SULPHITE PULPS FOR HWM-FIBRES

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It has generally been taken for granted that only high-alpha dissolving pulps possess the necessary qualifications to serve as a starting material for the production of fibres which would display the characteristics typical of high wet modulus fibres. As a result, HWM-fibres have so far been produced almost exclusively from high-alpha sulphate pulps, and moreover the spinning techniques have been developed principally for these pulps alone. This leads to higher costs of production, by reason of the higher price of the initial pulp, along with a lowering of the output capacity of the viscose mill.

As producers of pulp, we have naturally taken an interest in the influence exercised by the refining level upon the typical characteristics of HWM-fibres. The refining level can be expressed as an alpha-level, or as the percentage of low molecular weight material in the pulp. A study has been made with these two quantities as reference, using fibres spun by both the Polynosic and the modifier method.

The pulps chosen were five sulphite pulps, refined to various alpha levels by different methods of manufacture, and two prehydrolysis sulphate pulps. All seven dissolving pulps were manufactured on a mill scale, and were intended specifically as the raw material for modal-fibres. Analytical data in respect of the seven pulps are given in *Table 1.*

The sulphite group comprises two softwood pulps, and three hardwood

Table 1. Analytical data of seven dissolving pulps

	Sulphite pulps					*Prehydrolysed sulphate pulps*	
	A	B	C	D	E	F	G
Wood species	Hard	Soft	Hard	Hard	Soft	Soft	Hard
Alpha-cellulose (%)	87·3	89·6	93·0	94·2	95·5	94·8	96·0
Beta-cellulose (%)	3·8	1·5	2·5	2·6	1·1	2·1	2·1
Gamma-cellulose (%)	8·5	8·7	4·3	3·2	3·4	3·1	1·0
Viscosity, cuam (cP)	46	54	37	39	48	26	23
Alcohol extract (%)	0·33	0·34	0·15	0·14	0·14	0·51	0·14
Pentosans (%)	6·5	4·4	4·0	3·5	2·7	2·7	1·5
Copper number	1·4	0·9	0·7	0·6	0·5	0·5	0·5
Ash content (%)	0·06	0·04	0·05	0·03	0·03	0·10	0·05
DP < 200 (%)	12·5	11·5	13·5	9·0	8·0	8·0	7·0

pulps. The sulphate group contains one representative each of hardwood and softwood. In both groups, the pulps are arranged in accordance with increasing content of alpha-cellulose. It is observable that a comparatively broad alpha-range was chosen—from 87·3 to 96 per cent. It seems that the gamma-content becomes lower on an increase in the alpha, whereas in the case of beta-cellulose no clear tendency is discernible. The viscosity level of the sulphite pulps is distinctly higher than normal. For this reason, the percentages of short-chain material—as shown on the lowermost line—are considerably less than the customary values for sulphite pulps. The high extract of pulp F (0·5 per cent) has been proved to be due to an added surfactant, which may possibly affect the results of spinning. The amount of pentosans is clearly a function of the alpha content, and thus the effect exerted by pentosans on the results will be accounted for, and included in the influence exerted by the alpha-cellulose. This also applies to the copper number. Ash values are all on a normal level. Significant differences which would have affected the properties of the fibres spun were not detectable in the ash-composition.

It can here be mentioned that all seven pulps were found to display approximately equivalent reactivity on small-scale preparation of viscose[1].

Table 2. Viscose preparation

Type of fibre	*Polynosic*	*Modifier*
Ageing	—	To a viscosity of 180 sec
CS_2 amount (%)	55	40
Viscose: Cellulose (%)	5·0	6·75
NaOH (%)	3·5	5·80
Gamma value	62	45
Modifiers: Alkyl amine polyoxyethylene glycol (%)	0·05	1·0
Aliphatic polyoxyethylene glycol derivative (%)	0·1	2·0

Table 2 gives an idea of the conditions of viscose preparation. Pure steeping liquor alone was employed on mercerization. The Polynosic-type viscose was prepared without ageing of the alkali cellulose; however, some depolymerization occurred during the 30 min shredding stage, at 19°C. In the modifier-type of method, the ageing was allowed to proceed to a stage which corresponded to the falling-ball-viscosity of the viscoses of 180 sec.

The other features typical of the two procedures were as indicated in *Table 2.* Thus, the dosage of carbon disulphide and the gamma-value were higher in the Polynosic-type of method, and conversely, the percentages of cellulose and alkali were higher in the modifier-type viscose. In this process the amount of modifying agent considerably exceeded that in the Polynosic viscose.

