IMPROVEMENTS OF FIBRILLAR ARRANGEMENT AND PROPERTIES OF CELLULOSIC FIBRES

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INTRODUCTION

The efforts of the manufacturers of dissolving pulps have resulted in the production of wood pulp qualities which make it possible to obtain fibres of a technical value close to that of fibres made from linter cellulose, but offering certain special advantages, e.g. good filterability of the solutions.

In the same way, as soon as the use of cellulose staple fibres was developed in the traditional field of natural textiles, one tried to produce fibres which would permit the manufacture of fabrics having the same value in practical use as natural textiles, but in combination with other advantages of interest to the consumers.

The development of new types of fibres, now known under the name of HWM (high wet-modulus), the use of which is rapidly spreading, was due to important modifications in the molecular assemblage, or the formation of new structures, in the fibres. These fibres have at least two characteristics: (i) High conditioned, and wet tensile strength; and (ii) a high elasticity modulus, which enables the production of fabrics of high strength and dimensional stability.

Some of these fibres stand out by their special structure, close to that of natural textile fibres. This structure is characterized by the presence of well defined microfibrils with a particularly high degree of organization or crystallinity. This structure withstands the action of alkaline agents. The fabrics woven with these fibres can be treated like natural textiles, and they have a special hand and nervosity. It might be useful, to recall that, by itself, the presence of this structure, which can be obtained by quite different spinning processes, is not sufficient for ensuring the production of fibres leading to fabrics with satisfactory wear properties. For this reason, a fibre must not be described by the Trade name "Polynosic" unless it satisfies a set of criteria defining its textile quality.

The general level of the properties of the present Polynosic fibres has already given to them an important position in new fields of application, as well as in blends with natural or synthetic fibres.

At this stage we can at best consider that only part of our object has been fulfilled and that, with respect to certain aspects, the fibres developed do not entirely solve the problem, viz. the production of a fibre able to compete with natural textile fibres successfully in all fields of application.

Thus, the essential improvements which have to be effected with respect to the level of the mechanical and finished properties can be summed up as follows: (i) Wet tenacity of fabrics equalling that of cotton. (ii) No fibrillation in washing and wearing. (iii) High tenacity and tear strength and good wearability after chemical treatments.

All these properties seem closely related to the fibre's own structure; all the studies have a bearing on the question of how to obtain a basic modification of this structure.

An important point has to be made with respect to the strength of the woven goods. It is not only related to the tensile strength of the fibre but also to its work performance when used in a yarn. Thus, the increase of work performance at rupture is also a basic element which has to be added to the objects aimed at.

In modern fabrics cellulose fibres are more and more often chemically modified by the effect of reactive resins, and this improvement is particularly important when treatments of the Permanent Press type are applied. In finishing treatments of this kind the natural fibres lose a good part of their qualities.

It was possible to envisage a modification of the structure of the fibres so as to preserve their initial properties as far as possible after this treatment.

IMPROVEMENT OF THE PROPERTIES OF THE FIBRES AND THEIR STRUCTURE

The improvement of the properties of the Polynosic fibres has been the subject of extensive research in the past few years. This research has been directed mainly on the modification of the fibre structure since it is this structure which determines essentially the properties of the fibre.

It may be considered today that this modification was realized in two well defined successive steps: (i) The improvement of the structure of the microfibril, i.e. the achievement of higher organization through higher crystallinity. As a consequence, these fibrils are strongly oriented relative to the axis of the fibre. (ii) The creation of a new type of macro-structure in which the elementary fibrils possess an organization of the same order of magnitude as in the preceding case, but have on the contrary an inclined position relative to the axis of the fibre.

In the following report, we compare the structure and the properties of these two types of fibres so as to put into evidence the practical interest of this new type of structure.

The structure which is shown by the fibres with high fibrillar orientation, is called structure of the type (I). The structure of the fibres in which the fibrils are disposed in an inclined position relative to the axis of the fibre, is called structure of the type (8).

Improvement of the structure of the microfibril: Structure of type (I)

First of all we tried to improve the structure of the microfibril itself, i.e. to modify its internal organization so as to increase its energy at rupture. Incidentally, the improvement of the structure of the microfibril also brought about an increase in the resistance of the fibre to alkaline agents.

