of Selmec we-
re much lower than other electroconductive fibers.

Figure 10 shows the effect of Selmec static eliminator. The
residual voltages on the charged polyethylene film are measured re-
lated to the distance (mm) between static eliminator and charged
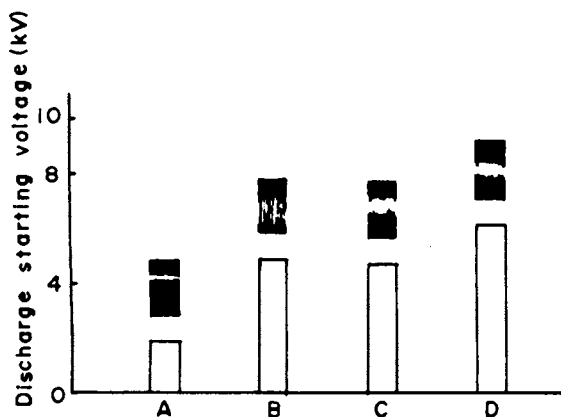
Figure 9. Comparison of discharge starting voltage and discharging current wave between Selmec and other electroconductive fibers. (A) Kuraray electroconductive fiber (Selmec); (B) stainless fiber (8μ) 10% blended yarn; (C) stainless fiber (30μ) monofilament; (D) electroconductive resin coated monofilament.
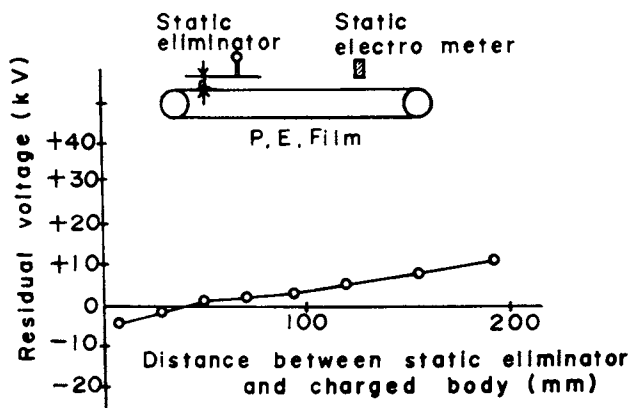
Figure 10. Static eliminating effect of Kuraray eliminator (Polyethylene film, speed 100 m/min, discharged voltage at the beginning +60 kV)

body. The residual voltage is nearly zero at the distance of about
50 mm.

Selmec is suitable to electroconductive working suit and acc-
essories. When worker stands under ultra high voltage transmission
line, the induced current run through human body is very much dec-
reased by use of Selmec working suit, through which almost all in-
duced current run away. When ordinary working suit is used, the
relation is reversed and the body current is very much increased.
The shielding effect is durable to repeated washing.

The Matrix-Fibril Bicomponent Fibers (Ecsaine, Clarino or Astrino)

Next, I will introduce some bicomponent or biconstituent fi-
bers made by special spinning technics.

One is an island-in-sea type fiber made in Toray Co. and used
for the manufacturing of man-made leather or suede named "Ecsaine".
Figure 11 shows an example of the conjugate spinneret used to make
this special fiber (8). Two kinds of molten polymer, A and B, are
conjugated in the spinneret, then many such a two component fibers
are again conjugated before they are spun out from the spinneret.
Thus, by this double conjugate spinning the filaments are obtained
which have the cross and longitudinal sections schematically shown
in the figure. These two components, A and B, may be any polymer,
but the combination of polyamide with polyester, polyamide with po-
lyolefin, and polyester with polyolefin are advantageously used.

When the sea component B is dissolved out by solvent, the fi-
lament composed of very fine microfilaments of A will be obtained.
By impregnating of the web composed of the bundle of such microfi-
lament with polyurethane, suede like materials, Ecsaine, can be ma-
de. Their microstructures are shown in Figure 12. As shown in Table
VIII, Ecsaine has reasonable tensile strength, elongation, modulus,
and high tearing strength, crease recovery, water vapor and air
permeabilities, and shows very low shrinkage by water boiling. They
give very soft man-made suede or high drape apparel.

