

# THE STRUCTURE AND CHARACTERISTICS OF POLYNOSIC FIBRES

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## INTRODUCTION

A wide variety of Polynosic fibres have been introduced into the industry during the past decade. These fibres differ in production methods and show different fibre structures and fibre performance. Polynosic fibres can be roughly classified into two groups. The first group is "Polynosic" fibres in the narrow sense, which has a high crystallinity and an advanced fibrillar structure. The second group is the so-called "high wet modulus (HWM)" fibres with a slightly lower crystallinity. In general, Polynosic type fibres show high wet modulus and high alkali resistance, and subsequently good dimensional stability. On the contrary, however, such fibre tends to be brittle due to its low elongation and low knot and loop tenacities. Consequently, this lowers the processability in spinning and weaving, and the flex abrasion resistance of the fabric becomes slightly reduced. It is true that a remarkable improvement has been made in some recent products, but this kind of problem still remains unsolved. Another drawback of the Polynosic type is the fact that it easily fibrillates, i.e. when they are abraded in the wet state, twig-like fibrils are formed on the fibre surface. This phenomenon is observed, for example, during the dyeing process of the fabric, which not only results in impairing the shade of the dyed fabrics, but also produces troubles in wearing. Compared with the above-mentioned Polynosic type, the HWM fibres generally show lower wet modulus and alkali resistance, and the dimensional stability of the fabric becomes slightly lower. The HWM-type fibre, however, exhibits lower brittleness and higher toughness and loop tenacity. In addition, it may be characterized by being hard to fibrillate. It has been found that a new fibre having the merits of both the Polynosic and HWM types in one fibre can be developed. This new type of Polynosic fibre is now in commercial production by Mitsubishi Rayon Co. under the trade name of Hipolan S (formerly designated Hipolan X).

This paper presents the results concerning the relationship between fibre structure and fibre properties with regard to various test Polynosic fibres and analytical results on the fibre structures of commercial Hipolan S in relation to fabric performance.

## RELATION BETWEEN FIBRE STRUCTURE AND PROPERTIES OF VARIOUS POLYNOSIC FIBRES

In general, the fibre structures of various viscose fibres depend on the conditions of viscose, acid bath, stretching, regeneration and so forth. In the case of ordinary rayon, in which an acid bath offering high coagulative and

regenerative powers is used, the major portion of the fibre structure is determined in the acid bath. For Polynosic fibres, however, in which a weak acid bath is employed, the regeneration and the crystallization of fibres in the acid bath are only carried out to a small extent, and the fibre structure is dependent not only on the acid bath conditions, but also on the stretching and the regeneration conditions. Consequently, a wide choice of fibre structures and properties is available by combining such factors, viscose, acid bath, stretching and regeneration.

Figure 1 shows the stained cross section of fibres from the same viscose and acid bath under different stretching and regeneration conditions. For skin staining, Kato's method<sup>1</sup> making use of blue direct dyestuffs was applied. For core staining, Solophenyl Fast Blue Green BL was used according to the Japanese Industrial Standard (JIS) method<sup>2</sup>.

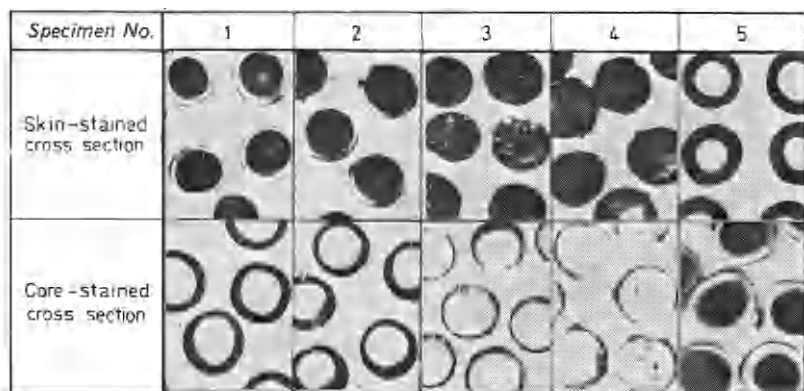


Figure 1. Photomicrographs: Stained cross section of test specimens (stretching and regeneration conditions varied)






In Figure 1, specimen Nos. 1-4 are the fibres of the Polynosic type and No. 5 is one example of a commercial HWM-type fibre. As evident from No. 1, the fibre gives a thick outer layer by the core staining. In specimen Nos. 2 and 3 this layer gets thinner and in No. 4, it disappears, showing total skin staining. The HWM-type shown in specimen No. 5 gives an outer layer by skin staining and an inner part by core staining. The mechanical properties of these fibres are shown in Table 1.