Radical changes in the production methods resulted finally in the development of a fibre, the fibrils of which are highly organized in structure, as evidenced by the formation of fibres with extremely high wet tensile strengths, in the range of 3·5–5·5 g/den., in the case of textile fibres[2]. These fibres have a very high wet elasticity modulus, due to the perfection of the organization of the fibrils, but their elongation at rupture is low, scarcely higher than 10–11 per cent. This becomes understandable if one examines their macro-structure.

These fibres are built up from well organized fibrils which are, however, straight, and arranged strictly parallel to the axis of the fibres. This is caused by the manufacturing method which comprises high stretching during the formation of the fibrils. Thus, the structure which had been created was close to that of best fibres.

Since the fibrils are perfectly defined, the lateral cohesion is weakened. Such fibres, therefore, have a strong tendency to fibrillate. Given the low elongation at rupture of these fibres, the work at rupture is not much increased.

These new fibres already constitute a considerable improvement over the known fibres of the same kind, because the more highly organized structure of their fibrils results in yarns with higher tensile strengths, and also improves the behaviour during the washing and mercerization operations; but the strong fibrillar orientation increases the tendency to defibrillation.

This explains why this type of fibre has not been developed any further, and more research work had to be done. This research ended in the development of a new type of fibre whose properties will now be described.

Modification of the macro-structure: Creation of the structure of type (8)

These fibres are produced by special methods resulting in macro-structures where the structure of the microfibrils is highly organized but the fibrils are arranged in an entirely different position relative to each other. These fibres have the same properties as those mentioned before, i.e. high wet tensile strength and elasticity modulus, moreover these fibres have a high elongation at break and their macro-structures give the fibres all the desirable properties which was the object of this work.

There is no doubt that the structural superiority of cotton is due to the special arrangement of its fibrillar elements, strongly inclined relative to the axis of the fibre, due to their spiral curling.

The work of the fibrils in actual use in textiles does not normally take place at their axis, and despite the perfection and rigidity of the fibrils the fibre performs well in the fabric, and the abrasion resistance in use is very satisfactory. Thus, it was reasonable to presume that the ideal fibre would have well characterized fibrils and arranged in a similar manner.

Considering the fibres mentioned above, one could, of course, envisage to destroy more or less the straightness of the fibrils so as to bring about a certain amount of internal disorganization. But such an operation always goes together with a decrease in the organization of the fibrils themselves and heterogeneity between the surface and the core of the fibre.

An attempt was, therefore, made—in spite of the technical contradictions inherent in the idea—to find a method for building up, in spinning, macro-structures where the fibrils, though having a highly organized internal structure, are formed in an inclined position relative to the axis of the fibre. And, finally, a new technique was found to attain this end.

The resulting fibres are characterized by an assemblage of perfectly well defined fibrils which are regularly arranged over the whole cross section of the fibre but are angularly disposed with respect to the axis of the fibre. Such a macro-structure causes an entanglement of the fibrils which considerably increases the cohesion and practically cuts out the tendency to fibrillation.

Consequently, such a structure is accompanied by an increase in elongation at rupture and, therefore, a considerable rise of the work at rupture, but without lowering of the wet tensile strength and modulus of elasticity since the level of organization of the fibril remains very high.

STRUCTURE OF THE NEW FIBRES

In order to show clearly the difference between the practical values of fibres with this new structure and highly oriented fibres we shall compare our results with those obtained on fibres of the latter type, both types of fibre having a tensile strength above the minimum value of 3·5 g/den. wet.

Let us consider first of all the basic differences which exist between the structures of these two types of fibres. The macro-structure has been studied by examining fibres swollen in a nitric medium and slightly disintegrated by crushing. This technique is the best to demonstrate the relative positions of the fibrils. According to the concentration of the swelling medium it is possible, either simply to show the arrangement of the fibrils without affecting the structure of the fibrils themselves, or to cause a complete separation of the fibrils in order to reveal more clearly their spatial position, in which latter case, however, the fibrils are slightly affected and swollen.

Figure 1 shows the position of the fibrils of a strongly oriented fibre in comparison with the position of the cotton fibrils fibre. In the latter the spiral structure gives the fibrils a strong inclination relative to the axis.

