THE CHEMISTRY OF PULP FIBRES

LEIF JÖRGENSEN

BILLERUDS AKTIEBOLAG, RESEARCH LABORATORY, SÄFFLE, SWEDEN

Summary

Spruce pulps have been prepared by various processes — sulphite, bisulphite, sulphate and multistage processes such as 'bisulphite-soda' and 'Sivola' — over a wide yield range. The carbohydrate composition of the pulp fibres, their hemicellulose content, as well as the carbohydrates present in some of the hemicelluloses have been determined. Some of the papermaking properties of the pulp fibres are presented and the results discussed in relation to the chemistry of the pulp fibres.

The data on the composition, hemicellulose content and hemicellulose composition of birch sulphite, sulphate and neutral semichemical pulps are presented for a limited high yield range.

Introduction

OUR knowledge of the chemical composition of woodpulp fibres is not very extensive. That variations exist between pulps prepared from different wood species, such as softwoods and hardwoods, as well as between pulps prepared by different processes but from the same raw material, has been recognised for a long time. Wise[1] summarises some of the main differences in a recent review article. It is, however, apparent that much more information is needed in this field.

The effect on pulp properties of the hemicellulose content of pulp fibres, defined as the alkaline extractable carbohydrate portion, has been known for

several years. Wise[1] gives an excellent review of the most important investigation in this field. In general, those pulps that contain more hemicelluloses, up to a certain level, have been found to beat faster and to develop greater strength than corresponding pulps containing less hemicellulose. Cottrall[2] discusses in detail the various aspects of the hemicelluloses of pulp fibres and the influence on their papermaking properties. It is clear that it is not only the amount and composition of the hemicellulose that determines the papermaking properties, but that other changes the fibres have undergone during the pulping process are of importance. Discussions especially related to differences between sulphate and sulphite pulps are found in papers by Jayme and A. v. Köppen[3] and Giertz.[4] Rather few data are available, however, to show the differences in chemical composition of these two classes of pulp and many of the hypotheses advanced are based on speculation and, as Wise[1] concludes — 'The differences between kraft and sulphite pulps remain as obscure as ever.' Very recent studies of Yllner and Enström[5] on the fate of xylan during the sulphate cook may open new views on this old problem.

The hydrolytic attack that the fibres are exposed to during a sulphite cook has frequently been put forward as one of the explanations for their inferior strength properties compared with sulphate pulps. The destruction of the fibre wall is regarded to be especially harmful after the delignification process has been carried to the point of defibration. A possible way of avoiding this destruction would therefore be to stop the delignification process at the point of defibration and continue the removal of the hemicelluloses and lignin to the desired content with an alkaline process. Another possibility is to use bisulphite cooking solution without excess of sulphur dioxide, perhaps combined with an alkaline treatment and thus avoid the strongly acidic conditions in the latter part of a sulphite cook.

New impetus to investigations on pulping processes of this nature, using sodium as the cation, has been given by the progress in recent years on the recovery of chemicals from spent cooking liquors. An investigation of some of these pulping processes and comparison of the papermaking properties of these pulps with those of the ordinary sulphite and sulphate pulps has been carried out by the pulping division of Billeruds Research Laboratory. At the same time, we thought it to be of interest to determine the carbohydrate composition of representative samples from some of the cooking series, as well as the hemicellulose content and composition of some hemicelluloses in the hope of shedding some light on the problem of chemistry of pulp fibres in relation to their papermaking properties.

Experimental part

Raw materials

The pulps were prepared from wood chipped in a mill, but screened in the laboratory. The wood material was either Swedish spruce (*Picea abies*) or in some cases birch (technical mixture of *Betula verrucosa* and *B. pubescens*). The cooking liquors were made up from sodium hydroxide and sulphur dioxide gas and, for the soda cooks, sodium carbonate.

Cooking conditions for spruce wood

All cooks were performed in 10 litre electrically heated digesters, with a liquor-to-wood ratio of 4:1.

In the acid sulphite cooks, the acid composition varied 5 — 7 per cent. total sulphur dioxide and 1 — 2 per cent. combined sulphur dioxide, the maximum temperature 130° — 160°c and the time at that temperature 1 — 4 hr.

In the sodium bisulphite cooks without excess of sulphur dioxide, called *bisulphite* cooks from now on, the total sulphur dioxide was 4.0 per cent., combined sulphur dioxide 2.0 per cent. and initial pH 4.0. The maximum temperature was 155°c and the time at this temperature varied 2 — 8 hr.

In the bisulphite/sodium carbonate cooks (called *bisulphite-soda*), the sodium (215 g./kg. wood) was introduced at the maximum temperature in the bisulphite stage and the digester either kept at that temperature for 2 — 5 hr. or the temperature raised to 170°c and kept there for 1 — 3 hr.

In the three-stage cooks (called *Sivola* cook after the patents of Y. Sivola[6]), the first stage was carried out with 1.8 — 2.7 per cent. total sulphur dioxide and 1.2 — 1.8 per cent. combined sulphur dioxide, pH 6, at temperatures up to 110°c. In the second acid stage, sulphur dioxide was introduced to make the total sulphur dioxide 5 — 7 per cent. and the temperature raised to 120° — 130°c. After 1 — 4 hr. at that temperature, the excess of sulphur dioxide was relieved, sodium carbonate introduced to a pH of 7.5 — 9.5 and the temperature raised to 155° — 170°c and kept there for 1 — 3 hr.

In the sulphate cooks, the temperature was raised to 170°c in 2½ hr. and the temperature kept there for 2 hr. The yield was varied by varying the amount of active alkali 140 — 220 g./kg. wood. The sulphidity was kept at 30 per cent.

Cooking conditions for birch wood

The sulphite cooks were, as in the case of spruce, like the sulphate cooks, although the active alkali varied at a lower level. The neutral sulphite cooks were performed with sodium carbonate, 160 g./kg. wood, of which 75 per cent. was converted to sulphite by sulphur dioxide gas. Temperature was increased to 170°c in 2½ hr. and kept there for 1 — 3 hr.

Pulp preparations

High yield pulps were first defibred twice in a laboratory Bauer refiner (clearance 3 thou.) and then screened and granulated as the other pulps. The beating was carried out in an original Valley beater and sheet formation and strength measurements made according to standard methods.

Analyses

Roe numbers were determined according to Swedish method CCA 9/41. Determination of alkaline solubilities were made according to method CCA 8/55 on lignin-free materials.

The chromatographic sugar determinations were carried out following an adaption of the method of Saeman *et al.*[7]

Spruce woodpulps

Yields and Roe numbers

The yield plotted against the Roe number for sulphite, sulphate and bisulphite pulps from spruce are found in Fig. 1. The plots are averages from a large number of cooks. The sulphite cooks represent also a two-stage cook with a neutral first step. We have found no significant difference in yields at the same Roe number for a sulphite, bisulphite or two-stage sulphite cook (*cf.* however [8, 9]). The yield curve for the sulphate pulps is always below that of the sulphite. The screening increases rapidly in the Roe number interval of 10 — 14.
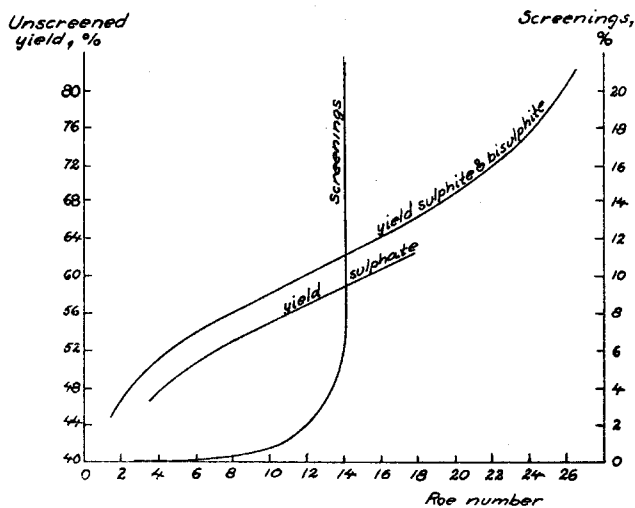

Fig. 1 — Yield against Roe numbers of sulphite, bisulphite and sulphate cooks

The influence of the sodium carbonate stage is illustrated in Fig. 2. The yield values lie within the shaded area; the exact value will depend upon how far the sulphite stage has been carried, as well as upon the excess of sodium carbonate and the temperature and time in the last stage. As exam-

ples, two lines are drawn to show the effect of a sodium carbonate stage when the sulphite stages have been stopped at Roe numbers 20 and 10.5, respectively.
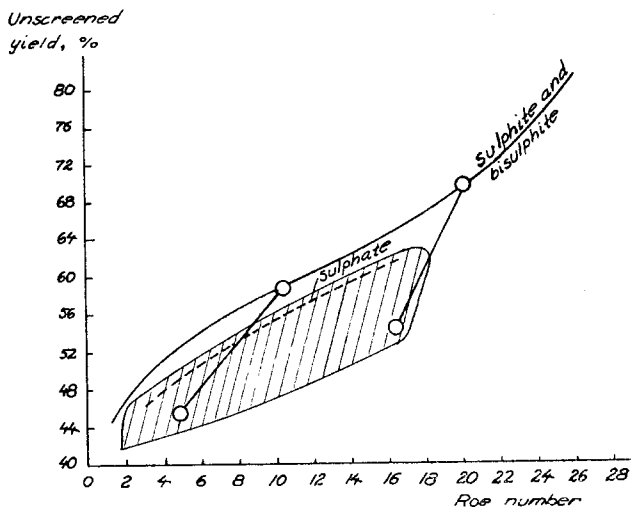

Fig. 2 — Yield against Roe numbers of sulphite and bisulphite cooks followed by a sodium carbonate stage (*see* explanation in text)

Carbohydrate composition of the spruce pulps

Tables 1 — 5 give the composition of the carbohydrate portion of the pulp fibres obtained by the various pulping processes and over a relatively wide yield range.

Besides glucose, all fibres contain mannose and xylose and sulphate pulps arabinose. Traces of arabinose have been found in bisulphite pulps also. Galactose was not found in any of the pulps, though the wood contains over 3 per cent. of it.