Both types of fibres were spun in the spinning machine shown in *Figure 1.*

Following many preliminary tests, the arrangement shown in *Figure 2* was decided upon for the Polynosic-type spinning. Here, the stretching of the yarn was effected in a concentric system of eight reels of increasing diameter. By this means, the total length of the stretching stage becomes 320 cm. The composition of the spinning bath and the dimensions of the

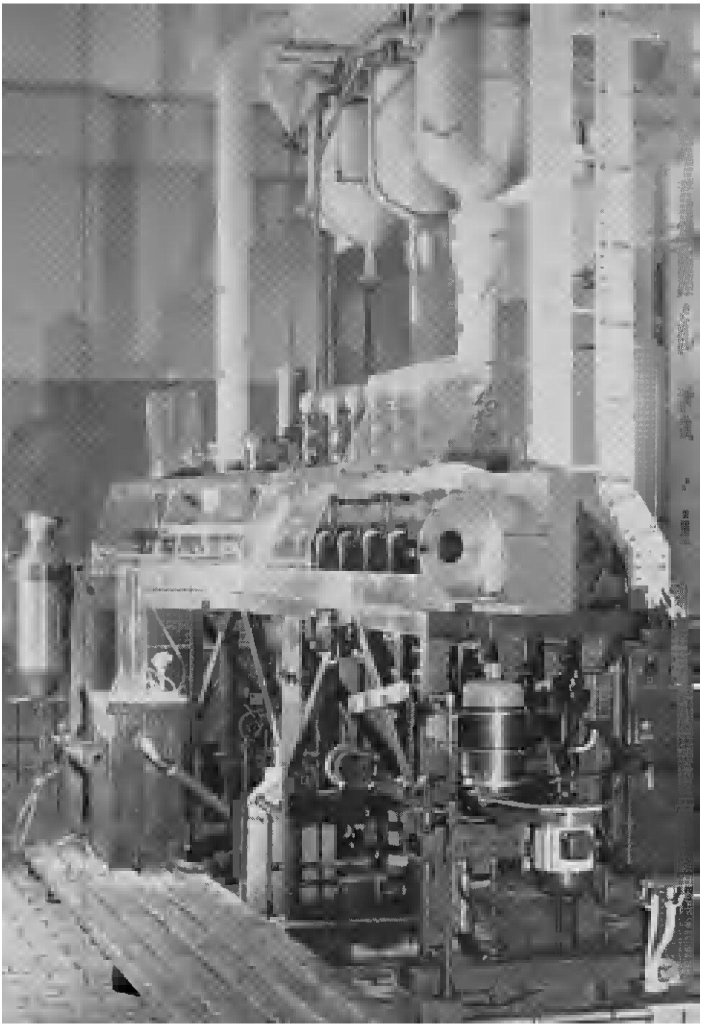


Figure 1. Pilot spinning machine

spinnerets are given in *Figure 2*, as are also the different stages of after-treatment. The rate of spinning was 25 m/min.

The spinning of the modifier-type fibres was carried out in accordance with the flow-sheet shown in *Figure 3*. The spinning was done vertically, with a depth of immersion of 40 cm. The stretching, which was 110 per cent, was effected in a separate bath, with an immersion distance of 50 cm. The compositions of the two baths and other conditions of test were as indicated in *Figure 3*. The spinnerets and the after-treatment, as well as the rate of spinning, were the same as in the Polynosic-type of spinning.

