

POLYNOSIC FIBRES FROM DIFFERENT TYPES OF DISSOLVING PULPS

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INTRODUCTION

During the usual work, carried out in our laboratories and pilot plants for research and development in the field of Polynosic fibres, several dissolving pulps have been examined some of which are suitable for preparing Polynosic fibres. I shall refer to the most significant cases hoping to contribute, to a certain extent, to the solution of the problems connected with the production of suitable dissolving pulps within the usual price range.

The fibres obtained in the cases studied have properties consistent with "Association Polynosic" standards, but show clear differences. I shall make an attempt to relate the characteristics of the fibres with some of the properties of the starting pulps.

The results of the present work have been discussed, since January 1966, in a rather detailed way with our pulp suppliers including some Finnish firms, who have kindly provided us with various samples. Since the source and nature of these dissolving pulps, as well as the process for converting them into fibres, is confidential, I shall be obliged to provide only a limited information in this report.

HIGH TENACITY (POLYNOSIC) FIBRES

Dissolving pulps used

Seven dissolving pulps (denoted as numbers 1-7) were taken up for the present investigation. The process described here for the transformation of these pulps into fibres was chosen out of the ones available at "Snia Viscosa". In principle, this method uses dilute and well dissolved viscose solutions (obtained from shortly aged and well CS₂-treated alkali-celluloses) which have been spun at a low rate in dilute acid and salt baths containing mainly carbonylic agents. This procedure gives high tenacity fibres with well defined Polynosic properties.

The various pulps used in this study are listed below.

Pulp No. 1: This is a prehydrolysed and sulphate processed hardwood pulp, having a high alpha-cellulose content. It is normally used for high performance Cord-rayon.

Pulp No. 2: This is a sulphite processed northern hardwood pulp. We found it suitable for our purpose because of its high γ/β ratio; since γ -cellulose dissolved in the steeping soda, it is possible to obtain alkali with high alpha content.

Pulp No. 3: This pulp should have been similar to the Pulp 2 in performance but some processing difficulties gave a different product, with a less significant γ/β ratio, and with larger values both of dispersion and average degree of polymerization.

Pulp No. 4: This is sulphite processed fir-tree pulp: no particular information was given about its production process; the supplier praised its high viscosity.

Pulp No. 5: This is similar to No. 4 but has lower viscosity.

Pulp No. 6: This is sulphite processed fir-tree pulp; the supplier praised its high viscosity.

Pulp No. 7: This is a common fir-tree rayon-pulp.

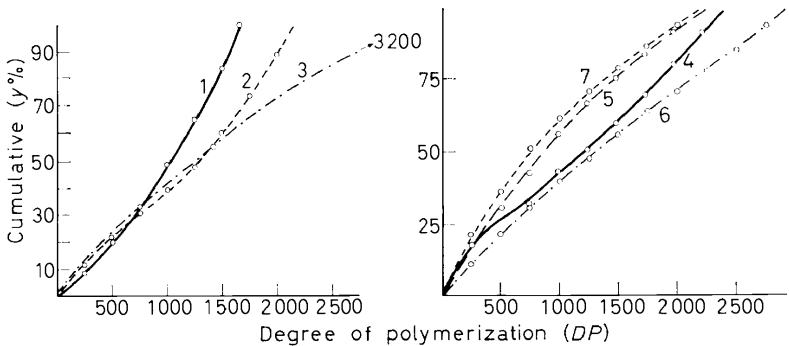


Figure 1. Chain length distribution of pulp by fractional solution. The numbers 1-7 refer to pulp numbers

Pulp No.	\overline{DP}	σ
1	975	41.2
2	1160	51.0
3	1300	57.8
4	1170	58
5	920	61
6	1300	61
7	860	63.7

In *Figure 1* are presented the curves of polydispersion, obtained by fractionating the nitro derivative, according to Jurisch. In all these curves are given the per cent dispersion σ of the degrees of polymerization (referred to the average value), as calculated according to the definition in *Figure 2*; σ represents the absolute value of the sum of the hatched areas, divided for the average degree of polymerization.