It is seen from Table 1 that, after an initial sharp decrease in mannose content and a slighter one in xylose content, the amount of these two carbohydrates remains fairly constant for sulphite pulps over a yield range of 60 — 50 per cent. It is only when the sulphite process is continued to a lower yield that a new sharp decrease in the mannose content is noticed.

The variation of the carbohydrate compositions of bisulphite pulps (Table 2) follows approximately the pattern of the sulphite pulps, as might have been expected from the yield data. The mannose and xylose levels seem to be somewhat higher, down to a pulp yield of about 55 per cent.

TABLE 1

Carbohydrate composition of spruce sulphite pulps

Cook No.	Yield, %	Roe No.	Carbohydrate composition, %		
			Glucose	Mannose	Xylose
1133	80.6	29.5	72.3	19.4	8.2
1654	73.7	22.5	79.5	14.0	6.5
1652	70.9	21.5	80.6	13.3	6.1
1495	62.5	14.0	85.5	9.4	5.1
1471	60.4	12.0	85.8	9.3	4.9
1493	56.8	9.5	85.7	9.2	5.1
1620	52.1	2.3	85.2	9.8	5.0
1893	47.2	1.6	90.2	5.4	4.4

TABLE 2

Carbohydrate composition of spruce bisulphite pulps

Cook No.	Yield, %	Roe No.	Carbohydrate composition, %		
			Glucose	Mannose	Xylose
1687	74.9	24.0	81.1	13.3	5.6
1685	70.0	21.0	80.2	12.3	7.5
1696	63.8	13.4	81.9	11.4	6.7
1678	56.7	9.6	82.3	10.8	6.9
1670	54.9	6.2	87.4	7.8	4.8

The data for sulphate pulps in Table 3 bear out the well-known fact that this pulp quality contains more pentosans than the sulphite pulp. The arabinose content decreases gradually as the yield goes down, whereas the xylose content remains remarkably constant over the investigated yield range from over 72 per cent. down to 47 per cent. The mannose content also remains at the same level from a yield of above 60 per cent. and downwards.

As mentioned in the experimental part, the yield variations of the sulphate pulps were achieved by varying the amount of active alkali at the

start of the cooking process. The cooking liquors have therefore undergone those variations that Yllner and Enström[5] have found favourable for the absorption (or crystallisation) of xylan. It is remarkable, however, that the amount of xylan, originally present and 're-absorbed', remains so constant over this wide yield range.

It is apparent from Tables 4 and 5 that the alkaline step in the two-stage bisulphite-soda or three-stage Sivola cooks causes a more selective removal of the carbohydrates containing mannose and xylose than ordinary sulphite or sulphate cooks do, compared at the same yield level. This is especially so for the Sivola process. Pulps of this type have really undergone a hot alkaline refining, only under conditions somewhat different from those ordinarily applied in the bleaching process. The ultimate yield and composition of the pulps are in these processes dependent on so many variables in the various stages that the figures shown in the two tables should be regarded only as an indication of what can be achieved in certain conditions.

TABLE 3

Carbohydrate composition of spruce sulphate pulps

Cook No.	Yield, %	Roe No.	Carbohydrate composition ,%			
			Glucose	Mannose	Arabinose	Xylose
1960	72.6	26.0	80.1	9.0	2.0	8.9
1130	67.4	—	80.8	8.2	2.1	8.9
1503	61.3	17.1	83.7	5.8	1.4	9.1
1084	56.6	10.0	83.4	6.4	1.3	8.9
1505	52.3	7.0	82.9	6.6	1.1	9.4
1529	47.6	3.6	85.0	6.0	0.8	8.2

TABLE 4

Carbohydrate composition of spruce bisulphite-soda pulps

Cook No.	Yield, %	Roe No.	Carbohydrate composition, %		
			Glucose	Mannose	Xylose
1689	60.9	15.1	84.7	10.2	5.1
1690	54.4	14.7	86.7	8.8	4.5
1688	51.9	11.9	88.0	7.4	4.6
1680	47.7	5.4	90.0	5.6	4.4
1681	42.6	2.2	90.6	5.2	4.2

TABLE 5

Carbohydrate composition of spruce Sivola pulps

			Carbohydrate composition, %		
Cook No.	Yield, %	Roe No.	Glucose	Mannose	Xylose
1643	59.2	18.0	89.7	6.3	4.0
1534	49.6	2.2	90.9	5.8	3.3
1501	47.6	2.3	92.2	3.8	4.0
1817	43.2	1.6	94.1	3.4	2.5

In Table 6, pulps from the same yield range are grouped together to permit a comparison of the carbohydrate composition for pulp fibres cooked by various processes. The table shows clearly that the distinct difference between sulphate and sulphite pulps — the higher xylose content of the former and the higher mannose of the latter — holds for the whole range of yields. It is only when the yield is brought down to about 47 per cent. that the mannose contents of these two pulp fibres become about the same, whereas the difference in xylose remains unchanged.

The mannose and xylose contents at the same yield figure are much the same for sulphite, bisulphite and bisulphite-soda pulps. The Sivola pulp, on the other hand, shows lower mannose and xylose contents than any other pulp does at the same yield.

In the last column, an attempt has been made to show how much 'true cellulose' has been lost in the various processes. Our present knowledge seems to indicate that the spruce wood used contains around 42 per cent. true cellulose. The lignin content of the pulps has been calculated by multiplying the Roe number for the sulphite and bisulphite pulps by 0.7 and by 0.8 for the sulphate, bisulphate-soda and Sivola pulps. It is also likely that the mannose is present as a heteropolymer glucomannan and, according to Timell,[9] one third of the mannose figure should be deducted from the percentages of glucose to correct for glucose in this hemicellulose. On this basis, the glucose contents necessary to account for all true cellulose are compared with the determined glucose percentages, less the amount of glucose present as glucomannan. Positive figures in the last column show the percentages of glucose present to be higher and negative figures to be lower than that necessary to account for true cellulose originally present in the

TABLE 6

Comparative data of the carbohydrate composition of various pulps at same yield range

Process	Cook No.	Yield, %	Roe No.	Composition of the carbohydrates, %				Percentage glucose difference from 'true cellulose'
				Glucose	Mannose	Arabinose	Xylose	
Sulphite	1654	73.7	22.5	79.5	14.0	—	6.5	+ 2.3
Sulphate	1960	72.6	26.0	80.1	9.0	2.0	8.9	− 3.9
Bisulphite	1687	74.9	24.0	81.1	13.3	—	5.6	+ 4.2
Sulphite	1471	60.4	12.0	85.8	9.3	—	4.9	+ 1.8
Sulphate	1503	61.3	17.1	83.7	5.8	1.4	9.1	− 6.7
Bisulphite	1696	63.8	13.4	81.9	11.4	—	6.7	+ 0.8
Bisulphite-soda	1689	60.9	15.1	84.7	8.8	—	4.5	− 4.2
Sivola	1643	59.2	18.0	89.7	6.3	—	4.0	− 6.3
Sulphite	1620	52.1	2.3	85.2	9.8	—	5.0	− 1.4
Sulphate	1505	52.3	7.0	82.9	6.6	1.1	9.4	− 9.3
Bisulphite	1670	54.9	6.2	87.4	7.8	—	4.8	+ 1.8
Bisulphite-soda	1688	51.9	11.9	88.0	7.4	—	4.6	− 13.0
Sivola	1534	49.6	2.2	90.9	5.8	—	3.3	+ 1.0
Sulphite	1893	47.2	1.6	90.2	5.4	—	4.4	− 2.8
Sulphate	1529	47.6	3.6	85.0	6.0	0.8	8.2	− 11.0
Bisulphite-soda	1680	47.7	5.4	90.0	5.6	—	4.4	− 8.9
Sivola	1501	47.6	2.3	92.2	3.8	—	4.0	+ 0.6

TABLE 7

Solubility of spruce sulphite pulps in caustic soda solutions

Cook No.	Yield, %	Roe No.	Percentage solubility in caustic soda of concentration—		
			5%	10%	18%
1133	80.6	29.5	25.7	32.5	33.6
1654	73.7	22.5	18.1	28.8	26.7
1652	70.9	21.5	13.2	24.4	23.5
1495	62.5	14.0	11.3	16.4	15.6
1471	60.4	12.0	10.5	16.6	16.2
1493	56.8	9.5	8.9	15.1	14.5
1620	52.1	2.3	8.5	15.6	14.0
1893	47.2	1.6	5.4	12.9	9.7

TABLE 8

Solubility of spruce bisulphite pulp in caustic soda solutions

Cook No.	Yield, %	Roe No.	Percentage solubility in caustic soda of concentration—		
			5%	10%	18%
1687	74.9	24.0	14.7	24.7	22.7
1685	70.0	21.0	13.4	20.9	19.5
1696	63.8	13.4	11.0	17.9	17.1
1678	56.7	9.6	9.6	16.9	15.7
1670	54.9	6.2	9.5	16.1	15.0

TABLE 9

Solubility of spruce sulphate pulps in caustic soda solutions

Cook No.	Yield, %	Roe No.	Percentage solubility in caustic soda of concentration—		
			5%	10%	18%
1960	72.6	26.0	22.4	30.5	28.5
1130	67.4	—	19.6	20.8	19.6
1503	61.3	17.1	12.4	17.9	17.3
1084	56.6	10.0	8.2	11.6	11.9
1505	52.3	7.0	8.3	13.0	13.1
1529	47.6	3.6	6.5	11.9	12.0

wood. As the fibres may contain glucose not belonging to true cellulose, the significance of the calculated figures is doubtful, but they give some information on the losses of true cellulose that have occurred.