Another one is the melt mix-spun fiber used to make a man-made
leather Clarino (called Astrino in the United States) made in Kura-
ray Co. For the production of this special fiber, two kinds of po-
lymers which have different solubility in a given solvent are melt
mix-spun through a nozzle hole. The island-in-sea structure of this
biconstituent fiber is influenced by various factors. Figure 13 sh-
ows the relation of mixing ratio and viscosity ratio with the form-
ation of island and sea phases of the mix-spun fiber composed of
nylon 6 and polystyrene. In the region under the curve, the island
phase is composed of nylon 6, and in the region over the curve the
island phase is polystyrene. Therefore, when polystyrene is removed
by solvent extraction, either porous or fine fiber bundle both com-
posed of nylon 6, as shown in Figure 14 and 15, will be obtained
depending on the structure of the melt mix-spun fibers. Figure 16
shows the stress-strain curve of nylon 6 special fiber after ext-
raction of polystyrene sea phase. This special nylon 6 fiber has

Cross section
of the filament

Longitudinal
section of
the filament
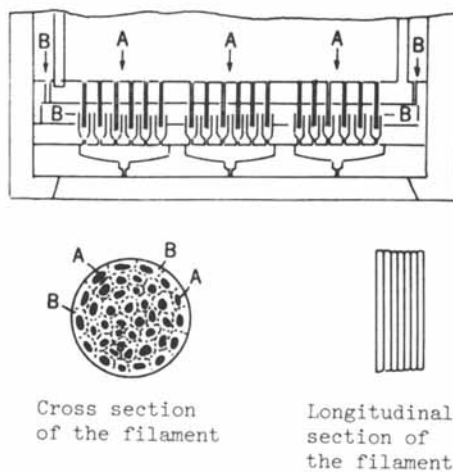
Figure 11. An example of the conjugate spinneret

Ecsaine   Natural suede
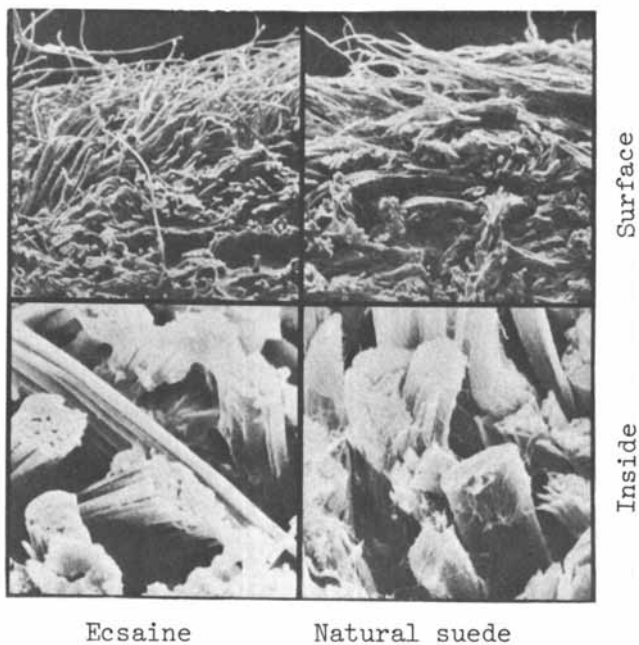
Figure 12. Microstructure of Ecsaine and natural suede
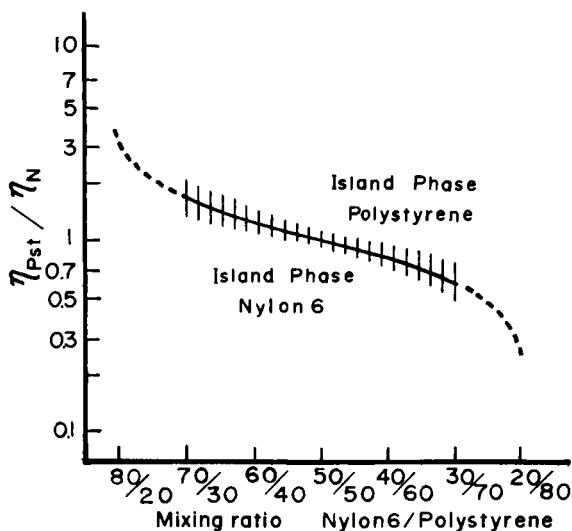
Figure 13.   The relation of mixing ratio and viscosity ratio with the formation of island and sea phases of the mix–spun fibers composed of nylon 6 and polystyrene