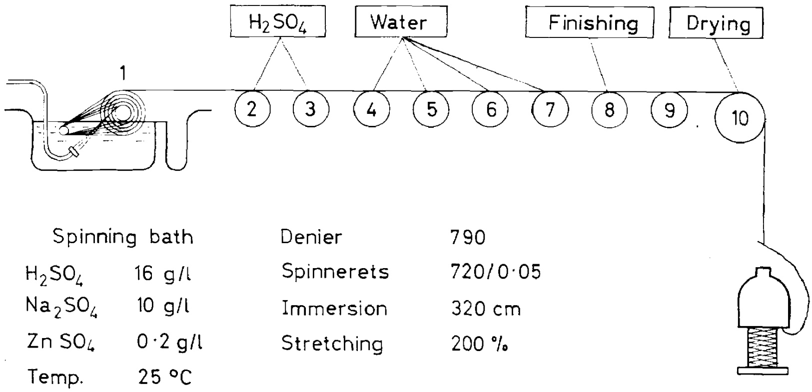


Figure 2. Polynosic spinning system

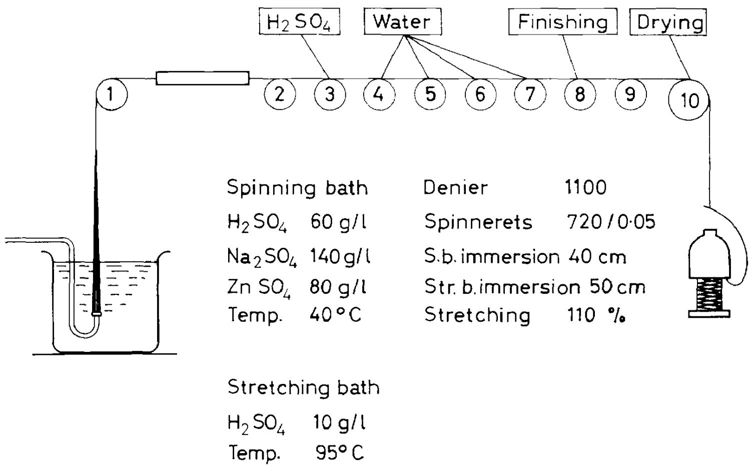


Figure 3. Modifier spinning system

All the viscoses were prepared from the seven initial pulps under constant conditions, and all the yarns spun under the same conditions, with a view to testing the different grades and types of pulp as regards their applicability to HWM-fibre manufacture. The spinning procedures described previously were selected with this aim in mind, and no attempts were made to optimize the process in any way to suit any particular type of pulp. For this reason, the fibres spun cannot in all respects be considered as comparable to some of the top class commercial fibres currently available. However, we believe that the fibres made from the different pulps can now instead be compared without the introduction of such cumbersome variables as processing methods.

Preliminary spinning tests were made with all seven pulps to ascertain the correctness of the method selected. Finally, six successive viscoses were made from each pulp, and the yarns spun from these viscoses tested with the Scott-tester to check that reproducible results were in fact obtained. Two lots of yarn were then selected to represent each grade of pulp. The samples were selected on the basis of the preliminary test results, with their properties lying as close as possible to the mean of the six lots examined.

The strength characteristics of the single filaments of each yarn sample were then arrived at with the Instron Tensile Tester as a mean of 25 measurements. The values presented in *Table 3* thus represent the mean of 50 single determinations. At first sight, one would be inclined to conclude that quite marked differences exist between the values in the Table; however, as will be seen shortly, these differences are attributable, by regression analysis, to differences in the alpha levels of the pulps. However, the method of manufacture exercises no effect upon the strength properties. The values of

Table 3. Fibre properties after Polynosic spinning

	Sulphite pulps					*Sulphate pulps*	
	A	B	C	D	E	F	G
Conditioned tenacity (g/den.)	4·94	5·06	4·80	5·33	5·18	5·18	5·42
Wet tenacity (g/den.)	3·58	3·83	3·79	4·07	4·37	4·25	4·61
Ratio T_w/T_c (%)	77	76	79	77	85	82	85
Conditioned elongation (%)	7·4	6·8	6·9	7·3	7·3	7·5	7·8
Wet elongation (%)	8·6	8·5	9·1	8·6	9·1	9·5	9·9
Loop tenacity (g/den.)	0·68	0·65	0·67	0·73	0·78	0·74	0·80
Wet modulus (g/den.)	41·2	42·6	40·2	45·0	46·2	41·0	46·9
Water retention (%)	56	59	55	54	54	58	54
Alkali solubility (5% NaOH) (%)	3·45	3·72	2·06	2·06	1·98	3·17	2·08
DP	623	634	635	679	652	634	614

Table 4. Fibre properties after modifier spinning

	Sulphite pulps					*Sulphate pulps*	
	A	B	C	D	E	F	G
Conditioned tenacity (g/den.)	4·60	4·70	4·52	4·60	4·98	5·37	4·86
Wet tenacity (g/den.)	3·17	3·15	3·21	2·89	3·48	3·94	3·36
Ratio T_w/T_c (%)	68	67	71	63	70	73	69
Conditioned elongation (%)	16·0	12·1	12·1	11·6	12·3	12·7	11·9
Wet elongation (%)	24·7	15·1	18·7	16·3	16·7	19·4	17·3
Loop tenacity (g/den.)	1·53	1·42	1·33	1·53	1·55	1·50	1·58
Wet modulus (g/den.)	12·3	17·4	16·4	16·2	17·2	17·4	18·4
Water retention (%)	67	68	70	70	65	65	70
Alkali solubility (5% NaOH) (%)	8·17	7·47	6·50	5·91	3·76	5·55	5·18
DP	475	486	514	498	485	499	524

water retention and alkali solubility—in 5 per cent sodium hydroxide—were determined from only one yarn sample. The water retention values are typical of Polynosic fibres, and seem independent of the initial pulp used. With an increase in the content of alpha-cellulose, the alkali solubility is seen to diminish.