TABLE 10

Solubility of bisulphite-soda pulp in caustic soda solutions

Cook No.	Yield, %	Roe No.	Percentage solubility in caustic soda of concentration—		
			5%	10%	18%
1689	60.9	15.1	11.4	15.6	15.1
1690	54.4	14.7	8.7	14.3	14.7
1688	51.9	11.9	7.8	13.7	12.9
1680	47.7	5.4	5.4	10.7	9.9
1681	42.6	2.2	3.6	8.4	7.6

TABLE 11

Solubility of Sivola pulps in caustic soda solutions

Cook No.	Yield, %	Roe No.	Percentage solubility in caustic soda of concentration—		
			5%	10%	18%
1643	59.7	18.0	7.9	15.2	14.9
1534	49.6	2.2	6.0	11.1	10.7
1501	47.6	2.3	5.4	10.0	9.3
1817	43.2	1.6	2.8	5.6	5.2

It is seen that cellulose is removed from the kraft pulps even in high yield pulps and that this removal increases as the cooking conditions are made more severe. A normal kraft paper pulp has lost about 9 per cent. of the cellulose originally present in the wood. Remembering that (apart from losses in arabinose) the carbohydrate composition of the kraft pulps was almost unchanged over a wide yield range, one must conclude that the components are removed in the same proportion, that is, are equally disposed to alkaline hydrolysis and dissolution. The sulphite process is more gentle towards the cellulose and a 'strong' papermaking pulp has lost less than 3 per cent true cellulose. The bisulphite process behaves again very much like

that for sulphite pulps, it preserves the cellulose somewhat better than does the sulphite process.

It is more difficult to get a clear picture from the multistage processes, because of the many variables in the cooking process. The figures indicate however, that if proper conditions are chosen these processes may be arranged to cause small losses in cellulose.
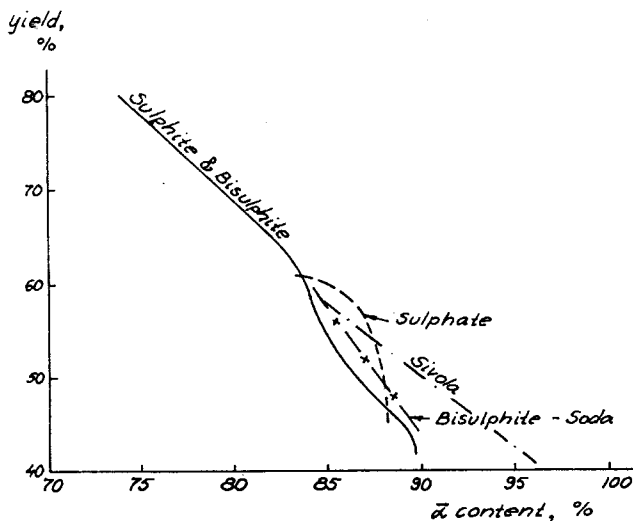
Fig. 3 — Yield against $\bar{\alpha}$-content — comparison of various processes

Alpha- and hemicellulose contents of spruce pulps

The solubilities of the delignified pulps in 5, 10 and 18 per cent. sodium hydroxide solution as an expression of the hemicellulose contents are found in Tables 7 — 11. The solubility in 18 per cent. caustic soda is a measure of the total hemicellulose content of the fibres and the solubilities in 5 per cent. caustic soda of the easily removable hemicelluloses that are dissolved in alkali without intramicellar swelling.

The alpha-cellulose content has been calculated as the average of the insolubility in 18 and 10 per cent. caustic soda and is denoted by $\bar{\alpha}$. This value has been found to agree with the standard alpha-cellulose determinations (for example, CCA 7). The variation of the alpha-cellulose content with the pulp yield for a large number of pulps has been plotted in Fig. 3.

The alpha-cellulose of the sulphite pulp first increases linearly with a lowering of the yield until the point of defibration — around 60 per cent.

yield. From there on, the alpha-cellulose content changes less with a continued decrease in yield. This apparently reflects a somewhat more selective dissolution of sulphonated lignin with little attack on the fibres in the yield range 60 — 50 per cent., until an alpha-cellulose content of 86 — 87 per cent. is reached. When it reaches 89 — 90 per cent., the yield decreases rapidly, now due to increased hydrolytic attack on the fibres. Alkaline solubility in 10 per cent. caustic soda increases at the same time.

Bisulphite and sulphite pulps follow each other closely in the yield range above 55 per cent.

TABLE 12

Solubility in caustic soda solutions compared at same yield range

Process	Cook No.	Yield, %	Roe No.	Percentage solubility in caustic soda of concentration	
				5%	18%
Sulphite	1654	73.7	22.5	18.1	26.7
Sulphate	1960	72.6	26.0	22.4	28.5
Bisulphite	1687	74.9	24.0	14.7	22.7
Sulphite	1471	60.4	12.0	10.5	16.2
Sulphate	1503	61.3	17.1	12.4	17.3
Bisulphite	1696	63.8	13.4	11.0	17.1
Bisulphite-soda	1689	60.9	15.1	11.4	15.1
Sivola	1643	59.2	18.0	7.9	14.9
Sulphite	1620	52.1	2.3	8.5	14.0
Sulphate	1505	52.3	7.0	8.3	13.1
Bisulphite	1670	54.9	6.2	9.5	15.0
Bisulphite-soda	1688	51.9	11.9	7.8	12.9
Sivola	1534	49.6	2.2	6.0	10.7
Sulphite	1893	47.2	1.6	5.4	9.7
Sulphate	1529	47.6	3.6	6.5	12.0
Bisulphite-soda	1680	47.7	5.4	5.4	9.9
Sivola	1501	47.6	3.3	5.4	9.3

The alpha-cellulose content of the sulphate pulps decreases rapidly when an alpha-level of 87 — 88 per cent. has been reached, which corresponds to the yield level of commercial kraft pulps.

The bisulphite-soda — and even more the Sivola — pulps have higher alpha-cellulose contents at same yield figures than do the sulphite pulps. This is especially so for the latter type of pulp and it appears possible to obtain fibres having an alpha-cellulose content of 95 per cent. with unbleached pulp yields as high as 42 — 43 per cent.

Chemistry of pulp fibres

In Table 12, the solubilities in 5 and 18 per cent. caustic soda are compared for pulps of same yield range. The amount of hemicellulose at approximately the same yields does not differ very much for the various pulp qualities, apart from the very high yield ranges. The sulphate pulps seem to have more hemicellulose than have the sulphite pulps, but perhaps less than the bisulphite pulps. The bisulphite-soda and even more the Sivola pulps have somewhat less hemicellulose than the other qualities do. The differences are, however, rather small.

TABLE 13

Composition of hemicellulose obtained with 5 per cent. caustic soda

Process	Cook No.	Yield, %	Roe No.	Solubility in 5% caustic soda	Carbohydrate composition of soluble material, %			
					Glucose	Mannose	Arabi-nose	Xylose
Sulphite	1654	73.7	22.5	18.1	14.2	43.4	—	42.4
	1893	47.2	1.6	5.4	13.5	28.3	—	58.2
Sulphate	1960	72.6	26.0	22.4	7.7	6.3	10.4	75.6
	1084	56.6	10.0	8.2	3.8	3.3	5.9	87.0
	1529	47.6	3.6	6.5	5.5	8.6	6.7	79.2
Bisulphite	1687	74.9	24.0	14.7	11.9	34.1	—	54.0
	1670	54.9	6.2	9.5	10.4	30.5	—	59.2
Bisulphite-soda	1689	60.9	15.1	11.4	12.0	36.7	tr	51.3
	1681	42.6	2.2	4.6	7.0	11.5	—	81.5
Sivola	1643	59.2	18.0	7.9	10.3	30.5	—	59.2
	1817	43.2	1.6	3.8	6.0	13.9	—	60.1

Table 13 gives the carbohydrate compositions of some of the hemicelluloses determined by solubility in 5 per cent. caustic soda. Whereas only slight differences were found in the amount of hemicellulose from the various cooks at similar yield levels, it is seen that the compositions are quite different.

Mannose and xylose are the main components in sulphite pulp hemicellulose. In high yield pulps, they are present in almost the same proportion, whereas xylose is more dominant in the low yield range. Relatively large amounts of glucose are also present. In sulphate pulps, the pentoses, arabinose and xylose, to a large extent, account for 85 — 90 per cent. of the hemicelluloses over the whole yield range. Mannose and glucose are present

only in smaller amounts. Bisulphite hemicelluloses are similar to those from sulphite pulps, but contain somewhat less glucose and more xylose.

TABLE 14

Carbohydrate composition of high yield birch pulps

Cook No.	Yield, %	Roe No.	Carbohydrate composition, %			
			Glucose	Mannose	Arabinose	Xylose
Sulphite birch						
1089	88.9	19.5	67.4	2.2	—	30.4
1091	72.0	17.7	73.7	2.0	—	24.3
1135	58.6	9.1	80.2	3.4	—	16.4
Sulphate birch						
1078	77.5	22.5	73.2	3.4	—	23.4
1073	69.0	18.1	76.4	tr	—	22.4
1076	62.7	10.9	76.2	tr	—	23.8
NSSC birch						
1121	81.3	20.5	66.2	3.7	—	30.1
1105	68.2	17.7	69.3	2.1	—	28.6

TABLE 15

Hemicelluloses from 5 per cent. caustic soda and their composition for birch pulp

Process	Cook No.	Yield, %	Roe No.	Percentage solubility in 5% caustic soda	Composition of the hemicellulose, %		
					Glucose	Mannose	Xylose
Sulphite	1089	85.9	19.5	33.6	3.1	1.9	95.0
	1135	58.6	9.1	17.1	3.3	2.8	93.9
Sulphate	1078	77.5	22.5	26.0	2.3	—	97.7
	1076	62.7	10.9	21.1	2.1	—	97.9
NSSC	1121	81.3	20.5	32.2	tr	tr	98.0
	1105	68.2	17.7	26.0	—	—	100

The hemicelluloses of the bisulphite-soda and Sivola pulps are for high yield pulps (60 per cent.) rather similar in composition to the sulphite hemicelluloses, mannose and xylose being the main components. The xylose content seems to be higher and the glucose lower than for corresponding

sulphite pulps. At low yields, however, xylose becomes the dominant component in the hemicelluloses, thus making the hemicellulose composition more like that from sulphate pulps.