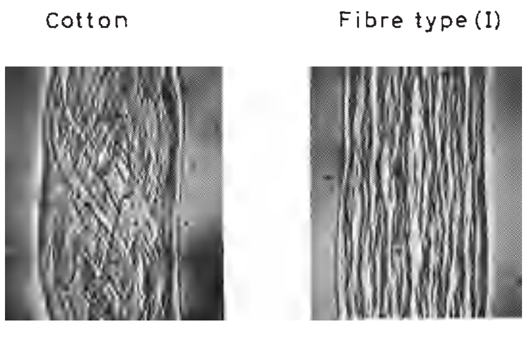

Figure 1. Fibrils of cotton and type (I) fibres

Figure 2 clearly shows the inclined and entangled position of the fibrils forming the new fibres, an arrangement which is similar to that of cotton. Though the photograph, on a plane, shows a similitude of position the fibrils are, of course, not arranged in spirals but obliquely from one side to the other of the fibre.

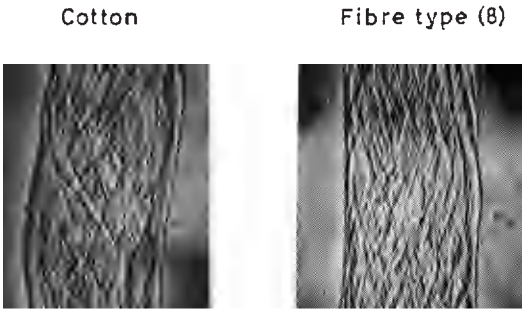

Figure 2. Fibrils of cotton and type (8) fibres

Figure 3 shows the fibrillar structure of the new fibres in comparison with that of fibres with the same tensile strength but having a strongly oriented structure. If one examines these two types of fibres with the classic x-ray diffraction technique, one observes clearly that the widening of the diffraction arcs, which corresponds to the different planes of the crystallites, is due to the opening angle formed by the fibrils; one gets in this manner a fibre diagram which is similar to that of mercerized cotton.

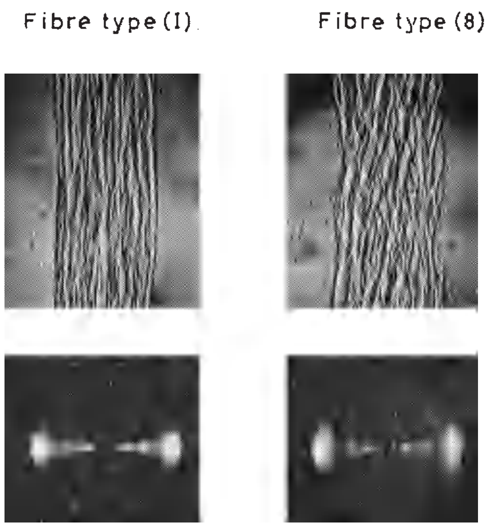

Figure 3. Fibrils of type (I) and type (8) fibres and their x-ray diffraction patterns

Figure 4 shows the effect of the action of a strong nitric acid solution on the position of the fibrils after their more complete separation from each other within the fibre; one sees that their inclined position is maintained after disintegration of the fibre structure.

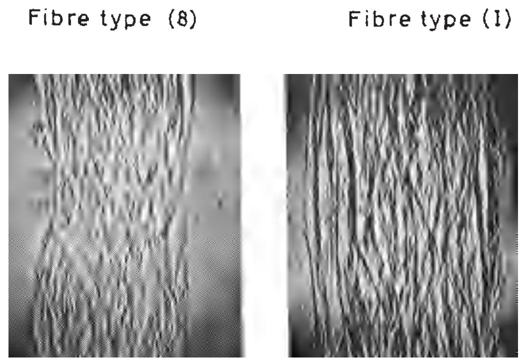

Figure 4. Fibrils of type (8) and type (I) fibres after the fibres have been treated with strong nitric acid

The same treatment, applied to a strongly oriented but heterogeneous fibre reveals the fact that while the fibrils forming the core of the fibre preserve their individuality, the surface fibrils vanish almost entirely, and separate distinctly from the core fibrils.