Characteristics of the pulps

In *Table 1*, the most important analytical data of these pulps are presented; we have described only those data which are the most relevant for our purpose. It can be seen from *Table 1* (from left to right) that the differences between the undissolved residue in 18 per cent and 10 per cent NaOH, the contents of aberrant sugars (with a particular reference to mannose), the solubilities in 7.14 per cent NaOH, and the per cent dispersion of the degrees of polymerization are all increasing.

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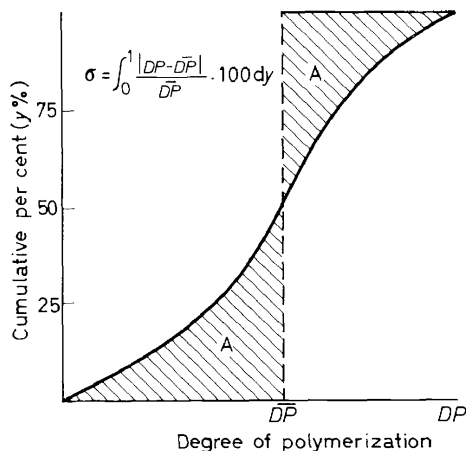

 Figure 2. Determination of the degree of dispersion (σ) of a pulp

Table 1. Chemical characteristics of the pulp samples

Characteristic Sample No.	1	2	3	4	5	6	7
α -Cellulose (%)	97.40	93.50	93.80	90.10	91.70	93.50	91.70
β -Cellulose (%)	1.80	1.70	2.00	2.80	3.70	3.23	3.80
γ -Cellulose (%)	0.80	4.80	4.20	7.10	4.60	3.27	4.50
R_{18} (insoluble in 18% NaOH) (%)	98.6	94.8	94.7	91.3	93.7	94.8	94.3
R_{10} (insoluble in 10% NaOH) (%)	97.5	93.0	92.4	88.6	90.5	91.5	90.7
Difference $R_{18}-R_{10}$ (%)	1.1	1.8	2.3	2.7	3.2	3.3	3.6
Rayon yield ($R_{18}-R_{10}$) (%)	99.0	95.0	94.5	91.6	93.7	94.7	94.0
Pentosans (GCA 24,27) (%)	1.50	2.50	3.00	1.30	2.15	2.20	3.20
Aberrant sugars (%)	2.40	3.40	4.20	4.70	5.20	5.30	5.70
Galactose (%)	Absent	Absent	Absent	Absent	Absent	Absent	Absent
Mannose (%)	1.00	1.20	1.40	3.40	3.20	3.40	2.60
Xylose (%)	1.40	1.90	2.80	1.30	1.70	1.90	2.00
Arabinose (%)	Absent	0.30	Traces	Traces	0.30	Traces	1.10
Alcohol-benzene extract (%)	0.07	0.22	0.29	0.40	0.25	0.15	0.21
S7.14 (Mahood index) (%)	5.10	9.30	9.60	1.1	12.50	13.50	14.00
Copper number (Schwalbe-Hägglund)	0.58	1.15	1.28	1.34	1.42	1.45	1.50
Ash ($840 \pm 10^\circ\text{C}$) (p.p.m.)	343	370	512	448	320	590	403
HCl insoluble (p.p.m.)	14.7	67.7	102	34.5	79	55.6	28.3
Calcium (p.p.m.)	70	169	161	225	99	222	138
Iron (p.p.m.)	4.15	3.50	6.12	4.80	4.20	4.40	6.70
Viscosity (TAPPI T206) (cP)	22	33	43	37	20.5	45.2	18.3
DP nitrate	975	1160	1300	1170	920	1300	860
DP dispersion (σ) (%)	41.20	51.00	57.80	58.00	61.00	61.00	63.70

Since we did not find other correlations regarding, for instance, alpha-cellulose content, viscosity, resins, ash, we related the properties of the fibres obtained to the above mentioned properties. As indicated in Figure 3 we notice that the average degrees of polymerization of the fibres are lower, the higher the dispersion σ of the starting pulps; the conditions of the transformation from pulp to fibre being strictly constant, the values of degree of polymerization drop considerably when σ values are higher than 52-54 per cent.