Composition and hemicellulose content of some birch pulps

For comparison, a few results from high yield sulphite, sulphate and neutral sulphite semi-chemical (NSSC) pulps are included. It is seen from Table 14 that xylose is the dominant non-glucosidic carbohydrate. Xylose is gradually removed in the sulphite process as the yield is lowered, whereas it remains constant in the sulphate pulps. The NSSC pulping process is definitely the process that leaves the greatest part of the hemicellulose in the fibres.

Table 15 shows the hemicellulose content determined as solubility in 5 per cent. caustic soda, as well as the composition of the hemicelluloses. All hemicelluloses are composed almost solely of xylose with smaller amounts of glucose and, in the case of the sulphite pulps, also mannose. There are thus very few differences between hemicelluloses from birch pulps prepared by different processes in the investigated yield range. This is in contrast to the results from the spruce pulps and is certainly mainly due to the difference in the carbohydrate composition of the birch and spruce.[11]

The figures show that almost all of the xylose in the pulps is found in the hemicellulose. This indicates that, even if the xylan is re-absorbed during the sulphate cook, it is easily removed by extraction without removing glucose and this makes it doubtful if the assumption of a crystallisation of the xylan into the cellulose lattice holds for high yield birch sulphate pulps.

This investigation does not give a complete picture of the chemistry of pulp fibres. Among others, carboxyl contents of the pulps have not been determined. Reference should be made here to investigations by Saarnia et al.,[12, 13] who have shown that sulphate pulps contain practically no carboxyl and sulphite pulps a somewhat varying, but low, quantity.

No attempt has been made to determine the configuration of the hemicellulose components. Our present knowledge seems to indicate that perhaps all mannose is present as a heteropolymer glucomannan in a 1:3 or 1:4 proportion of glucose to mannose (*see* very recent work of Immergut and Rånby[17]). In sulphite pulp, xylose is found either as a pure (neutral) polymer or as a heteropolymer containing glucuronic acid units as side chains. In sulphate pulps, the uronic groups are absent, but arabinose might here be part of the xylan structure.

Papermaking properties and relation to chemical composition

The implication of the term *papermaking properties of a pulp* is by no means clear. Characterisation by the conventional strength determinations at a certain degree of beating has, however, become the usual way of comparing these properties and will also be used here.

The paper strength properties have been determined on unbleached pulps and the effect of the lignin has therefore to be taken into account when
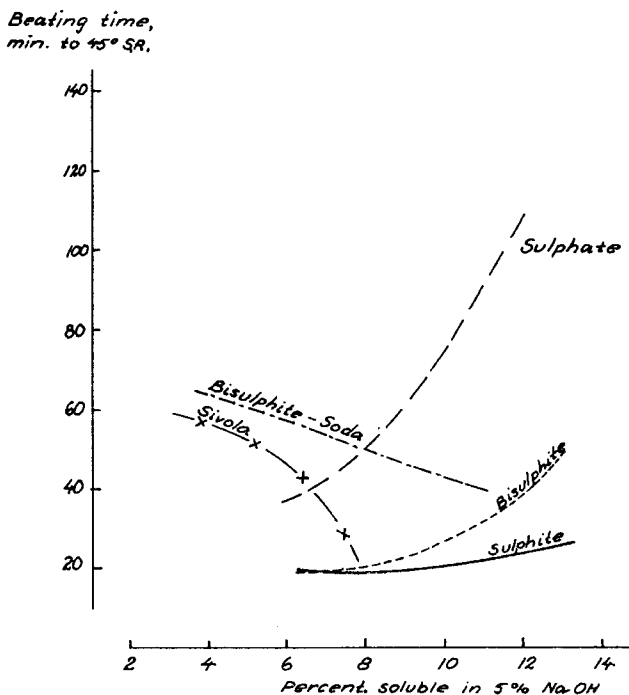

Fig. 4 — Beating against hemicellulose content for various spruce pulps

evaluating the results. The hemicellulose, determined as solubilities in 5 per cent. caustic soda, has been chosen as the variable against which to plot the pulp properties. The hemicellulose content varies with the yield and the standard procedure for handsheet preparation gives more fibres in handsheets prepared from pulps with lower yield than from higher yield, whereas the comparison ought to be made at the same number of fibres in the sheet to obtain precise information on the influence of the hemicelluloses. As this investigation

is mainly concerned with comparison of different pulp fibres and, as it has been shown that there are only minor differences in hemicellulose contents at the same yield range for various pulps, no corrections have been attempted.

Fig. 4 shows the beating time to 45° s.r. As previously mentioned, it is usually considered that the greater the percentage of hemicellulose, the shorter is the beating time. It is probable that at the high hemicellulose contents, which correspond to high lignin contents, the lignin retards the beating process. The curve for the sulphite pulp that shows a rather flat minimum at about 7 per cent. hemicellulose should very likely have continued
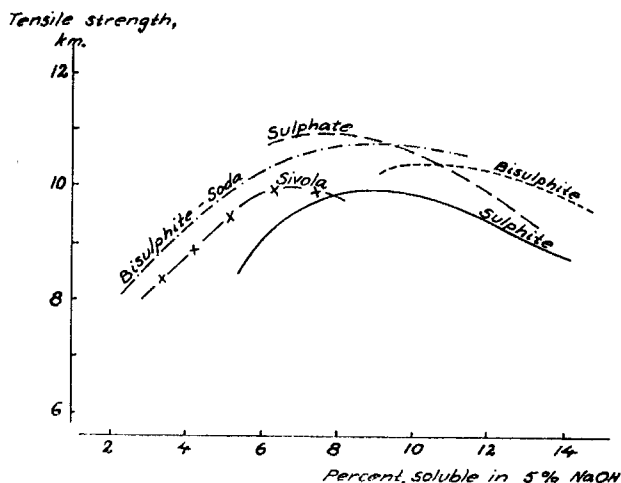
Fig. 5 — Tensile strength at 45° s.r. against hemicellulose content for various spruce pulps

downwards at higher contents, if the fibres were lignin-free. The lignin content of sulphate pulps increases more rapidly with increasing hemicellulose than it does for sulphite pulps (Table 12) and this might partly account for the steeper curve shown by the former compared with the latter. Even at hemicellulose levels when the influence of lignin ought to be negligible, however, the sulphate pulps need twice as long a beating time as do the sulphite pulps. The difference in hemicellulose composition (the higher mannose content in the sulphite hemicellulose) might account for this difference, as it is thought that hemicelluloses from hexoses with more hydroxyl groups hydrate more easily than do those composed of pentoses.

The beating curve of the bisulphite-soda and Sivola pulps might give some information here. These curves show a continued increase in beating time with less hemicellulose. At higher hemicellulose levels, when the composition of the hemicelluloses in the Sivola and sulphite pulps are rather similar, the beating times of the two pulps are almost the same and, as the hemicellulose in the Sivola pulp decreases and becomes richer in xylose content (that is, more like a sulphate hemicellulose), the beating time increases markedly above that of sulphite pulp.
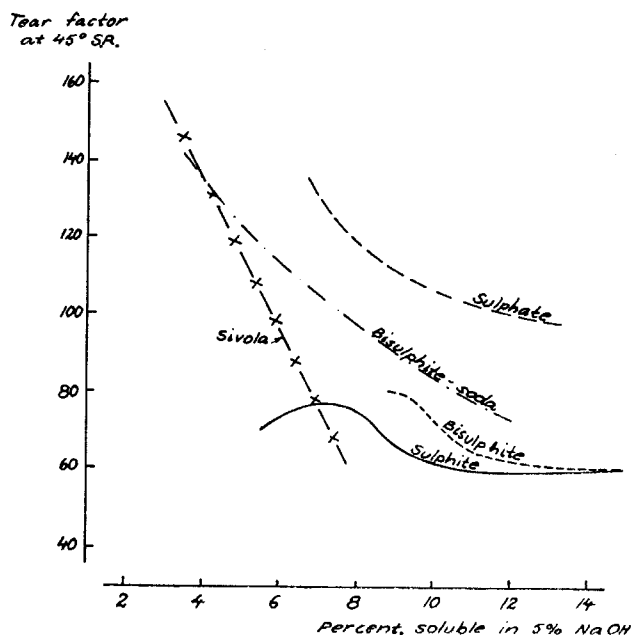
Fig. 6 — Tear factor at 45° s.r. against hemicellulose content for various spruce pulps

Swelling experiments on various fibres in iron sodium tartrate complex recently recommended by Jayme *et al.*[14] have shown that, in conditions when sulphite and bisulphite fibres readily develop balloon swelling, Sivola and bisulphite-soda fibres behave more like sulphate fibres and swell much more slowly, if at all.

Fig. 5 shows the plot of tensile strength against hemicellulose content. All pulps show curves of similar character, with a maximum at a certain

hemicellulose level. The optimum strength differs for the different pulps and is reached at different percentages of hemicellulose. The higher strength of the sulphate compared with the sulphite pulp of the same hemicellulose content is clearly shown. It is interesting to note that bisulphite fibres, which in chemical composition have been shown to be rather similar to sulphite fibres, develop definitely higher tensile strength. It might be that the more severe acid conditions in the sulphite process are of some importance. The influence of the alkaline stage in the bisulphite-soda and Sivola processes seems to be a continuation of the maximum strength level found for the bisulphite and sulphite pulps at lower hemicellulose levels, even a certain strength increase at the same level.

That a relationship exists between tensile strength and hemicellulose content is apparent, but the same amount of hemicellulose influences the strength property in a different way for different fibres. A partial explanation might be found in the different chemical composition of the hemicelluloses. It could be argued that the high xylose content in the sulphate hemicellulose gives the higher strength of the sulphate pulps; however, it is seen that the higher strength of bisulphite-soda and Sivola fibres, compared with bisulphite and sulphite fibres, is developed even when the hemicellulose compositions of the former pulps are similar to those of the latter. That xylan hemicelluloses are more beneficial than are mannan hemicelluloses is also contrary to the results of other investigations.[1]

Fig. 6 gives the tear factor plotted against the hemicellulose content. The increase in tearing strength with decreasing hemicellulose content is well known. The decrease in the tearing strength of sulphite pulps at low hemicellulose contents is most certainly due to the hydrolytic attack on the fibres when the sulphite process is continued towards low yields.