Figure 5 shows a typical aspect of a strongly oriented high tenacity fibre obtained by electron microscope examination. For these photographs, which were prepared by a very special technique, 400 Å longitudinal sections were used after chemical shadowing of the fibre. The empty spaces

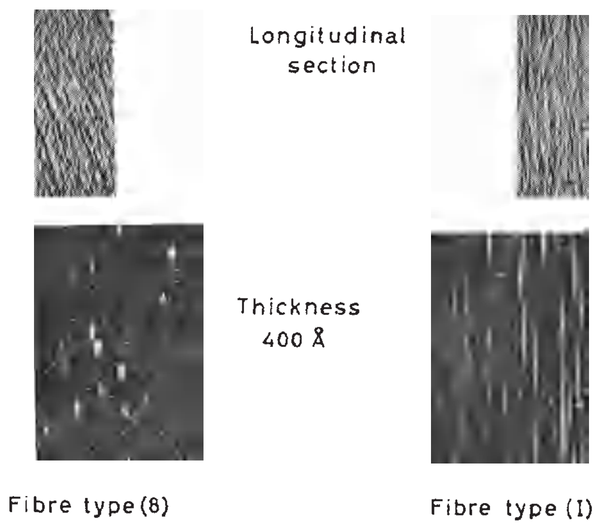

Figure 5. Electron micrographs of type (8) and type (I) fibres

between the fibrils are revealed, and they clearly show the straight position of the fibrils which they delimit.

The same kind of photograph but of a fibre with oblique and entangled fibrils does not show clearly defined interstices, which means that their possible width does not go beyond 400 Å. However, one can see that the few vacuoles present in the fibre which apparently correspond to some voids in the entangled structure of the fibrils, have rounder, and even rhombic shapes, related to the crossed positions of the fibrils.

The level of tenacity attained in the new fibres in itself is a proof of the perfection of the organization of the fibrils. It is possible to demonstrate it by measuring on the fibres a total organization factor by an x-ray test (crystallinity) based upon the use of a constant intensity radiation and the measurement of the intensity diffracted by pellets made of fibres cut into pieces of regular length.

Figure 6 shows that: (i) Organization factor of these fibres is definitely higher than that of the ordinary fibres; (ii) organization factor of these fibres equals that of highly oriented fibres with the same tensile strength. This confirms the fact that, despite their lower orientation, the fibrils were formed with the same perfection as in the highly oriented fibres.

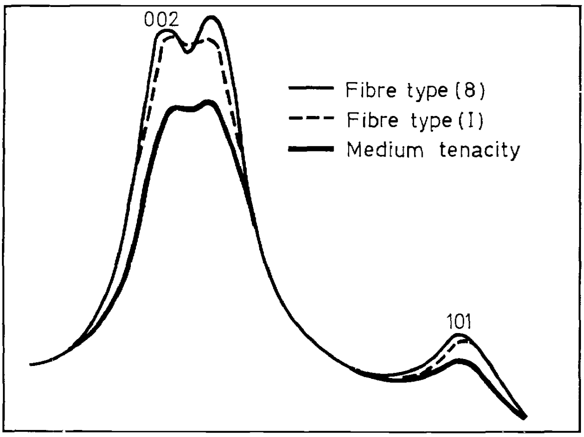

Figure 6. Organization factors of fibres

Type of fibre	*Wet tenacity* (g/den.)	*Organization factor*
Fibre type (8)	4·5	0·48
Fibre type (I)	4·5	0·47
Medium tenacity	3·2	0·38

The wet tenacities measured on the fibres correlate with their organization factor, and that the type (8) fibres have the same tenacity as type (I) fibres.

Mechanical properties

Thus, these structure studies have shown that it is possible to produce fibres with a structure comprising highly organized microfibrils, and a macro-structure where these fibrils are no longer arranged parallel to the axis of the fibre. A structure of this kind should give the fibres the following mechanical and physical properties.

1. A high wet tensile strength together with a high wet elasticity modulus; this modulus is slightly lower than that of the oriented fibres, but the dimensional stability should not be affected since it is related to the possibility of deformation of the fibril itself.
2. A distinctly higher elongation at rupture, which implies much greater work at the rupture as a consequence of this elongation, which is related to the possibility of deformation of the fibrils. From this property we can expect a better yield of fibre tenacity in the spun yarns.
3. The resistance to alkaline agents is distinctly increased.
4. The transverse strength, which is in direct relationship with the fibrillar entanglement is very high. One, therefore, attains a very satisfactory abrasion resistance. The peculiar arrangement of the fibrils also increases to a great extent the bending strength, the loop strength, and the knot strength.