Furthermore, as shown in Table 2, the lowering of the average degree of polymerization in the transformation from pulp to fibre is considerable the higher the corresponding value of the starting pulp, and the higher is the

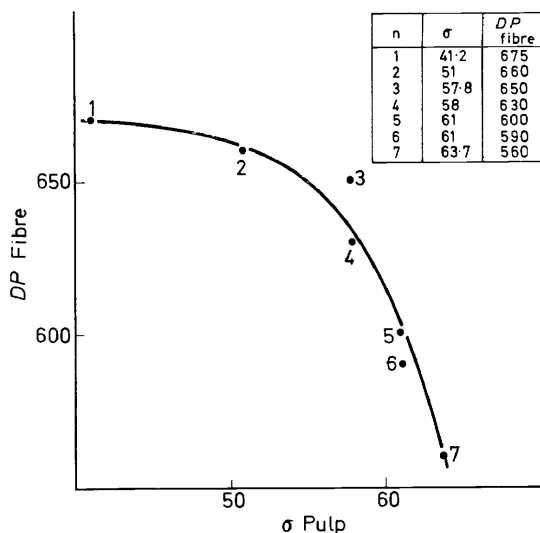


Figure 3. Average degree of polymerization of the fibre versus DP dispersion of the starting pulp

Table 2

Sample No.	$\overline{DP}_{\text{pulp}}$	$\overline{DP}_{\text{pulp}} - \overline{DP}_{\text{fibre}}$	σ_{pulp}
7	860	300	63.7
1	975	300	41.2
5	920	320	61
2	1160	500	51
4	1170	540	58
3	1300	650	57.8
6	1300	710	62

per cent dispersion, as inferred by considering the case of pulp Nos. 3–6 and 1–7.

Characteristics and performance of the K66 and K65 fibres

In *Table 3* are given the chemical and textile characteristics of the fibres and yarns at $N_{ec} = 20$ in the case of K 66 and K 65 fibres. The chemical process for obtaining both fibres is the same, only the mechanical treatment is different; the drawing ratio of K 66 and K 65 fibres being respectively 300 and 150 per cent. As can be seen from *Table 3* the K 66 fibre has very high conditioned and wet tenacities and rather small elongations. The K 65 fibre, on the contrary, has lower tenacities and higher elongations. The yarns thus obtained reach a maximum break length of 30 km in the first case, and of 23 km in the second case.

In the case of both fibres proceeding from left to right, we notice a slow and constant lowering of all properties—in fact, tenacity of fibres and break

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Table 3. Dynamometric characteristics of K 66 and K 65 fibres obtained by different starting pulps