The sulphate fibres are seen to develop much higher tear factors than do the sulphite fibres at all levels of hemicellulose. The very rapid increase in tearing strength of the bisulphite-soda and Sivola fibres with decreasing hemicellulose content is an interesting property of these fibres and the explanation may, at least for the Sivola pulps, be found partly in the fact that the lowering of hemicellulose content in this pulp has been brought about with an alkaline extraction process, whereas in the sulphite process it is due to an acid hydrolysis, which also attacks the fibre wall.

It is evident that pulp fibres from the same wood material, but prepared by different processes, show markedly different papermaking properties at the same hemicellulose content. Part of the explanation for this difference might be found in the different chemical composition of the various hemi-

celluloses, but it is hard to believe that this alone accounts for the whole effect.

A factor that has not yet been discussed is the influence that different degrees of polymerisation (D.P.) of the hemicelluloses might have. The work of Thompson *et al.*[15] makes it probable that, if the D.P. of hemicellulose goes much below 100, its influence on papermaking properties diminishes sharply. The differences in strength properties extend, however, to regions where the hydrolytic degradation in the sulphite process ought to be small. The recent work of Immergut and Rånby[17] indicates strongly that the degradation of the hemicelluloses takes place early in the sulphite process. No data are available however, for sulphate pulp hemicelluloses.

The effect that the dissolving and the following re-absorption of the xylan taking place in a sulphate cook might have on the properties of the hemicellulose is unknown. It is unlikely that the xylan undergoes a similar process in the Sivola cook, because the xylose content does not remain constant as in a sulphate pulp. This point might, however, be worth investigating.

One of the explanations for the inferior strength properties of sulphite pulps to sulphate pulps has been the effect attributed to the greater lignin content on the outer surface of the former pulp fibres. It is again difficult, however, to invoke this explanation when discussing the bisulphite-soda and Sivola pulps, in which the delignification takes place almost solely in the bisulphite or sulphite stage of the process respectively.

The birch wood was found to give sulphite and sulphate pulp fibres, as well as hemicelluloses, of almost the same carbohydrate compositions (Table 15). An investigation along the same lines as this one with birch wood and including determination of molecular weights and uronic acid contents might therefore show better to what degree the chemical composition of the fibres and their hemicelluloses are of importance for their papermaking properties. Investigations along these lines are in progress.

It seems possible, however, that Centola and Borruso[16] might be right in thinking that the determining factors for the papermaking properties of a fibre are not to be found in the hemicelluloses, but are "a collateral phenomenon and that the predominating action of reagents and conditions employed in the pulping lies in modifications imparted to the structure of the fibre and particularly to that of the surface."

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DISCUSSION

PROF. H. W. GIERTZ: The question has been discussed earlier today whether the total material in the fibre is just a mixture of cellulose chains and hemicellulose chains or whether we have to consider two separate phases. The last point was raised by Prof. Frey-Wyssling a long time before the electron microscope was in operation. His idea was that we had certain cellulose strands or microfibrils in the fibre and that these were embodied in a matrix of hemicellulose material. As I understand it, Prof. Hirst is of much the same opinion.

Other aspects have been argued in the last 10-15 years. It has been said that the fibre wall (S2) is more or less a homogeneous body with a pronounced tendency to split longitudinally (in the same way as asbestos does) and that the microfibrils are not natural units but artefacts, the size of which depends on the intensity of the grinding or ultrasonic treatment; that the cellulose and hemicellulose molecules are blended very much into each other and are partly co-crystallised; and that the cellulosic material occurs in an overlapping amorphous/crystalline system without sharp borderlines. Thus, the wall of native fibres should be fairly homogeneous, like a viscous rayon filament and regions of different densities go continuously over into each other. I would like to discuss this point today, mixing a little the physical and chemical aspects of the problem.

At the Fibre Chemistry Section of the Swedish Forest Products Research Laboratory, we attacked the problem by treating delignified spruce fibres mainly in two different ways — by partial acid hydrolysis and by fractionated dissolution.

1. When treating a cellulosic material with hot dilute acids, as suggested by Nickerson, one part of the material is very rapidly hydrolysed, whereas the rest is attacked only slowly. By following the reaction kinetically, the amount of the easily accessible regions of the fibre can be calculated. We have performed this experiment on the same pulp, but with varying acids (2 – 5 N HCl; 3.5 N HCl + 0.6 M FeCl$_3$; 2 – 4 N HBr; 3 – 7 N H$_2$SO$_4$) and at different temperatures; in all cases, the same amount of accessible material was obtained. This was taken as an indication that the borderline between accessible and non-accessible regions must be rather sharp. The amount of non-accessible material in a series of different spruce sulphite pulps was always 42 — 43 per cent. of the wood, whereas the accessible part varied 5 — 21 per cent. of the wood, depending on pulp quality.
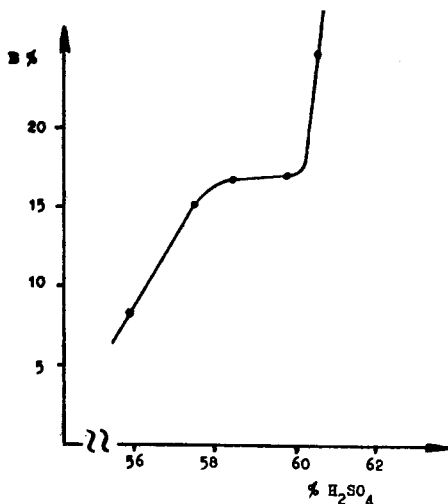
Fig. H — Strong sulphite pulp extracted with sulphuric acid — amount of extracted material against acid concentration
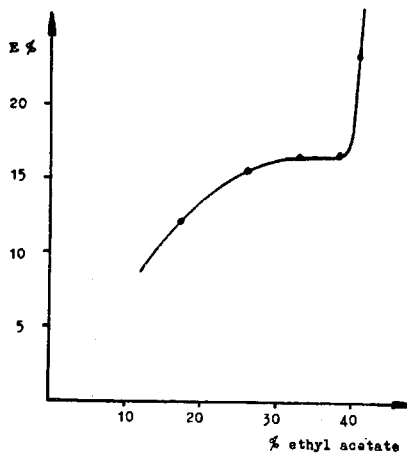
Fig. J — Nitrated strong sulphite pulp extracted with mixtures of ethyl alcohol and ethyl acetate — amount of extracted material against solvent composition

2.   Cellulose fibres swell considerably in sulphuric acid in the concentration range 50 — 58 per cent. At the same time, parts of the cellulosic material dissolves, as shown in Fig. H. The interesting feature in this dissolution process is that the amount of dissolved material increases with the acid concentration up to about 56 — 57 per cent. sulphuric acid solution, but then levels out despite the fact that the dissolving power of the acid is continuously increased with the concentration. At about 59 — 60 per cent., the rest of the cellulosic material dissolves. At this point, the swelling changes from inter-fibrillar to intrafibrillar in nature. This treatment is nothing but a fractional dissolution and, not being continuous, it seems to divide the fibre material in two main fractions. The resistant part amounts to about 42 per cent. of the wood in different spruce sulphite pulps, whereas the easily soluble part varies according to pulp yield.

3.   Exactly the same feature is obtained when a nitrated sample is treated with mixtures of ethyl alcohol and ethyl acetate of different composition, as shown in Fig. J. In this case, the solvation power is continuously increased with increasing ethyl acetate content of the solvent. In the region 65/35 parts per volume ethyl alcohol/ethyl acetate, however, dissolution ceases and increases markedly again at a mixture composition of 60/40, which shows

that the dissolution in this case too is typically fractionated. The resistant part corresponds to 42 per cent. of the wood.

In all these experiments, the cellulosic material has been separated into two main fractions, of which the resistant part amounts to 42 per cent. of the spruce wood. It must be kept in mind that the fractionation technique, however, has been essentially different in the three cases. Hydrolysis attacks and degrades the material continuously and quantitative estimation is based on the difference in reaction velocities for the two fractions. The treatment with sulphuric acid involves no chemical attack, but a strong interfibrillar swelling and partial dissolution. The same is the case with the nitrated fibre, but here the fractional dissolution has been performed on a derivative and not on the native fibre.

This separation into two main fractions becomes more interesting when the fractions are analysed for their chemical constituents. The resistant part consists mainly of glucan (Table 1), whereas the accessible part is a mixture of polymers of glucose, mannose and xylose.

TABLE 1

Chemical composition of the resistant fraction

Treatment	Pulp	Yield of wood, %	Chemical composition, %		
			Glucose	Mannose	Xylose
3.5 N HCl, 95°C	Strong sulphite	40.0	99	0.5	0.5
59% H_2SO_4	Strong sulphite	41.2	94	4	2
57% H_2SO_4	Rayon grade sulphite	41.0	96.5	2	1.5
65/35 ethyl alcohol/ ethyl acetate denitration	Nitrated strong sulphite	41.8	100	nil	nil

From these experiments, we have drawn the conclusions that the cellulosic material in spruce wood fibres is composed of two discrete fractions, the borderline between which is relatively sharp, excluding extensive transition areas. The resistant part consists of pure cellulose and, taking the results of modern electron microscope investigations into consideration, constitute the microfibrils. This fraction is the *true cellulose* and it amounts to about 42 per cent. in spruce wood. Consequently, the accessible material constitutes the interfibrillar substance. It seems to consist mainly of gluco-mannans and xylans, so there is good reason to keep the old term *hemicellulose*

for this fraction. In wood, there are other hemicellulose compounds such as galactan, araban, glycuronans and pectic substances. As these wood polyoses, part of which are laid down in the middle lamella, are extremely accessible, they do not occur in technical pulps.

From a practical point of view, the main difference between cellulose and hemicellulose is not because of chemical composition, but is their physical nature. The cellulose of the microfibrils is highly crystalline; it does not swell in water and chemical attack is a surface reaction. In contrast, the interfibrillar hemicellulose, probably owing to its heterogeneous composition, is of an amorphous nature; it swells in water and is easily accessible to acids and other chemical agents. It seems likely that the microfibrils also contain disordered, X-ray amorphous regions to some extent, but these are much denser than is the interfibrillar hemicellulose.