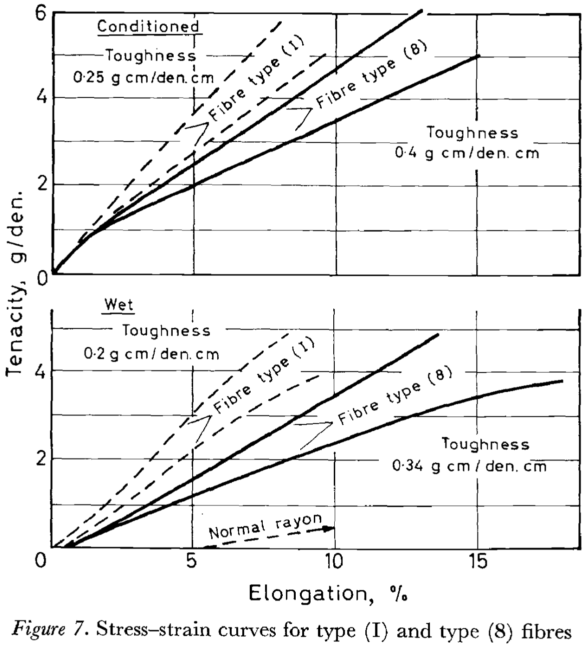

Figure 7. Stress–strain curves for type (I) and type (8) fibres

The stress–strain diagram (*Figure 7*) compares fibres having the same wet tensile strength but the two different structures, viz. highly oriented (type I), and new type structure (type 8). For each type of structure, we plotted curves for two different types of fibres having the same work of rupture, although their respective levels of tenacity were different. The work at rupture of the fibres of the new type is about 50 per cent higher than that of the fibres with an oriented structure.

It is important to stress the point that with this new type of fibre one can attain wet elongations beyond 17 per cent while the modulus of elasticity remains very high, and these properties bring about an excellent fibre/yarn tenacity ratio, of the same magnitude as that of classic fibres.

Table 1. Properties of the fibres

Property	*Fibre type (8)*	
	a	*b*
UNTREATED FIBRE		
Denier	1·45	1·45
Conditioned tenacity (g/den.)	5·1	6·1
Wet tenacity (g/den.)	3·8	4·9
Conditioned elongation (%)	15	13·6
Wet elongation (%)	17·5	14·2
Wet elongation under a load of 0·5 g/den. (%)	2·5	1·8
Loop tenacity (g/den.)	1·05	1·25
Degree of polymerization	580	580
Toughness g cm/den. cm (Cond.)	0·38	0·42
Toughness g cm/den. cm (Wet)	0·32	0·34
AFTER TREATMENT WITH 5% NaOH		
Denier	1·52	1·49
Wet tenacity (g/den.)	3·4	4·6
Wet elongation under a load of 0·5 g/den. (%)	4·0	2·7

Table 2. Properties of the spun yarn

Property	*Fibre type (8)*		*Am. Combed Cotton*
	a	*b*	
Yarn (N° cc)	41	41	41
Twist (t.p.i.)	21	21	24
Conditioned tenacity (g/den.)	2·3	2·85	1·6
Wet tenacity (g/den.)	1·9	2·55	2·2
Conditioned elongation (%)	10	9·5	7
Wet elongation (%)	12·6	12	8
Lea Skein	2800	3680	2200

Tables 1 and *2* show on a comparative basis, the general properties of the fibres having the structure of type (8), as well as the mechanical properties of the corresponding spun yarns. It is clear from *Tables 1* and *2* that the wet strength of the spun yarns is very close, if not superior, to the wet strength of high quality combed cotton yarns.

5. The high transverse strength due to the macro-structure gives the fibre a better resistance to fibrillation as one can see from *Figure 8*. Separation of the fibrils has been obtained in this case by violent steering-action in water, at great speed, in a mixer.

And, while fibrillation is very pronounced on the highly oriented type (I) fibres, the type (8) fibres remain unchanged or show just a very slight beginning of fibrillation.

This survey of the properties of the fibres justifies the conclusion that the modification of the structure has brought about great improvements in the practical value of the fibres and that, therefore, the end use properties of the finished products should be very satisfactory.