There are no more than minor variations in the average degrees of polymerization of the fibres produced from the different initial pulps. These variations, free from trend, do not interfere when examination is made of the dependence of the strength characteristics of the filaments upon the other variables selected.

Table 4 presents the corresponding results arrived at on testing the filaments of the modifier-type spinning. It will be shown by regression analysis that the variables chosen, viz. the alpha and low-DP contents respectively, explain well the differences in the strength characteristics of the filaments. A typical feature of modifier-type fibres is their high values of water retention, considerably higher than for Polynosic-type fibres. However, it is observable that the values for the different samples vary but slightly, and that the differences are by no means significant. The type of spinning is reflected also in the values for the alkali solubility, which are distinctly higher than for the Polynosic-type fibres in *Table 3*. In part, this higher solubility can be explained by the lower DP-values for these fibres, a direct consequence of the ageing stage introduced.

Figure 4 shows the stress–strain diagrams of some typical HWM-fibres, as well as those for the fibres produced in our investigation. Here the black curves depict the characteristics of some well-known HWM-fibres.

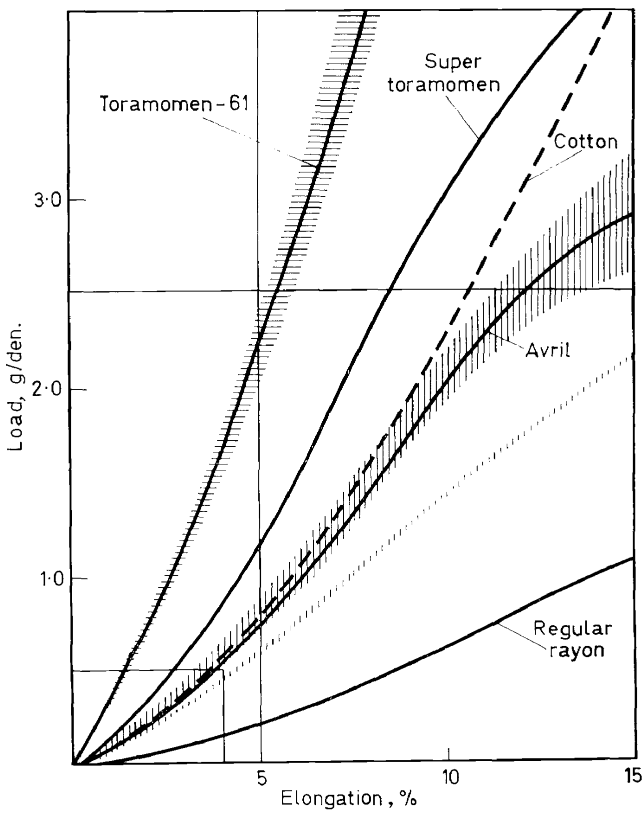


Figure 4. Stress–strain diagrams in wet state

All the stress–strain curves of our Polynosic-type fibres fall within the left-hand shaded region, and, with the exception of the curve for sample A, all the modifier-type fibres fall within the shaded region shown to the right. Indeed, the Polynosic-type fibres spun by us very well correspond to the typical representatives of their class, and meet the requirements for Polynosic fibres—that the elongation at 0·5 g/den load should not exceed 4 per cent. With the one exception mentioned, these fibres also come up to the requirements for modal-fibres, the elongation at 2·5 g/den load being less than 15 per cent. It can thus be remarked that also pulps of comparatively low alpha content are suitable for the manufacture of Polynosic-type fibres. However, it appears that modificr-type fibres are more sensitive as regards raw material.

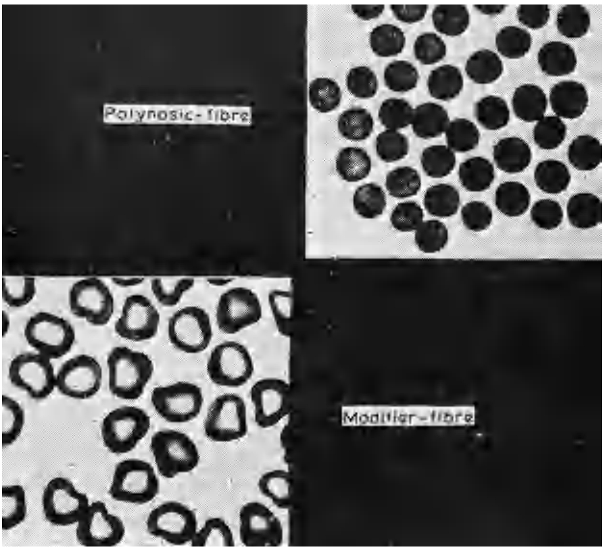


Figure 5. Cross-sections of HWM-fibres

The fibre cross-sections in *Figure 5* show the typical features of the HWM-fibres spun, and reveal the difference in the spinning methods.