DR. B. G. RÅNBY: Prof. Hirst commented upon the relationship of the strength of a bond between glucuronic acid and a xylose unit, which has been well known to us for the last four or five years. The question is whether a carboxyl group — on the sixth carbon atom, for example — can increase the rate of hydrolysis of a cellulose chain. The point was that the glucosidic bond on one side of the glucuronic acid unit could be strengthened, but we do not know about the strength of the bond on the other side. If it is so easy to isolate the aldobiouronic acids from a xylan by hydrolysis, this could be so because the bond between the glucuronic acid and the xylose is so much stronger, but it may also be so because the adjacent bonds in the xylan chain are so much weaker — that is, easier to open by hydrolysis. I do not wish to stress this point about the influence of carboxyl groups, because the chains also contain some residual aldehyde groups resistant to oxidation by sodium chlorite. These groups might also influence the stability of the cellulose chains.

MR. J. R. SIMMONS: I notice that Dr. Jörgensen has only given carbohydrate analyses of the 5 per cent. caustic soda extracts. I wonder if he has carried out any such analysis on the 10 per cent. caustic soda extracts? We have carried out such analyses at various strengths and, at about 10 per cent. caustic soda concentration, we have found something rather different. Besides mannan and xylan, we get an appreciable amount of acid-precipitable matter, which appears to be degraded cellulose, since the hydrolysate consists essentially of glucose. We have found that this acid-precipitable degraded cellulose fraction from the 10 per cent. caustic soda extract has a detrimental effect on the strength properties of the pulp rather greater than the beneficial effect of the natural hemicellulose content of this

extract. The larger the amount of this degraded cellulose fraction, the weaker the pulp will be in general.

DR. L. JÖRGENSEN: For the pulps described in the paper, we have not analysed any 10 per cent. fraction, but a few 18 per cent. fractions — I do not think anything more is gained by plotting solubilities in 10 per cent. caustic soda against strength properties. We have plotted the ordinary alpha-cellulose contents against the strength factors and obtained curves similar to those shown.

DR. G. O. ASPINALL: We found, in carrying out structural investigations of the hemicellulose group, that there is a certain amount of the glucomannan fraction that is, to all intents and purposes, similar to cellulose and is extracted by approximately 10 per cent. alkali. It comes out with the gluco-mannans, but thereafter it becomes insoluble. We have examined one such fraction and, so far as we can see, it is quite indistinguishable from normal cellulose, except for the difference that it is of lower molecular weight.

PROF. GIERTZ: When I spoke some minutes ago about the resistant and the soluble parts of the fibre, I did not want to go into the general problem of alkali solubility, because the swelling and solution phenomena are much more complicated in this case.

In Fig. K (*a*)–(*d*) are shown some typical alkali solubility curves. The analysis has been performed according to CCA 8:55 and the PE fraction (beta-cellulose) has been precipitated in cold solution (about 0°C) with the aim of keeping the SE fraction (gamma-cellulose) in as solvated a condition as possible, thus avoiding the adsorption of the soluble substances on the precipitate. To avoid misunderstanding, I want to use the following terms. The resistant cellulose is called the R fraction and the extract the E fraction. After neutralisation, the latter is divided into precipitate and soluble extract, called the PE and SE fractions, respectively. When using 18 per cent. caustic soda solution, these fractions correspond to alpha-, beta- and gamma-cellulose.

It is of interest to note that, for all pulps examined, the SE fraction is more or less constant within a wide alkali concentration range (10 — 22 per cent. caustic soda), whereas the PE curves show typical maxima at about 10 per cent. caustic soda. Furthermore, the amount of SE in sulphite pulps decreases with cooking degree (that is, acid hydrolysis), whereas the PE fraction increases with hydrolysis and oxidation. Obviously, the SE and PE fractions must be of different natures, physically or chemically.
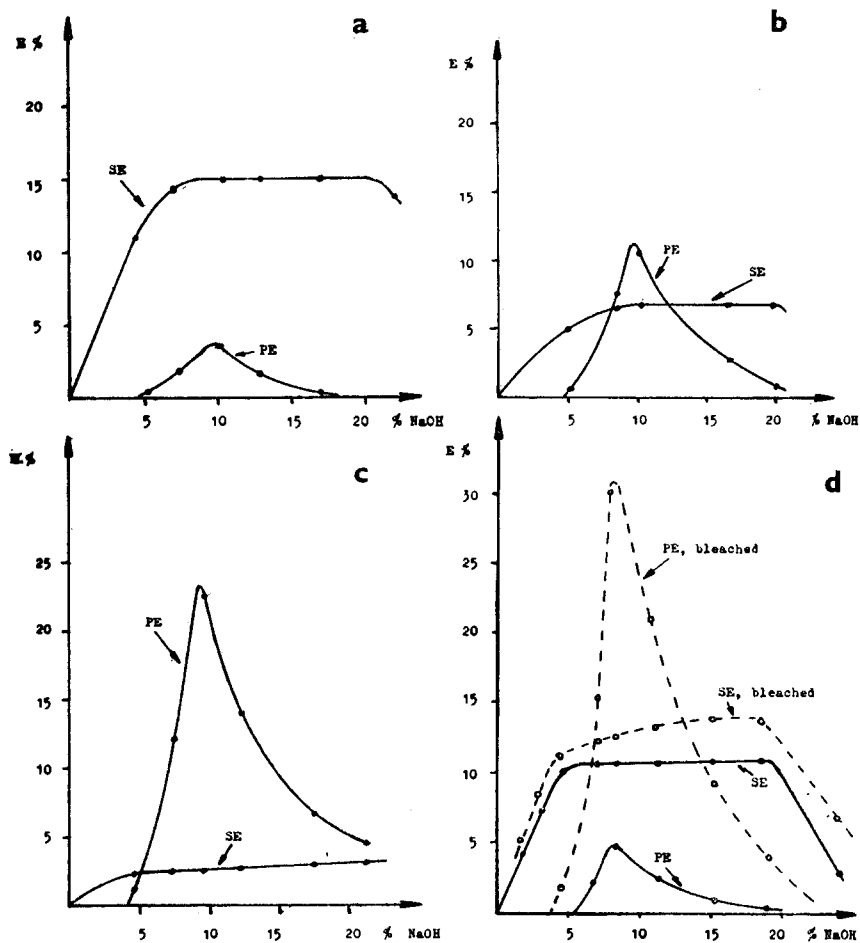
Fig. K — Alkali solubility curves — amount of soluble extract (SE) and precipitable extract (PE) as a function of caustic soda concentration

(*a*) Strong sulphite pulp
(*b*) Rayon grade sulphite pulp
(*c*) Overcooked sulphite pulp
(*d*) Paper grade sulphite pulp before and after strong hypochlorite bleaching

The fact that the amount of SE is constant within a wide alkali concentration range, independent of the swelling and dissolving power of the alkali, indicates that it is a discrete fraction and thus resembles the soluble fraction in treating native fibres with 57 per cent. sulphuric acid solution or nitrated fibres with a 65/35 mixture of ethyl alcohol/ethyl acetate, as mentioned earlier. Quantitatively, the SE fraction corresponds to the amount of soluble substance in the latter cases and chemically it consists of polymers of glucose, mannose and xylose, as shown in Table 2. There can be no doubt about it that we are dealing in these three cases with one and the same fraction of the cellulosic material; thus, the SE fraction (or gamma-cellulose) of spruce sulphite pulps is nothing but hemicellulose.

It is a well-known fact that alpha-cellulose, when isolated in the ordinary way, does not consist of pure cellulose. If, however, the analysis is performed under certain conditions, the R fraction consists of pure glucan (as is shown in Table 2) and, having a typical microfibrillar structure, it obviously consists of cellulose.

Being soluble in strong alkali, beta-cellulose is commonly supposed to belong to the hemicelluloses. This is misleading, however; no beta-cellulose occurs in chlorite holocellulose. It is formed during the different pulping and purification operations (hydrolysis, oxidation). In spruce sulphite pulps, the sum of the R and PE fractions is constant and amounts

TABLE 2

Chemical composition of the R, PE and SE fractions after alkali solubility determinations

Treatment	Pulp (sulphite)	Yield of wood %	Chemical composition, %		
			Glucose	Mannose	Xylose
R fraction					
15% NaOH	Paper grade	39.7	96.5	2.5	1.0
18%+18%+4% +4% NaOH	Paper grade	40.3	99	0.5	0.5
8% LiOH	Rayon grade	39.1	99	0.5	0.5
PE fraction					
10% NaOH	Paper grade	1.9	96	2	2
SE fraction					
8% LiOH	Paper grade	4.5	17.5	58.5	24
8% LiOH	Paper grade, overbleached	—	28.5	52	19.5

to 42-43 per cent. of the wood. It seems likely therefore that the PE fraction is nothing but degraded cellulose, which has been verified also by Rånby with the electron microscope. As a consequence, the PE fraction should consist of glucosan, which is the case (Table 2).

There is one thing more I want to mention about the nature of beta-cellulose. As can be seen from Fig. K (*a*)–(*d*), the PE fraction starts to appear at a concentration of about 4 per cent. caustic soda and reaches its maximum at about 10 per cent. This behaviour runs parallel with the intramicellar swelling of cellulose, changing the lattice from cellulose I to alkali cellulose (mercerisation), which phenomenon also starts at an alkali concentration of 4 per cent. and is completed within 8-10 per cent., as has been shown by Rånby in X-ray and moisture regain studies. It is tempting therefore to suspect a connection between mercerisation and the formation of the PE fraction. In Stockholm, we have been able to show that the PE fraction always shows the typical and very sharp X-ray pattern of alkali cellulose, whereas the R fraction shows the pattern of cellulose I with no trace of the lines of alkali cellulose, when isolated with 4 per cent. and 6 per cent. alkali solution. The lines of alkali cellulose first start to appear at a concentration of 8 per cent. caustic soda.