Characteristic	K 66							K 65						
	1	2	3	4	5	6	7	1	2	3	4	5	6	7
Denier (den.)	1.30	1.30	1.30	1.30	1.30	1.30	1.30	SINGLE FIBRES 1.30	1.30	1.30	1.30	1.30	1.30	1.30
Conditioned tenacity (g./den.)	7.0	6.8	6.5	6.3	6.3	6.2	6.2	SCHOPPER DYNAMOMETER 4.7	4.6	4.5	4.3	4.2	4.4	4.3
Conditioned elongation (%)	10.0	9.7	9.5	10.0	9.2	9	9.9	13.7	13.0	13.0	13.0	14.0	12.8	14.8
Wet tenacity (g./den.)	5.6	5.1	4.95	4.9	4.9	4.85	4.75	3.5	3.15	3.0	2.9	2.85	2.85	2.75
Wet elongation (%)	12.0	11.0	11.0	11.2	11.5	10.6	10.8	16.6	16.8	16.0	16.0	18.0	14.9	18.0
Wet tenacity (g./den.)	5.5	5.4	5	4.85	4.8	4.8	4.7	INSTRON DYNAMOMETER 3.4	3.3	3.1	3.1	2.85	2.78	2.75
Wet elongation (%)	9.0	8.6	8.5	8.2	9.0	8.7	8.7	11.5	12.0	11.0	11.0	13.0	10.15	13.0
Wet elongation at 0.5 g./den. (%)	1.16	0.97	0.95	0.85	0.90	1.00	1.11	2.20	2.15	2.00	2.00	2.50	2.04	2.20
Wet Young's modulus (g./den.)	47	50	48	49	47	48	50	26	26	26	26	21	26	22
Wet tenacity (g./den.)	5.2	4.9	4.7	4.6	4.6	4.5	4.4	AFTER TREATMENT WITH 5% NaOH 3.05	2.8	2.7	2.6	2.5	2.5	2.4
Wet elongation at 0.5 g./den. (%)	2.0	1.3	1.6	1.5	1.5	1.7	1.8	4.4	3.8	5.2	4.0	5.0	4.05	4.2
Loop strength (g./den.)	0.60	0.55	0.50	0.50	0.55	0.50	0.55	0.60	0.60	0.50	0.50	0.50	0.54	0.60
Solubility in 6% NaOH (%)	0.70	1.60	2.00	2.10	2.40	2.80	2.95	1.50	2.40	2.70	3.50	4.00	4.25	4.90
D.P. of fibre	675	660	650	630	600	590	560	675	660	650	630	600	590	560
Number (N/g)	20	20	20	20	20	20	20	YARNS 20	20	20	20	20	20	20
Conditioned break length (km)	30.100	28.500	27.900	27.200	27.000	27.000	26.400	23.600	22.500	22.000	20.000	19.800	19.600	18.200
Conditioned elongation (%)	6.2	6.0	6.0	6.2	5.9	5.7	6.1	7.5	7.8	7.5	7.5	8.1	6.8	8.3
Wet break length (km)	23.300	21.200	20.600	20.300	20.100	20.000	19.300	18.000	17.000	17.000	15.000	14.500	14.400	13.500
Wet elongation (%)	6.6	6.3	6.4	6.5	6.3	6.0	6.3	9.0	9.8	8.8	8.5	9.3	8.5	9.7
Wet conditioned ratio (%)	75.0	74.2	73.7	74.7	74.5	74.0	73.0	76	76	77	75	73	73.5	74

length of yarns decrease, solubility in 5 per cent NaOH increases, the average degree of polymerization decreases. The wet elastic moduli are of the same order of magnitude, because they are essentially the results of the chemical and mechanical process used. In fact a remarkable difference is noticeable for the elastic moduli between the fibres K 66 and K 65.

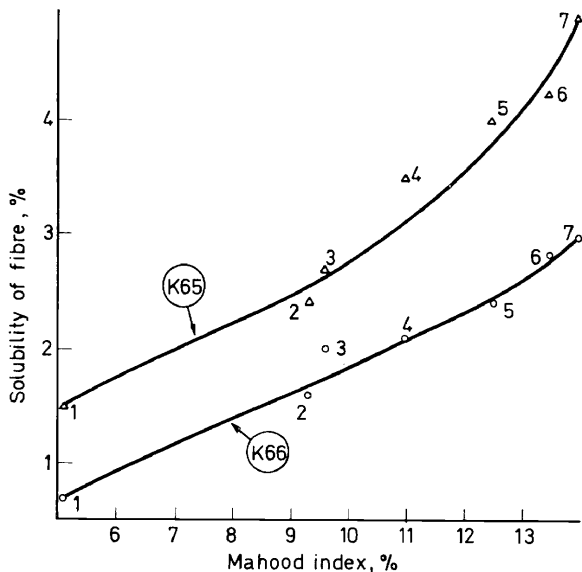


Figure 4. Solubility of fibres in 5 per cent sodium hydroxide versus Mahood index

In Figure 4 is plotted the solubility of the fibre in 5 per cent NaOH, as a function of the solubility of the starting pulp in 7.14 per cent NaOH. There is a certain proportionality between these values when the solubility of the pulp is lower than 10 per cent; afterwards the curve becomes exponential especially for the K 65 fibre, which is more soluble.

In Figure 5 wet tenacity (for untreated fibres and after treatment with 5 per cent NaOH) is plotted against solubility of the starting pulp in 7.14 per cent NaOH. In this case too, the lowering of tenacity is the more remarkable, the more soluble is the starting pulp. In Figure 6, the same values of wet tenacity are plotted against the dispersion degree σ of the starting pulp. In Figure 7, the same properties are plotted versus content of aberrant sugars—the results are the same as above mentioned. In Figure 8, the same situation is described as a function of the difference ($R_{18} - R_{10}$).