Porous fiber   Fine fiber bundle
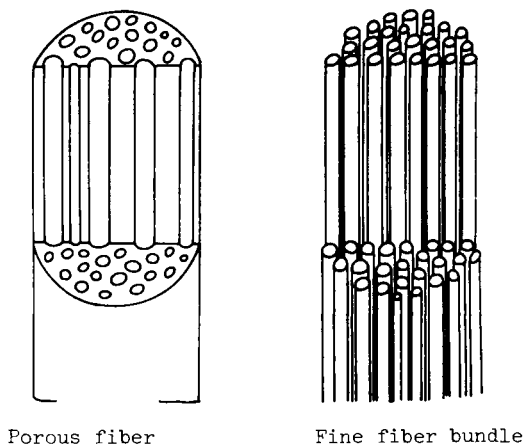
Figure 14.   Mix–spun and solvent extracted fibers for Clarino. (left) Porous fiber; (right) fine fiber bundle.
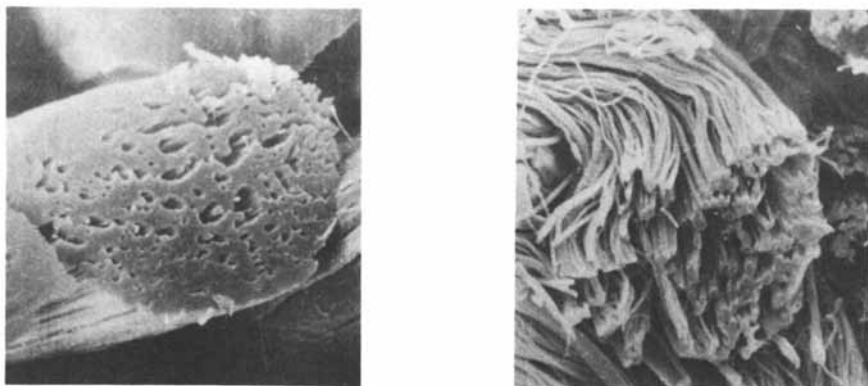
Figure 15.   Mix–spun and solvent extracted fibers for Clarino. (left) Porous fiber; (right) fine fiber bundle.
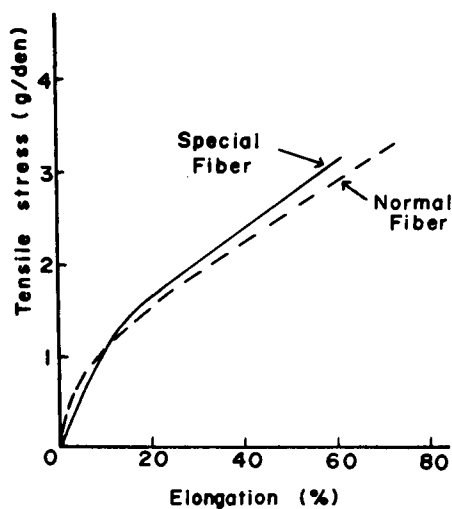
Figure 16.   Stress–strain curve of the special fiber of nylon 6 after the extractive removal of the sea phase component

substantially the same characteristics as those of conventional nylon 6 fiber.

Table VIII.   Comparison of the Properties of Ecsaine and Natural Suede

	Ecsaine	Sheep Suede
Thickness (mm)	0.85	0.83
App. Density (g/cm^3)	0.27	0.60
Tensile Strength (kg/cm)	7.9 x 6.7	20.0 x 6.6
Elongation (%)	86 x 105	35 x 37
Initial Modulus (kg/cm)	7.5 x 4.4	26 x 7.3
Tearing Strength (kg)	2.9 x 3.0	1.0 x 1.1
Abrasion Resistance (weight decrease %)	6.3	18.4
Crease Recovery (%)		
Dry	89 x 82	69 x 67
Wet	86 x 82	29 x 27
Water Vapor Permeability (mg/cm^2·hr)	30.9	29.8
Air Permeability (cc/cm^2·sec)	8.3	0.3
Shrinkage by Water Boiling (%)	2.0 x 0.9	49 x 45