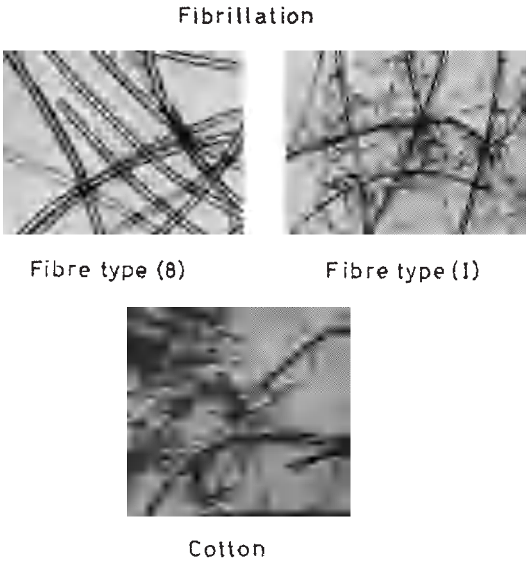

Figure 8. Fibrillation of type (I) and type (8) fibres as compared to that of cotton fibre

PRACTICAL UTILIZATION VALUE OF THE NEW FIBRES

We have tested the properties of experimental fabrics woven with fibres of this new type. Since our objectives were the creation of fibres having properties about the same level as cotton, comparative tests have been run with high quality combed cotton fabrics: (i) If one considers first the resistance to chemical and mechanical attacks during washing in a drum washing machine, where each wash ends with a strong hypochlorite bleaching, it is noticed that not only the initial dry properties are far superior to cotton, but that even the wet strength values are in the cotton range and even after 40 washes the properties of the new fibre and of cotton are still quite close; (ii) one knows already that the Polynosic fibres show after the treatment with reactive resins a very small loss of strength as compared to cotton, but as a consequence of the rigidity caused by the resin treatment the abrading resistance decreases.

It seems justified to believe that the oblique arrangement of the fibrils and the higher elongation which it causes, will give the fibres in the fabric after a strong finishing treatment a greater flexibility, and consequently the abrasion resistance should be satisfactory.

Figure 9 gives the data obtained on fabrics treated with a finish of the "Permanent Press" type and from which it is apparent on one hand, that

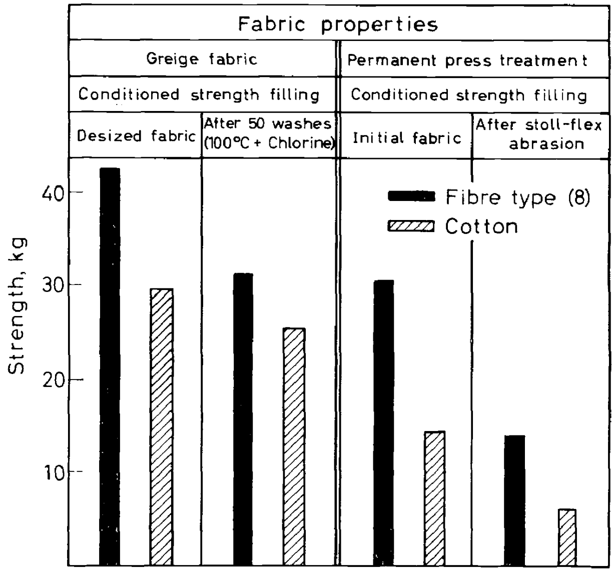

Figure 9. Properties of fabrics made from type (8) and cotton fibres and treated with a finish of the "Permanent Press' type

the strength of the fabrics after the treatment is considerably greater than that of cotton, and that on the other hand strength after a defined abrasion test also remains high; better than that of the cotton which is greatly affected by this treatment. The latter property gives these fibres special importance, seeing the considerable spreading of this type of treatment, especially on blends with cotton or synthetic fibres.

It should be pointed out that so far treatments of this kind on pure cotton fabrics, while they give excellent results with respect to their stability, lower the end use properties to such a degree that the development of such treatments on pure cotton fabrics is at present very much restricted.

Blends of cotton with this fibre should improve the end use properties of the fabrics containing a high percentage of cellulosic fibres.