From this experiment, we have drawn the conclusion — though still not definitely proved — that the formation of the PE fraction is a direct consequence of the intramicellar mercerising swelling. This swelling must involve appreciable forces within the microfibril and, if this has been weakened by hydrolysis or oxidation at some spots, it seems likely that the swelling stresses will cause the fibril to break at these weak points. The short fibril fragments formed will peptise as such in the alkali solution; but, after neutralisation, they will easily precipitate because of the hydrophobic nature of crystalline cellulose.

Looking at the problem in this way, the beta-cellulose is an artefact and is of no primary interest when dealing with papermaking pulps. Its amount is certainly an indication of the degree of degradation that the microfibrils have been subjected to, but this effect can more easily and more accurately be measured by an ordinary viscosity determination.

Summing up, the alpha-, beta- and gamma-cellulose analysis gives quite a lot of information about the cellulosic material. When dealing with papermaking pulps, however, the gamma-cellulose value is of greatest interest, because it gives the amount of hemicellulose in the pulp. The alkali solubility (the sum of beta- and gamma-cellulose) is obviously of no interest.

It should be pointed out that analytical methods based on solubility in sodium (or potassium and lithium) hydroxide solutions are not ideal, the main disadvantage being that mercerisation takes place before optimum hemicellulose dissolution occurs, which makes a separation into PE and SE fractions necessary.

This kind of fractionation is more complicated when dealing with sulphate pulps and birch pulps.

MR. L. G. COTTRALL: Do I understand Prof. Giertz correctly that he thinks beta-cellulose is produced during the extraction and not during the pulping process? From the practical point of view, does it really matter whether the pulping process actually breaks off little bits and pieces or whether it merely weakens some of the stuff so that bits and pieces are produced when you carry out the extraction?

PROF. GIERTZ: You are quite right, the $beta_{10}$ fraction certainly indicates the amount of attack. The problem, however, is that the PE curve always has a very sharp peak around 10 per cent. caustic soda, but is not always exactly at the same concentration. Thus, it seems difficult to develop a simple and accurate method. I think it will always be easier to get a value for the degree of degradation by an ordinary viscosity determination.

MR. COTTRALL: We are dealing here, I think, with two effects. We have the building up of strength, because of the natural hemicellulose in the pulp, which does contribute towards the strength, although maybe only up to a certain value in hemicellulose content. Then you have the deterioration of the cellulose, if it has deteriorated during the pulping process, which reduces the strength. You have the balance of those two factors. I think that is what Mr. Simmons means. I do not think he means that the strength goes down always when the extract of caustic soda is high at 10 per cent. Sometimes the strength is high at 10 per cent. extraction and sometimes it is lower.

MR. P. E. WRIST: I should like to ask Prof. Giertz why the amount of extractable material that is precipitable decreases when you exceed 10 per cent. alkali.

PROF. GIERTZ: Because the swelling and dissolving properties of the sodium hydroxide solution are highest at 10 per cent. You do not get better swelling properties by increasing the concentration. When this is done, the water is taken up so much by the sodium hydroxide that the swelling power falls. With sulphuric acid, however, this does occur and, with the

mixture of ethyl acetate and alcohol, the swelling power increases progressively with the amount of acetate.

THE CHAIRMAN: I think that this question of the relationship of hemicellulose content to strength is a very important one. I was particularly impressed by the concluding sentence of Dr. Jörgensen's paper, which seemed to swing the pendulum back to the time I entered the industry some 25 years ago, when it was believed that the physical condition of the cellulose might have a good deal to do with the physical qualities of the paper.

PROF. GIERTZ: It is an old experience of papermakers that the higher the hemicellulose content, the stronger the paper or, the higher the pentosan content (as it was known in the 1930s), the better the strength. This relationship holds well for sulphite pulps. The very important question is, however, whether this is a primary correlation, involving cause and effect or only a secondary phenomenon.

As pointed out by Dr. Jörgensen today, we have always to remember that sulphite cooking means acid hydrolysis. Hydrolysis is needed to liberate and dissolve the lignosulphonic acid and, at the same time, the hemicelluloses are partly saccharified and the cellulose attacked and degraded, which latter means a weakening of the cellulosic framework and lower fibre strength. Thus, during a sulphite cook, the weakening of the fibre will always run parallel with hemicellulose dissolution. Paper strength has been related to the hemicellulose content, but it might as well be to fibre strength — this is the factor determining the optimum paper strength.

DR. RÅNBY: The effect of the hemicellulose will be further discussed tomorrow in connection with the beating of fibres. From what we know about beating today, especially when you have seen the latest pictures from the Forest Products Research Laboratory in Stockholm of the fibre-to-fibre bonds in paper, it seems reasonable to assume that it is largely a question of making the fibres so soft that the bonding surface, fibre-to-fibre, can be increased in size and you can get more effective hydrogen bonding from one fibre to another. The plasticising effect in a wetted pulp fibre is largely related to the content of the hemicellulose. If you bring that aspect in, you do not have to assume that the hemicellulose makes the glue in the paper; it is only that its presence makes the beating so much more possible. If you do not find so much fibrillation in beating, the main effect would be to make the whole fibre so much softer.

PROF. GIERTZ: I agree exactly. The amount of hemicellulose definitely has an effect on how readily the pulp is beaten. We are now coming, however,

to such matters as swelling, water imbibition, fibrillation and fibre flexibility, on which the hemicelluloses seem to have a considerable effect.

MR. H. W. EMERTON: We must resist the temptation to explain the effect of hemicelluloses in black and white terms. It seems to me unlikely that this is purely chemical or purely physical: almost certainly both effects are present. What we are trying to do this week is to find where to put the emphasis.

There is one aspect that has not been touched upon. It was pointed out by Jayme and von Köppen (*Das Papier*, 1950, **4** (19/20) 373; (21/22), 415; (23/24), 455) that under certain cooking conditions — chiefly those obtaining in sulphite digestion — the surface layers of the fibre are weakened by hydrolysis. Extensive bonding may occur between the surface layers of adjacent fibres, but, because the surface layers are not well anchored to their parent fibre, the whole interfibre link may be comparatively weak.

DR. F. MULLER: The impression that I get from this discussion is that softwood acid sulphite pulp is rather a poor material for studying the influence of hemicelluloses on the strength properties of paper. The experience we have had with strawpulp in this respect, I think, is much clearer and shows the hemicelluloses have a preponderant influence on the strength of paper-making pulps.

Since I read a paper on this subject last year in London (*Tappi*, 1957, **40** (6), 470), I do not think it is necessary to refer at length to our results, but I wanted to point out this difference as well as the further difference with the hardwood pulps studied by other workers.

PROF. B. STEENBERG: I have very much enjoyed listening to the talks today, but I am rather surprised that nobody has mentioned what happens if you take a highly purified cellulose fibre and proceed with graded methylation of it to see how its papermaking properties change. I think that reference to work of that type would be of some interest for those who advocate the extreme importance of the hemicelluloses in the cellulose group. Why does nobody talk about it?

THE CHAIRMAN: Prof. Steenberg has thrown down the challenge. Would either of the original speakers like to reply to it?

PROF. STEENBERG: Well, that is a good enough answer for me.

MR. EMERTON: Is Prof. Steenberg asking what the effect of substitution of hydroxyl groups is?

PROF. STEENBERG: No, we know that. I thought everyone knew that if you take a highly purified pulp having very poor papermaking qualities and partially methylate it, increased swelling and better strengths result. An increase in the number of methyl groups passes through a maximum until methyl cellulose is finally obtained, which does not swell in water at all and has no papermaking properties. Introduction of a group that obviously requires some space, opens up the structure, making it more bulky. Swelling can take place and bonding comes as a result. When there are too many of these groups, the material becomes hydrophobic and swelling diminishes. Here is a case of something not native in the material like hemicellulose, but something added later; the added groups — not capable of hydrogen bonding — open up the structure and make it possible for water to penetrate. Loose ends get into the tacky state and bonding can occur, but it is not due to a specific tacky material.

I thought this observation, well known to most of you, was very difficult to harmonise with any assumption that a specific group (or a specific carbohydrate type) would be the only important substance for beating, etc. In short, it very much corroborates Dr. Jörgensen's idea.

THE CHAIRMAN: That has cleared up a point of which the audience were perhaps more in ignorance than Prof. Steenberg thought.

MR. WRIST: I wish to take up the question of the importance of hemicelluloses in pulp strength, particularly the proposition that increasing the one inevitably results in an increase of the other. The use of additives to a pulp affords a method of studying the effect of amount of adhesives in a pulp without changing the fibres in other respects. I believe that many of the commercial additives such as guar gum or starch derivatives approximate sufficiently in behaviour to hemicelluloses to allow this generalisation.

Such a test on a variety of hardwood pulps, softwood pulps and groundwood, prepared by a wide variety of pulping and bleaching methods, has failed to reveal any trend so simple as that proposed. Contradictions were many, even between pulps of a similar type. In many instances, especially in the case of strong softwood pulps, additional bonding resulted as evidenced by increased burst and tensile strengths and loss of opacity. These changes were of the same order as could be achieved by small additional beating and no other advantage was realised.

Very weak pulps were relatively insensitive to the addition of adhesives. Weak softwood pulps and most hardwood pulps, however, did not exhibit any such common trends. Cases were obtained of improvements in strength

exceeded by those obtainable by additional beating; others have even shown losses of strength, particularly of tearing and folding strengths, without improvements in tensile or bursting strengths.

I would prefer to say that hemicelluloses or other adhesives enhance bonding, but whether or not increased hemicellulose proves advantageous to paper strength is dependent on many other factors such as fibre flexibility, fibre surface strength, extent of degradation of the fibre structure during pulping and bleaching and the strengths of the fibres themselves.