It is generally said that the low molecular weight portion of the pulp exerts a significant influence on fibre tenacity. To check this statement, molecular fractionations from cadoxene solutions were made in accordance with the fractional precipitation method developed at the Finnish Pulp and Paper Research Institute[2]. *Figure 6* shows the results of these fractionations of the initial pulp, alkali cellulose immediately subsequent to mercerization, and the final Polynosic fibre. The results are given as three staples; the left one represents the proportion of material with a degree of polymerization lower than 200, the middle one shows the DP-range of 200–1000, whereas the staple on the right gives the fraction of long chains with a DP exceeding 1000. The differences evident in the original pulps can be explained by the

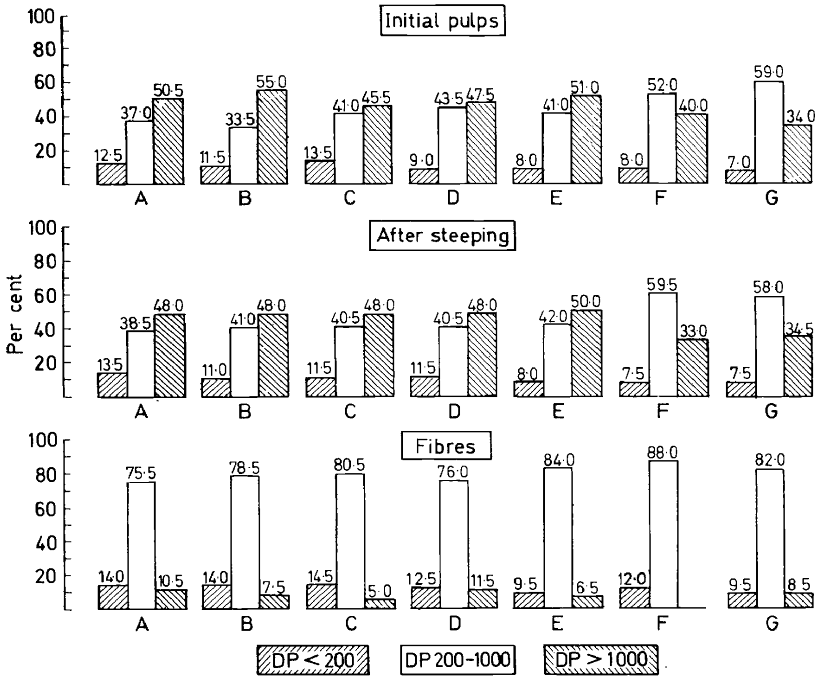


Figure 6. Results of molecular fractionations. Polynosic-type process

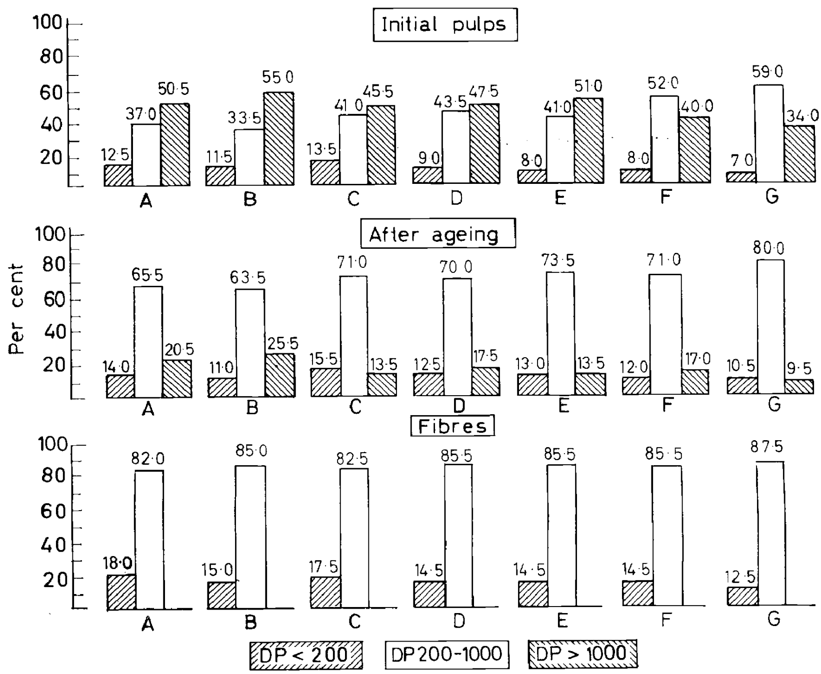


Figure 7. Results of molecular fractionations. Modifier-type method

different alpha content of the pulps; however, the amount of long chains also depends on the viscosity level of the pulps. It is observable that the situation is not appreciably changed on mercerization. Nevertheless, the mol. wt. distribution of the final yarns differs significantly from the distributions indicated in the two upper rows. This clearly implies that depolymerization has taken effect during the process, despite the absence of an ageing stage proper. A closer study reveals that the proportion of low molecular weight material has not increased appreciably from the amount initially present in the starting material; it follows that the effect of low mol. wt. material can be studied as a function of the amount found in the initial pulps. However, the effect of long chains, with DP over 1000, can be studied on the basis of molecular fractionations alone. The staples of the final fibres still exhibit the influence exerted by the alpha level, although there is no indication that the different methods of pulp manufacture have any effect.

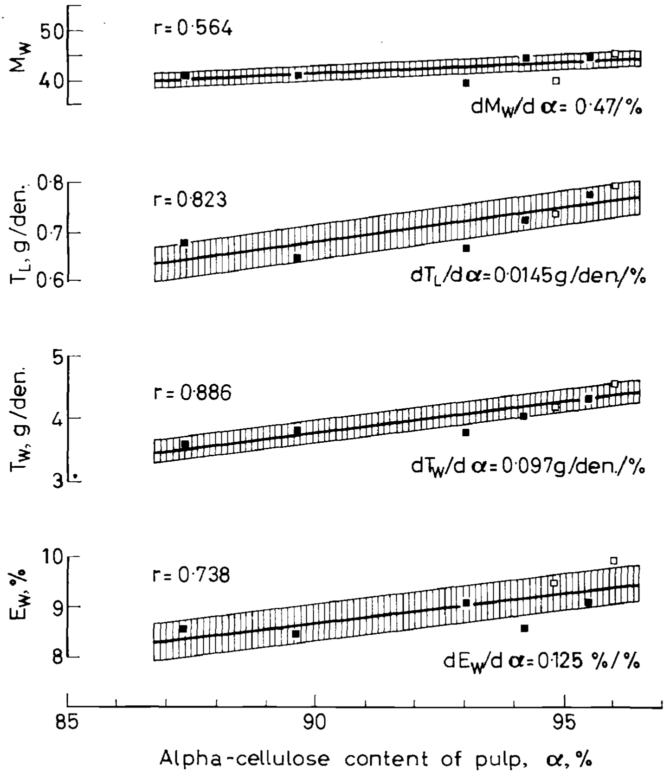