We have insisted on wet tenacities, because they are more significant, in order to characterize a Polynosic fibre. No particular advantages are noticeable, as given by a high alpha-cellulose content, or by a high average degree of polymerization, especially when, to this latter, a marked contribution is made by the high D.P. fraction.

On the contrary, the importance of both dispersion of the degrees of polymerization and solubility in 7.14 per cent soda of the starting pulp is very clear. This could be explained in this way: the need to obtain high

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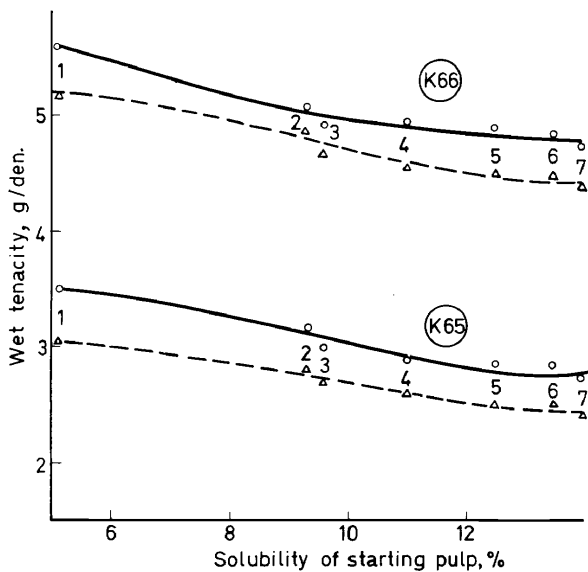


Figure 5. Wet tenacity of fibres as a function of 7.14 per cent sodium hydroxide solubility of the starting pulp [\circ — \circ untreated; \triangle --- \triangle after treatment with 5 per cent sodium hydroxide]

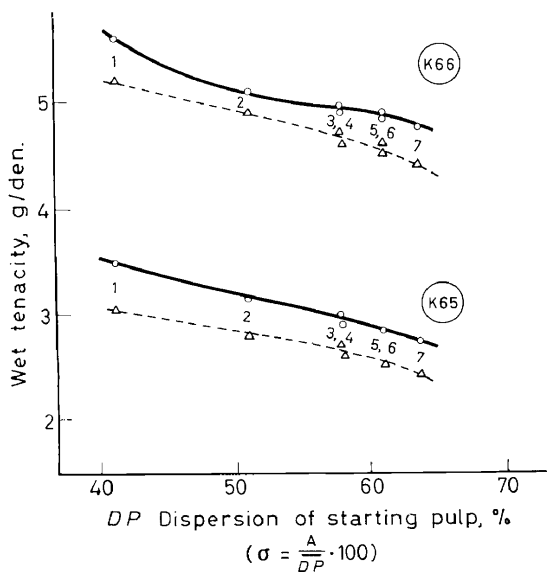


Figure 6. Wet tenacity of fibres as a function of DP dispersion of the starting pulp [\circ — \circ untreated; \triangle --- \triangle after treatment with 5 per cent sodium hydroxide]

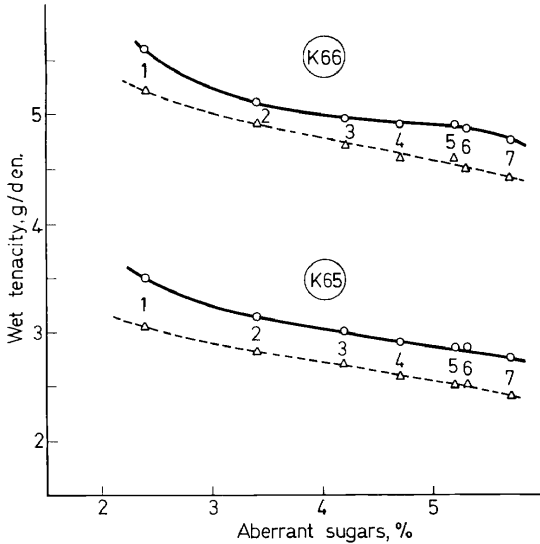


Figure 7. Wet tenacity of fibres versus aberrant sugar content of the starting pulp [\circ — \circ untreated; \triangle --- \triangle after treatment with 5 per cent sodium hydroxide]

average D.P. on the fibres makes it necessary, to shorten the ageing of alkali cellulose as much as possible and, as a consequence, to give up its equalizing action on the dispersion of D.P. On the other hand, pulps which are weak on this point, do not recover by means of a high viscosity, as samples 3 and 6 indicate. From this point of view, we think that caustic refined pulps are more suitable, though less reactive.