Needle-punched web of these special fibers is impregnated with polyurethane resin to make sheet materials. Porous fibers free of island phase are used for Clarino of relatively hard type, and the bundles of fine fibers free of sea phase are used to make Clarino sheet for clothing and other soft application. Figure 17 and 18 show the sectional view and surface of Clarino.
The stiffness or flexibility of the sheet material is influenced to great extent by the condition of bond between fiber and resin. When one of the components in the fiber mat or web is extracted with a solvent before the impregnation with resin dope, a high density, high tenacity, rather stiff sheet is obtained, because the fiber and resin closely contact as seen in Figure 19.A. But if the fiber web is impregnated at first with resin dope and coagulated before the removal of one fiber component by extraction, the bond between fiber and resin is broken by solvent extraction, thus leaving a flexible sheet (Figure 19.B). In the type C method one of the component fibers is dissolved to impregnate the web and followed by coagulation. Since the extracted polymer dose not need to be recovered, this method has a commercial advantage. However, it is said in view of the latitude of the resin selection, quality, productivity and other factors, Clarino is manufactured basically by method B. Figure 20 shows the stress-strain curves of various sheet materials. The curve of Clarino is similar to that of calf suede.

Figure 17.   Cross section of Clarino
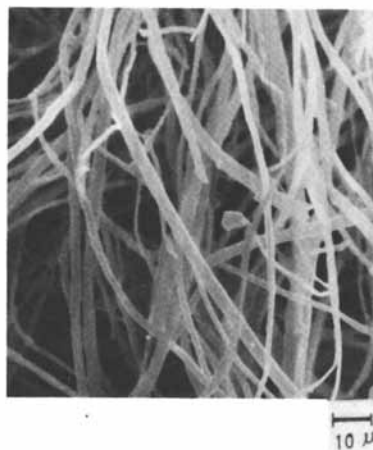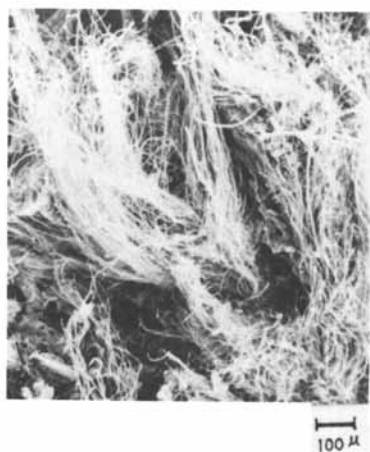
Figure 18.   Surface of Clarino