Corresponding changes in the molecular weight distribution related to the processing of modifier-type fibres are given in *Figure 7*. It can be noted directly that to a major extent the ageing stage has levelled off the differences which existed initially. The depolymerization has obviously proceeded during the subsequent stages, so that long chains no longer occur in the final fibres. The relative amount of short chains is also larger than in the Polynosic fibres, the difference from Polynosic-type fibres also being evident from the values for the alkali solubility.

REGRESSION ANALYSIS

The data arrived at in this study have been treated by statistical mathematics, to find possible correlations between the refining levels of the initial pulps and the properties of the fibres produced. A very great deal of information has been acquired, and it is not possible in this connection to discuss the dependence upon variables other than the alpha level and the amount of low molecular weight material.

Figure 8 shows the dependence of the strength properties of the Polynosic fibres upon the alpha-cellulose content of the initial pulp. It should be stressed that a discussion of the effect of the alpha content necessarily includes the net influence exerted by all variables related to the alpha level. Thus, chemical analyses indicated that for example the amount of pentosans and extractives depends on the alpha content.

In *Figure 8*, each point represents two spinnings, and is a mean of 50 tensile tests. The continuous line in the middle of the shaded field is the statistically computed regression line; the shaded field proper gives the statistical area of standard deviation from the regression line. It appears that all the strength characteristics are improved on an increase in the alpha content of the starting material. The correlation coefficients are seen to range between 0·56 and 0·9, and, with reference to the Table of significance levels, given beneath *Figure 8*, these r-values are all significant on a confidence level better than 92 per cent. It is observable that the loop tenacity increases by 0·015 g/den. when the alpha content increases by 1 per cent. A very good correlation exists between the alpha content and the wet strength, a 1 per cent rise in alpha bringing about, on the average, an