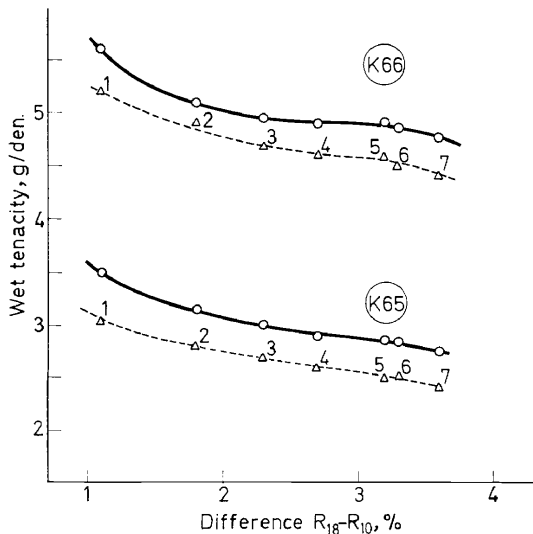


Figure 8. Wet tenacity of fibres versus difference ($R_{18}-R_{10}$) of the starting pulp [\circ — \circ untreated; \triangle --- \triangle after treatment with 5 per cent sodium hydroxide]

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Because of the nature of pulps, and the particular process of their transformation into fibres, we could not detect noticeable differences in the content of gel particles of the viscose solutions: many counts, performed at the Coulter Counter and at the microscope gave fluctuating results which were all comprised within the limits of reproducibility of these measurements. We can therefore point out that no gel particles larger than $35\ \mu$ were detected in any case. The viscose solutions were very clean and were fed to spinning with high γ -indexes. In addition to this, the xanthates, proceeding from samples 1-7 were less and less dry, according to the Mahood index. Xanthate No. 1 was perfectly floury, while No. 7 was like paste. We hope that this information is useful to the pulp producers, giving them some guidance in order to supply the fibre producers with a suitable pulp, without increasing the price.

Actually, the cost of these fibres is such that they are looked upon with a certain suspicion: the share of the cost of special pulps, which in the most cases are used as raw material is very high. We think that a pulp with usual alpha-cellulose content, low D.P. dispersion, low solubility in NaOH and low content of aberrant sugars, can be suitable enough for our purpose. We must add, however, that a more appropriate policy of utilization of the fibres could compensate the producer for this unavoidable additive cost.

We refer to the possibilities of using these fibres in the washable clothes industry, which has been, till now, the uncontested domain of natural fibres, generally, and particularly of cotton. Cotton represents 65 per cent of the world consumption of all fibres; 75 per cent of cotton is employed in the washable clothes, this amount being 49 per cent of the total world consumption of all fibres.

The high elastic moduli and the high wet tenacities, together with the small attachability by caustics of these fibres, guarantee the dimensional stability of their fabrics, while their microfibrillar structure, similar to that of natural fibres, rules, in the same way as the latter, the exchange equilibria with room moisture.