A

B

C
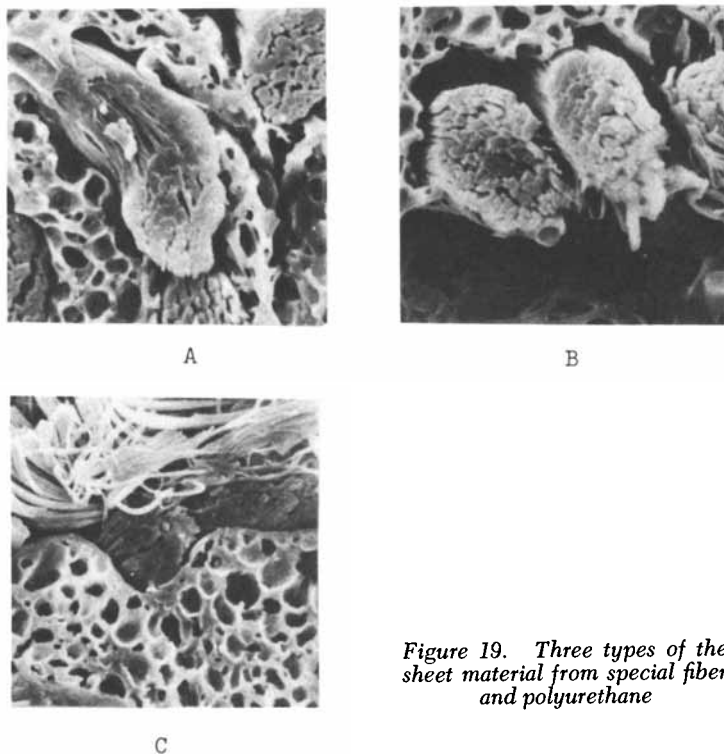
Figure 19.   Three types of the
sheet material from special fiber
and polyurethane
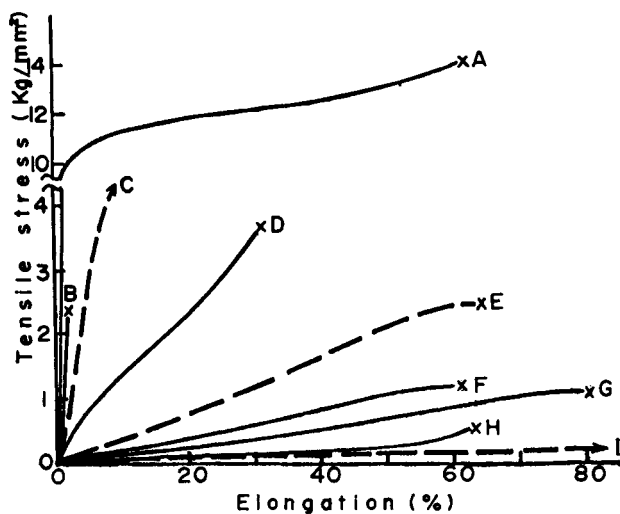
Figure 20.   Stress–strain
curves of various sheet
materials. (A) Polyester
oriented film; (B) paper;
(C) cotton suede for man-
made leather; (D) plain
weave fabric; (E) natural
leather (kip); (F) Clarino;
(G) calf suede for apparel;
(H) needle-punched non-
woven; (I) soft rubber.

Emulsion Mix-Spinning of Polyvinyl Alcohol and Other Synthetic Po-
lymers

     Professor I. Sakurada, Professor S. Okamura and Tsuji et al.
in Kyoto University developed more than fifteen years ago a new te-
chnic of the emulsion mix-spinning of polyvinyl alcohol (PVA) with
other various synthetic polymers (9-12).
     Water dispersions of various synthetic polymers are mixed with
aqueous solution of PVA and spun into a concentrated aqueous solu-
tion of sodium sulfate. Fibers thus obtained are heat-stretched,
heat treated and formalized similarly to the ordinary PVA fiber
(Vinylon or Vinal).
     As an example, Figure 21 and 22 show the cross and longitudi-
nal section of a mix-spun PVA fiber containing polyacrylonitrile
(PAN) emulsion particles. This fiber is not yet heat-stretched, so
the PAN particles are separated each other. However, when this fi-
ber is heat-stretched at about 180°C, these PAN particles are ad-
hered together, and stretched and oriented along fiber axis. This
is shown by x-ray diffraction diagram of such fiber as shown in
Figure 23. The diffraction pattern shows that both PVA and PAN mo-
lecules take orientation along the fiber axis in the mix-spun fi-
ber. This aspect is also seen in Figure 24 for PVA-polyethylene
mix-spun fiber. If PVA is removed out by formic acid after heat-
stretching, typical fibril structure of polyethylene remains.
     Thus, PVA fibers containing as high as equal quantity of vari-
ous synthetic polymers such as PAN, polyvinyl chloride (PVC), poly-
vinyl acetate (PVAc), polyethylene (PE), polystylene (PSt), poly-
vinylidene chloride (PVdC), etc. are obtained. As shown in Table
IX, they show the ordinally level of tenacity, elongation, modulus
and low shrinkage in hot water. It is notable that those fibers
which contain large quantity of the polymers having low softening
or melting temperature such as PVAc, PVC or PE, do not shrink until
about 150°C as shown in Figure 25.