IMPORTANCE OF THE FIBRILLAR STRUCTURES IN PAPER MAKING

The growing importance of structure on paper making fibres deserves a mention here since the Congress is attended by an audience who are equally interested in paper. In this field of application, we tried to produce not textile fibres, but quite to the contrary fibrillar structures by forcing to a maximum the tendency of fibres to fibrillate, so as to transform the fibres into fibrils as long and as fine as possible.

The material so obtained presents extremely interesting properties alone or in blends with classic paper making fibres, resulting in paper which can be considered as felts, the long and very fine fibrils giving cohesion to the assemblage (*Figure 10*). These fibres which easily divide into fibrils designed for the paper making industry offer a special interest for the manufacture of thin papers or felts.

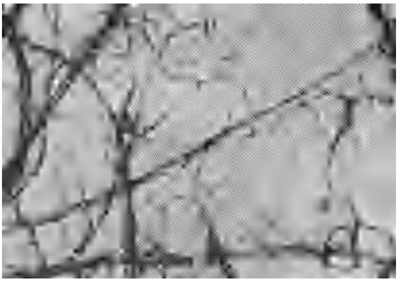

Figure 10. Fibrillation after beating in the case of BX 55–80° SR paper

One of the new properties consists in the possibility of producing with these fibrils very opaque papers without the necessity of adding mineral filling or loading material, as can be seen from *Table 3* which compares the characteristics of paper made from 100 per cent natural fibre and 100 per cent BX 55 fibre, respectively. These papers have another very interesting quality: their very high porosity.

Table 3. Characteristics of paper made from 100 per cent natural fibre and that from 100 per cent BX 55 fibre

Paper composition	*Loading material* (%)	*Opacity*	*Porosity*
100% Flax	15	76	140
100% BX 55	0	80	>1000

One of the first applications of these papers on a commercial scale has been the manufacture of cigarette paper without loading that has inherently a high degree of porosity, while up to now this porosity was only obtained by purely mechanical means, viz. perforation.

It should be noted that for this application it is necessary to produce highly fibrillar fibres of great chemical purity, so as to avoid a disagreeable taste while smoking.

In this respect an extremely interesting observation has been made regarding the composition of the combustion products. The tars produced in the combustion of this fibre, have a composition different from that of tars produced from the usual fibres. Particularly, these tars contain very small quantities of benzopyrene[3].

Many other fields of application are open to these fibres.

For the use of these fibrillated fibres in blends with paper fibres for the purpose of making very thin paper, one of their properties of use which is outstandingly important is the considerable increase in the wet strength of the paper on the machine, as can be seen from *Table 4*. This property

Table 4. Wet strength of paper made from different fibres

Paper composition	*Wet strength (g)*
100% Wood pulp–85° SR	160
100% Fibre BX 55–87° SR	500
{90% Wood pulp–35° SR {10% BX 55–87° SR	150

can be used advantageously for the preparation of blends to be processed on paper machine, while reducing considerably the beating of the other pulp components.

In a certain way these fibres are still high modulus fibres with undoubtedly interesting qualities, but in this case fibrillation becomes a considerable advantage, while for textile purposes work it was absolutely necessary to avoid it.

CONCLUSION

Our main efforts have been directed first towards the improvement of the structure of fibres. It is true, however—as it was in the case with tyre cords—that the improvement of the structures has not minimized the importance of the quality of the pulps for attaining a very high level of mechanical properties, and resistance to wear.

Incidentally, it should be noted that for textile applications it is more important to consider not only the apparent qualities of the fibres, but also the influence the quality of the pulp may exercise on the practical properties in use of the finished products, especially after strong treatments with reactive resins. The problem is obviously complex, and it would be worthwhile to make it the subject of further meetings.

Finally, we express our conviction that the new possibilities already offered by the Cellulosic chemical fibres have become even greater now, thanks to the development of fibres with structures which are still better adapted to the needs of the consumer. On the basis of the results already obtained, the use of the new type of fibre, either alone or in blends with cotton or synthetic fibres, should make it possible to produce goods with wear properties giving entire satisfaction, stimulating a new rise in the use of chemical pulps.

References

[1] N. Drisch. *Reyon und Zellwolle* **7**, 431 (1959).
[2] B.F. Patent no. 1 266 492; U.S. Patent no. 3 139 467.
[3] *Bulletin du Cancer* No. 1/66.