In *Figure 9*, we describe the deformations, which occur on three calicot

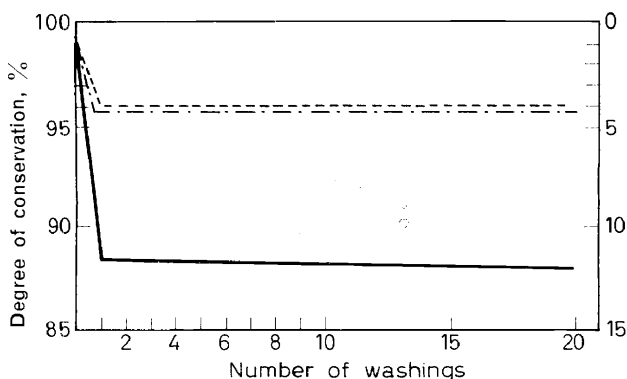
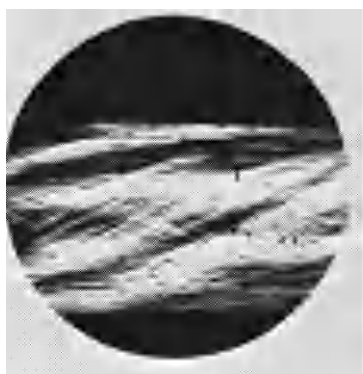
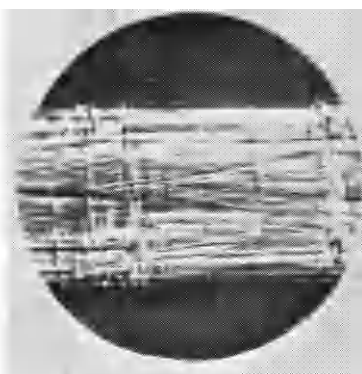


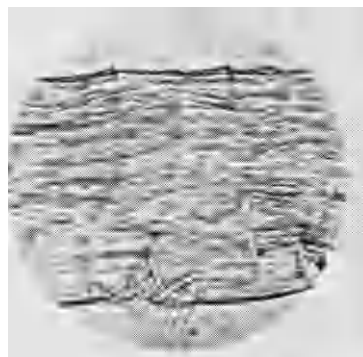
Figure 9. Behaviour in the wash. Deformations of three different calicot fabrics as a function of the number of washings [— normal staple fibre; —·— high modulus staple fibre; - - - American cotton]



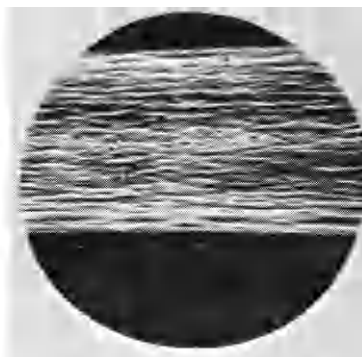
(a) Cotton



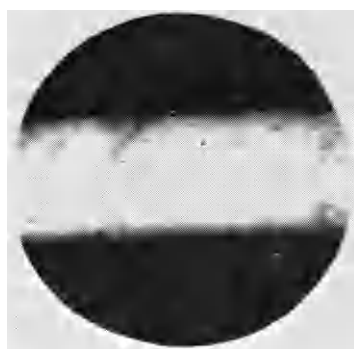
(b) Flax



(c) Wool



(d) Polynosic



(e) Cord Rayon

Figure 10. Photomicrographs of sodium hydroxide-swollen fibres ($\times 1080$, r. p. 0.4μ)

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fabrics, made respectively with American cotton, Polynosic fibres and viscose staple fibres, as a function of the number of washings.

The fabrics made with cotton and Polynosic fibres, after a small initial settlement, due to the re-adjustment of the weaving tensions, are perfectly stable, while the viscose staple fabric shrinks very markedly at the beginning, and afterwards it shrinks slowly but constantly during the following washings. In *Figure 10* are given the photomicrographs of several types of fibres after their swelling with caustic soda to the same extent. The micro-fibrillar structure is present in the natural fibres and in the Polynosic one.

Owing to this structure, the fibre has a large surface in contact with the air; on this surface there are intense and immediate exchange equilibria which generate heat at higher relative humidity and adsorb heat at lower relative humidity. In these cycles, the fibre behaves as a proper thermal fly-wheel. In this regard, the behaviour of wool is typical. This effect is due to the microfibrillar structure, because the limit values of regain are not very different, being, for instance, for cotton and wool, respectively equal to 295 and 320 cal/g of adsorbed water.

The high side orientation of the substance, constituting the contact surface, limits the intra-fibrillar adsorption of water, and the fibre is always fresh—in this regard the behaviour of flax is typical.

The fibres, in which water can be adsorbed in the intra-fibrillar spaces, accumulate it inside. In this way, water is not available for the exchanges with the room, owing to the low surface of vaporization; so the fibre remains damp and the thermal effects are poor.

For practical purposes, this particular structure is the most valuable property and is the first, though not perfect, solution of an old and important problem, which had till now prevented the use of man-made fibres in the washable clothes industry.