Table IX. The Properties of Emulsion Mix-Spun Fibers

Mixing Ratio Polymer/PVA		Heat Drawing Ratio	Shrinkage in Hot Wa-ter (%)	Tenacity (g/d)	Elong-ation (%)	Young's Modulus (kg/mm²)
PAN	1/6	3.0	1.0	4.15	18.7	517
	1/3	3.8	3.7	3.73	21.8	509
PVC	1/4	3.3	5.9	5.44	18.7	–
	1/2	2.2	5.2	2.66	26.6	386
	1/1	2.4	4.9	2.33	26.4	301
PVAc	1/2	2.7	3.6	4.09	18.3	497
	1/1	2.7	5.6	1.86	19.2	354
PE	1/2	2.7	2.1	2.09	19.4	308
	1/1	3.0	3.7	2.39	19.1	267

     This principle of emulsion mix-spinning is being utilized in
Japan to produce Cordelan of Kohjin Co., which contains about equal
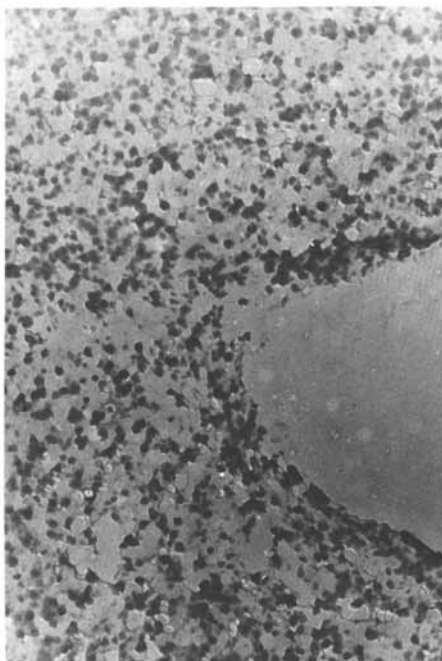
Figure 21. Cross section of a mix–spun PVA fiber containing polyacrylonitrile (PAN) emulsion particles (PAN/PVA = 1/4, unheat-stretched)
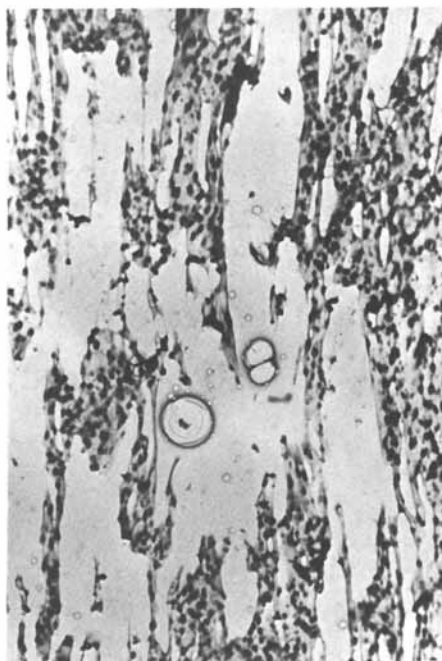
Figure 22. Longitudinal section of a mix–spun PVA fiber containing polyacrylonitrile (PAN) emulsion particles (PAN/PVA = 1/4, unheat-stretched).

Emulsion mix-spun
fiber (PAN/PVA:1/3,
heat-stretched)