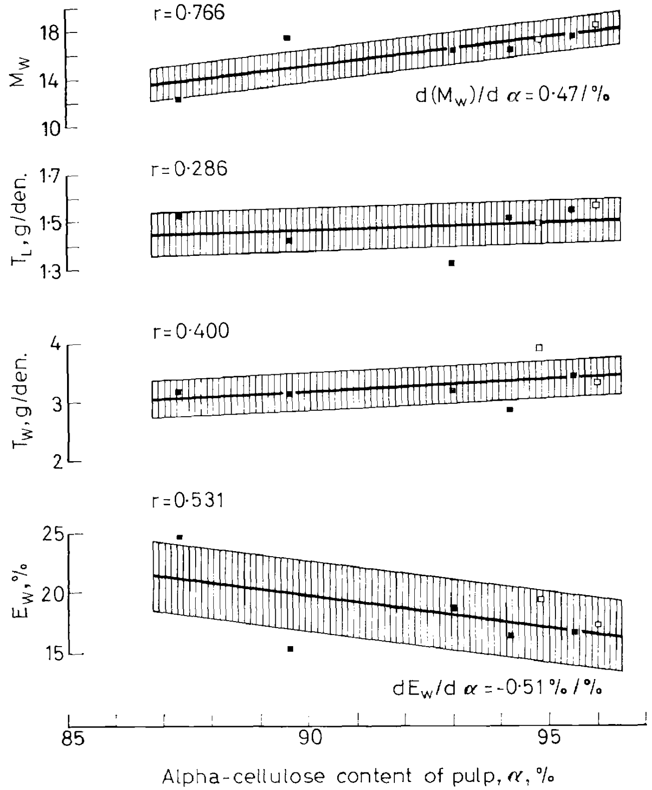
Level of significance	90%	95%	99%
r	≥0·50	≥0·67	≥0·84

Figure 8. Tensile properties of Polynosic-type fibres as function of alpha-cellulose content of initial pulp

improvement of 0·1 g/den. in the wet strength. Nonetheless, this figure does not represent more than 2·5 per cent relative improvement, and in practice significant improvements are noted only when the differences in alpha level are very large. These remarks also apply to the wet elongation regression given in the lowermost diagram.

In *Figure 9*, there are given the corresponding regressions for the modifier-type fibres. Here, the correlation is weaker than in the case of the Polynosic fibres, and it seems that a statistically significant correlation exists only as regards the wet modulus. Again, the effect per percentage-unit of alpha is rather slight; in practice the influence is almost negligible.

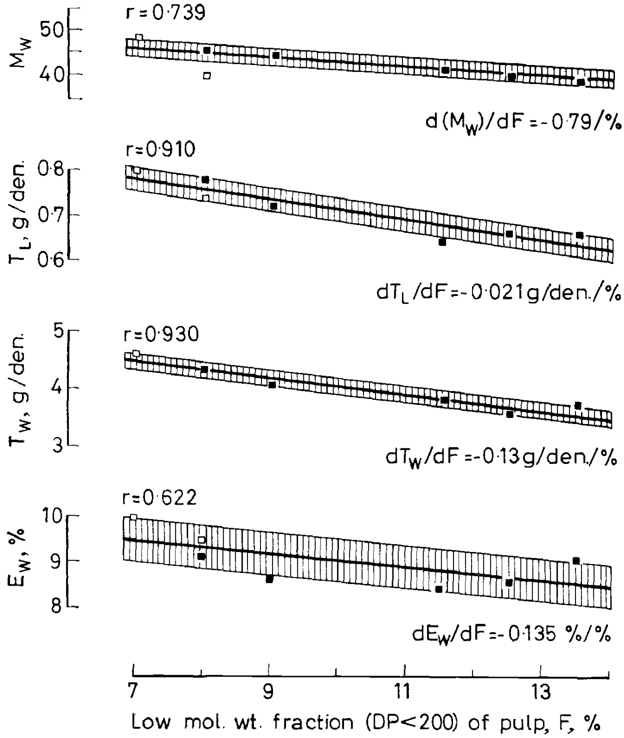
We can thus conclude that a definite statistical trend exists toward improvements in quality with increase in the alpha content of pulp, although the relative improvement seems to be too low to be of real practical importance. Moreover, it can be concluded that dissolving pulps on the same alpha level are equivalent, irrespective of their origin or method of manufacture.