DR. RÅNBY: On this question of the hemicellulose content and its effect upon the colloidal properties of the fibres, we did some work about five or six years ago using colloidal sols of cellulose micelles in aqueous solution (*Faraday Soc. Disc.*, 1951, **11**, 158). It was shown that one could easily coagulate and precipitate these cellulose sols by adding small amounts of electrolytes. The cellulose micelles were classified as hydrophobic colloids. One could also stabilise the sol against precipitation with electrolytes by adding extracted hemicellulose in water or just as well by adding water soluble cellulose derivatives like carboxymethylcellulose (CMC) or ethyl hydroxyethylcellulose (Modocoll). These experiments show that one action of hemicellulose on cellulose is that of a protective colloid. Hemicellulose can apparently be replaced by water soluble cellulose derivatives. In this way, we apply a concept from classical colloidal chemistry.

MR. G. F. UNDERHAY: I was very interested in Prof. Giertz' references to the usefulness of density as well as strength measurements and I could not help thinking when Dr. Jörgensen referred to Schopper-Riegler data that it was rather like introducing a mongrel to a Cruft's dog show. The Schopper-Riegler determination of freeness is a bad method of measuring a property that, in any case, is mainly incidental and is not essential to finished paper properties and I felt a little bothered whether that was the right thing to do. I should be glad to have Dr. Jörgensen's comments.

DR. JÖRGENSEN: I agree that it is better to have sheet densities against strength factors instead of °s.r. or any other similar measurement. In this case, however, we found that the comparative picture did not change and decided to use the most common method — that is, to plot the strength properties at a certain level of beating measured as °s.r. against the amount of material soluble in alkali.

MR. D. MCNEILL: Is there any way other than beating to treat pulp to give good sheet formation? Could the addition of a small amount of rayon pulp

reject, such as Prof. Steenberg was talking about, which is near enough to pure cellulose, followed by wet rolling as on an MG cylinder give the same effect in density as in beating without using so much power?

PROF. GIERTZ: There are some pulps it is not necessary to beat to obtain high paper strength. One kind is the sulphate pulp studied by Jayme and co-workers, which is obtained by cooking quite fresh spruce wood by the ordinary sulphate process (Jayme, G., Kohler, L and Haas, W. L., *Das Papier*, 1956, **10** (21/22), 495). Such pulps have been called biological pulps. The unbeaten pulp shows the following paper strength characteristics — breaking length 8 700 m., tear factor 390 and 21 000 double folds, of which the latter two especially are extremely high.

Another type of pulp is that obtained by cooking spruce or pine with a slightly acidified sodium sulphite liquor (pH 6 – 3; 170°C). Despite the fact that the yield is about 65 per cent., delignification has been extensive enough to allow complete separation of the fibres as in the ordinary sulphite cook and no special machine is needed as in the semichemical process (Bölviken, A. and Giertz, H. W., *Norsk Skogind.*, 1956, **10** (10), 344).

Judging from the high yield figure, it must be expected that some of the hemicelluloses from the middle lamella are present on the fibre surface. The unbeaten pulp has the same slippery feel as a highly beaten greaseproof pulp has and the paper strength properties are quite high — breaking length 8 300 m., tear factor 107 and 2 800 double folds.

I think that every one of us will agree that some hemicellulose or some other swollen substance — maybe in a very thin layer — is needed on the surface of the fibre to produce the effect of gum or glue. Ordinary acid sulphite and sulphate pulps seem to be lacking such surface substances and therefore we have to beat them perhaps with the aim of removing the primary wall and thus disclosing fresh internal surfaces. In the case of the pulps just mentioned, however, the fibre surface seems to be covered with hemi-cellulosic material. Characteristic of the biological pulps is that the paper strength decreases markedly at the very beginning of beating, then increases again and that the high strength is lost on drying the pulp.

PROF. G. CENTOLA: Dr. Jörgensen closed his paper by quoting a sentence from an article that Dr. Borruso and I published about 8 years ago and presented at the second congress of A.T.I.P. in Paris.

I will repeat the reasons that led us to emphasise structure modifications, especially the surface structure modifications, instead of underscoring chemical composition.

The amount of the chemical constituents determined by analysis is an average value of the total fibrous mass. On the other hand, the chemical constituents fraction that is directly involved in the beating process and consequently contributes to the formation of fibre-to-fibre bonds is only located in the outer surface layers.

About 10 years ago, I had the opportunity of reading some papers in which an attempt was made to correlate the amount of hemicelluloses present in some pulps and the behaviour of such pulps on beating. Generally, the experiments were carried out by preparing a series of pulps characterised by different amounts of hemicellulose by extraction with alkali at various concentrations. The effect of hemicellulose extraction on pulp properties did not seem right — or only to some extent. I thought it necessary, first of all, to take into consideration other phenomena related to structure changes. In fact, repeating the same experiments on cotton linter pulps, we obtained changes in pulp properties very similar to those observed for the woodpulps when beating was related to the alkali concentration in the extraction.

It is well known that above certain concentrations the alkali can act so that the fibres become inert to beating action. Apart from the structure changes, it is necessary to consider not only the distribution of the substances that accompany the cellulose in the fibre, but also the state of combination in more or less sensitive complexes to the swelling and plasticising action of water. This consideration, together with other of our tests on the tendency of cellulose to delaminate have led us to direct our studies to plasticising fibres obtained either by modifying the structure or by introducing substances able to increase the rate of beating by favouring the swelling of the cellulose lamellae and consequently the cleavage of the fibre. We will refer to these arguments in our paper for session 4.

DR. F. L. HUDSON: I want to draw attention to the paper by M. N. Fineman (*Tappi*, 1952, 35 (7), 320). He was dealing with wet strength and proved, so far as the paper went, that urea- and melamine-formaldehyde resins did not produce wet strength in pulps that were substantially free from hemicellulose. Even cotton contains sufficient hemicellulose to be important in this respect, as he showed that extraction with caustic soda prevented it reacting with resins to give wet strength to the paper.

Is there any evidence that any particular hemicellulose or hemicelluloses in general are likely to react readily with amino resins or to react with formaldehyde?

MR. F. BRIDGE: Some time ago, I was concerned with a similar problem, though not with the production of wet strength in paper: I was asked to

provide pulps with varying lignin contents. This presented the problem of removing the lignin without touching the hemicellulose material. I resorted to the holocellulose method, which, I think it is generally agreed, leaves only the carbohydrate fraction. It was found that wet strength was definitely a function of the lignin content and not of the hemicellulose content.

Samples of a fairly raw-cooked sulphate pulp were subjected to different degrees of treatment with sodium chlorite and a range of pulps prepared in stages of decreasing lignin content. These pulps were then made into standard sheets incorporating a urea-formaldehyde resin for the wet-strengthening process. As the percentage of lignin in the pulp decreased, so did the retention of resin and the wet strength, until with a pulp of zero permanganate number the retention was virtually nil. (A full account of this work will be found in *Proc. Tech. Sect. P.M.A.*, 1947, **28**, 239: Schofield, G. and Harrison, H. Ainsworth, 'Some factors affecting the retention of amino resins by woodpulps'.)

PROF. GIERTZ: I wish to take up another point in this discussion on the hemicelluloses. If a researcher wants to show that paper strength depends on the hemicelluloses, of course, he needs to make a pulp without any hemicellulose to see if it is possible to get good paper strength from it.

The easiest way to get rid of the hemicelluloses is to extract the pulp with 10 or 18 per cent. sodium hydroxide solutions. By such treatment, the hemicelluloses are more or less fully extracted, but, at the same time, quite a number of other things happen to the pulp. When treating with a sodium hydroxide solution of mercerising strength, the whole cellulose lattice is changed; native cellulose I is converted to alkali cellulose; the whole fibre is extremely swollen. When washing away the alkali, the lattice of cellulose II is obtained and the fibre is still somewhat swollen. By drying, this swollen fibre shrinks and collapses and a type of fibre is obtained that is quite different from the native one. It is very dense, homogenised glassy fibre, which will not swell in water nor fibrillate on beating. When native fibres are beaten, opacity decreases; with this type of fibre, however, the opacity increases, which shows that cutting takes place, but no hydration. Hemicellulose extraction with a mercerising solution has thus formed quite a new kind of pulp, therefore all experiments based on comparisons with this kind of fibre are of no value.

MR. A. R. SMITH: I should like to make one comment about this question of applying amino-formaldehyde resins. The mechanism of the production of wet strength by this method is not understood and I think it is not at all

clear whether it is necessary for the resin to be within the cellulose structure or whether the mechanism is an external one of bonding the fibres together.

It must be appreciated in a case like this, when it is found that wet strength has not been produced under certain conditions, that it may be because the affinity of the resin for the cellulose has been lost or because the resin is not having the same effect on the cellulose as it does under normal conditions. So, to say that, because the hemicellulose has been removed, the resin is no longer effective may not be the full story. It should be appreciated that the resin may not have been picked up by the pulp at the stage of addition and, therefore, although resin was originally added to the pulp suspension, it may not be present in the final paper. Unless this is known (and I am not acquainted myself with Fineman's paper), it would appear that we must look further to find the explanation of the phenomena observed.

DR. W. GALLAY: It so happens that I assisted in directing the work of Fineman reported. This was not a question of resin pick-up, but rather one of the strength of the bridge between the amino-formaldehyde and the fibre through the hemicellulose.

DR. MULLER: Fibre cellulose consists of very long chains united in a more or less crystalline lattice and, therefore, they are not easily detached. The hemicellulose chains are much shorter and not arranged in a crystalline structure and so they are more easily detached. You need some detachment of these hemicellulose or other chains to obtain sufficient hydrogen bonding for the fibre-to-fibre bond strength of the paper. In my opinion, that is what is actually done in beating.

Another thing comes into play and that is, if you illtreat a fibre sufficiently, either by hydrolysis or by some other means (perhaps, some oxidation process, especially in an alkaline medium), the cellulose may be broken down and its lattice structure loosened so much that there is some detachment of the cellulose chains as well, so that it can take up the role of the hemicellulose. There is no prior reason that a glucose β–1, 4– chain should not be able to form hydrogen bonds as well as a hemicellulose chain does. I think the same will hold good for the development of wet strength with the urea-formaldehyde resin, because this resin has to attach itself to the fibre surface. The more chain fragments that are taken out, the greater possibility there will be of the urea-formaldehyde attaching itself to the fibre.