Acrylic fiber

*Figure 23. X-ray diffrac-
tion patterns of the emul-
sion mix–spun fiber, ac-
rylic, and PVA fibers.*
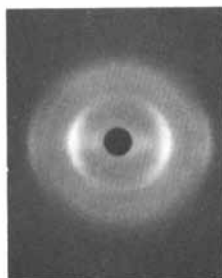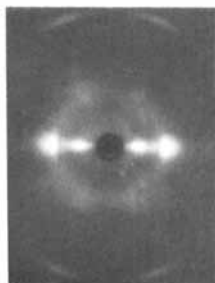
PVA fiber (Vinylon)
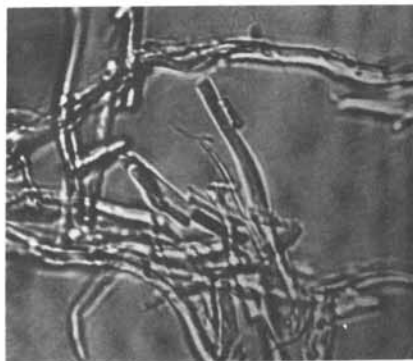
*Figure 24.   PVA–polyethylene mix–spun fiber. PVA was removed with formic acid after
heat-stretching.*

```
1.  PAN/PVA : 2/3
2.  PE/PVA  : 1/1
3.  PVAc/PVA: 2/1
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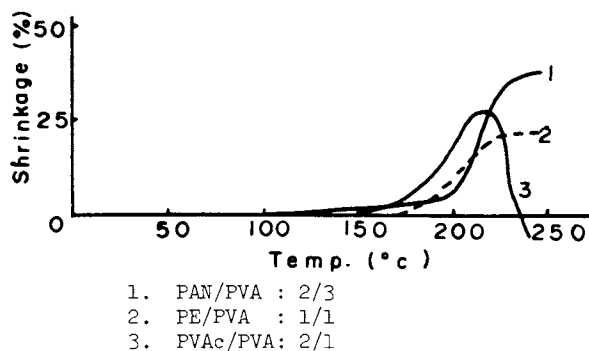
Figure 25. Heat shrinkage of the emulsion mix–spun fibers. (1) PAN/PVA: 2/3; (2) PE/PVA: 1/1; (3) PVAc/PVA: 2/1.
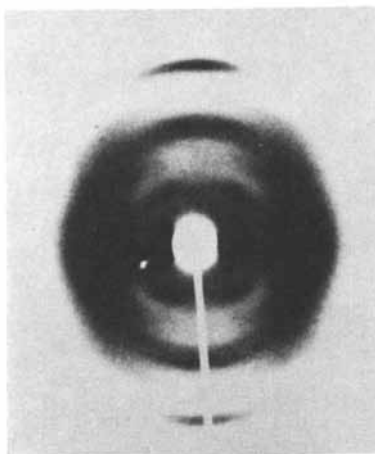
Figure 26. X-ray diffraction pattern of collagen spun fiber

quantity of PVA and PVC and has high flame retardant property.

Regenerated Collagen Man-Made Fiber

Finally, I would like to introduce briefly the collagen man-made fiber developed by Nippi Co. (**13**).

Natural collagen is an insoluble fibrous protein composed of rigid rod-like molecules called tropocollagen. Three subunit poly-peptide chains of tropocollagen are held in helical configulation. On the end of tropocollagen molecule there are so-called telopeptide regions in which the aminoacid composition and helical configulati-on are different from those of the major portion of tropocollagen. The telopeptide regions are recognized as the location of intra and intermolecular crosslinkings. Recently, some methods were introduc-ed to solubilize the insoluble collagen fiber at high yield by di-gesting the telopeptide region without destroying the inherent mo-lecular configulation. Thus the way to make collagen man-made fiber was developed.

Thus the aqueous solution of collagen, the pH of which is 3-4, can be prepared. Several percent aqueous solution of solubilized collagen is spun into slightly acidic concentrated aqueous solution of sodium sulfate and regenerated collagen fiber is stretched, dri-ed, and finally treated with conventional chrom tanning agent to improve hot water resistance.

Collagen spun fiber gives the x-ray diffraction pattern simi-lar to native collagen fiber as shown in Figure 26. Collagen spun fiber has excellent dry and wet tenacity compared with other rege-nerated protein fibers as shown in Table X. It does not shrink in water until near to 100°C. Collagen spun fiber is considered to ha-ve low antigenicity, and various medical uses are being developed, such as surgical suter, artificial skin, artificial tendon, etc.

Table X. Physical Properties of Collagen Spun Fiber Treated
          with Chrome Tanning Agent

Denier		1 - 5
Tensile	Dry	5 - 6
Strength (g/d)	Wet	3 - 4
Elongation (%)	Dry	18 - 22
	Wet	11 - 13
Young's Modulus (kg/mm²)		600 - 650
Knot Strength (g/d)		3.0 - 3.5
Melting Temperature (°C)		200 - 220
Shrinkage Temperature in Water (°C)		90 - 100

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INDEX

279