Level of significance	90 %	95 %	99 %
r	≥ 0·50	≥ 0·67	≥ 0·84

Figure 9. Tensile properties of modifier-type fibres as function of alpha-cellulose content of initial pulp

In a way, the percentage of low-molecular weight substance in pulp is a measure of the refining level of pulp. In the previous examination of the results of the molecular fractionations, it was pointed out that the amount of low-molecular weight material in the fibre was associated with the corresponding figure for the initial pulp. *Figure 10* indicates the dependence of the strength values upon the short-chain fraction, designated F, in the initial pulp. It can be remarked that all the strength characteristics are reduced with increase in the F-value, and in most instances the coefficient of correlation is very high, even exceeding 0·9. The influence exerted by an increase of one per cent in the low-molecular weight fraction can be read from the slopes of the regression lines; the loop tenacity is affected by 0·02 g/den., the wet strength by 0·13 g/den., and the wet modulus by 0·79 g/den. The effect on the wet modulus is without practical importance, and in the cases of loop and wet tenacity, the adverse effect of the low-molecular weight material does not become significant until the increase in the F-value is large indeed.



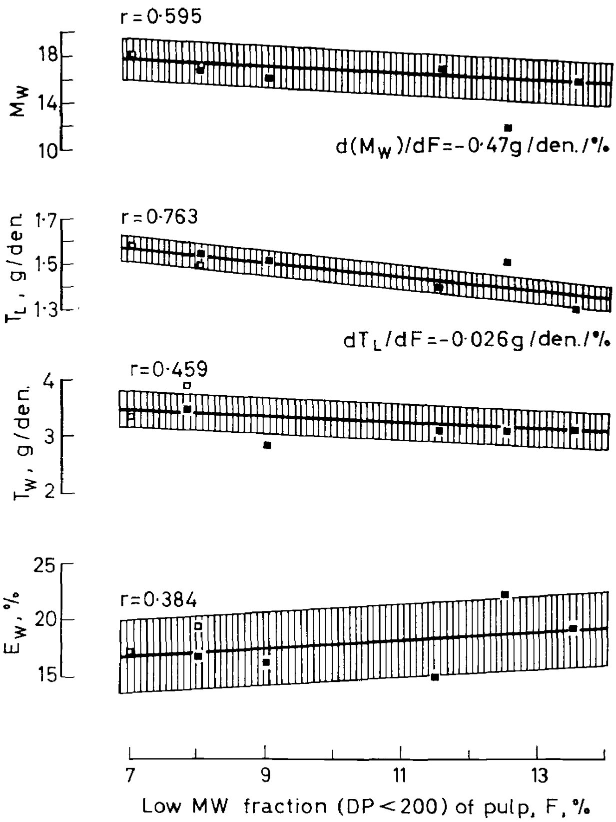
Level of significance	90%	95%	99%
r	≥0·50	≥0·67	≥0·84

Figure 10. Properties of Polynosic-type fibres as function of low-molecular weight fraction of initial pulp

The corresponding graphical representation for the modifier-type fibres is given in *Figure 11*. Statistically significant correlations exist only as regards the wet modulus and the loop tenacity, whereas in the cases of wet strength and elongation the trend alone is discernible. An ascending line was obtained for the elongation. However, in this case the standard deviation is large.

It can accordingly be concluded that in the F-range of 7 to 13·5 per cent the percentage of low-molecular weight material affects the strength properties of modal-fibres to a comparatively minor extent.

In published papers, the main emphasis appears to have been laid on the comparison of sulphite and sulphate pulps at the same viscosity level. The sulphite pulps studied here were specifically intended as a raw material for modal-fibres; the viscosity was thus preserved at a higher level. This probably explains why both sulphite and sulphate pulps fit the same regression equations, and why the method of pulp manufacture is no longer reflected in the properties of the modal-fibres. Thus the division of pulps into two sharply marked groups must now be considered as outdated.



Level of significance	90%	95%	99%
r	≥ 0·50	≥ 0·67	≥ 0·84

Figure 11. Properties of modifier-type fibres as function of low-molecular weight fraction of initial pulp

Sulphite pulps, of which the viscosity level is high, are capable of imparting to yarns the special characteristics typical of HWM-fibres; to this end, the alpha level does not necessarily have to be exceedingly high, as the strength properties can be improved to a greater extent by developments in the spinning techniques.

This investigation was made jointly by G. A. Serlachius Oy, Lielahti (formerly Ab J. W. Enqvist Oy), Oy Kaukas Ab, Rauma-Repola Oy, and the Finnish Pulp and Paper Research Institute. The Polynosic-type spinning was done at the Kaukas pilot plant, the modifier-type of spinning at Rauma-Repola Oy, and most of the analytical investigations and the fibre tests at the Finnish Pulp and Paper Research Institute. The authors are indebted to the staffs of the mills and the Institute for the skilful work done, which made this joint study possible.

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[2] L. Laamanen and H. Sihtola. *Paperi ja Puu* **46**, 419–422 (1964).