In Table 1, the Polynosic-type fibres Nos. 1-4 show widely different mechanical properties according to their skin-core structure. In particular, this skin-core structure of the fibre has a definite effect on its knot and loop tenacities, i.e. it seems that, the thicker the outer layer is, the less brittle the fibre becomes.

Figure 2 shows the wet fibrillation properties and fibrillar structures of these fibres. Photomicrographs for wet fibrillation characteristics were taken of a fibre, cut to 5 mm, dispersed in water and beaten for 15 min using a home mixer at 3000 rev/min. Figure 2 also shows such a fibrillar structure as obtained when fibres are hydrolysed in 1N sulphuric acid at 45°C for 1 h and then beaten 200 times with a wooden rod.

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Table 1. Mechanical properties of test specimens (JIS Method)

| Specimen                        | 1   | 2   | 3   | 4   | 5   |
|---------------------------------|---|---|---|---|---|
| Tenacity wet (g/d)              | 4.0   | 4.2   | 4.5   | 4.2   | 3.2   |
| Elongation wet (%)              | 17  | 13  | 11  | 9   | 16  |
| Knot tenacity conditioned (g/d) | 3.0   | 2.3   | 1.7   | 1.1   | 1.9   |
| Loop tenacity conditioned (g/d) | 2.7   | 2.0   | 1.4   | 0.8   | 1.6   |
| Degree of dyeing (%)            | 91  | 75  | 46  | 33  | 23  |
| Skin - stained cross section    |  |  |  |  |  |

With the Polynosic specimens, there is a very clear relationship between fibrillation and skin-core structure, i.e. the fibres having a thicker core-stainable layer in the outer part show little fibrillation, while those having skin-stainable layer in the outer part show considerable fibrillation. With the HWM-fibre, on the other hand, no fibrillation is observed, although they show distinct skin staining in the surface region.

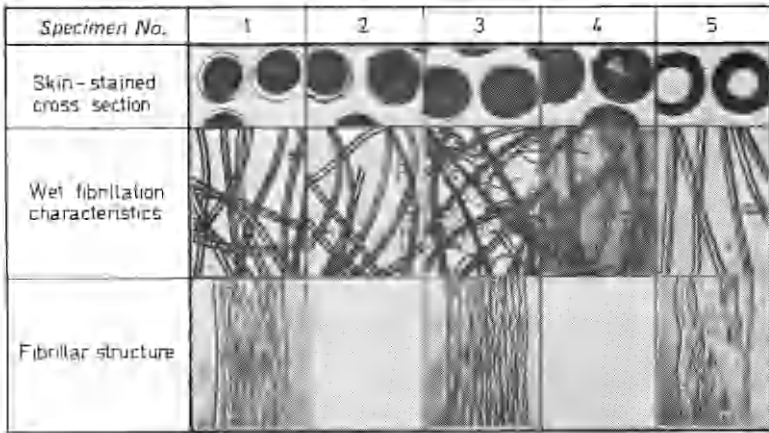


Figure 2. Photomicrographs: Stained cross section, wet fibrillation characteristics and fibrillar structure of test specimens

As for fibrillar structures, the totally skin type Polynosic fibres, like No. 3, have a well-developed fibrillar structure all over the fibres as seen in most of the commercial Polynosic fibres, while the HWM-fibre gives a less fibrillar structure.

Polynosic fibre No. 1 shows a high fibrillar structure in its inner part similar to No. 3, but its outer part is hard to fibrillate as in the case with the HWM-fibre.

Figure 3 shows the lateral order distribution of the fibres determined according to Maeda's method<sup>3</sup>. Polynosic fibre No. 1 has the highest lateral

order. On the contrary, No. 5 which is a HWM-type, gives a much lower lateral order. As is expected from this fact the fibre No. 1 gives the highest alkali resistance; e.g. retention of wet tenacity after treatment in 5 per cent sodium hydroxide solution is the highest with No. 1, and the lowest with No. 5.

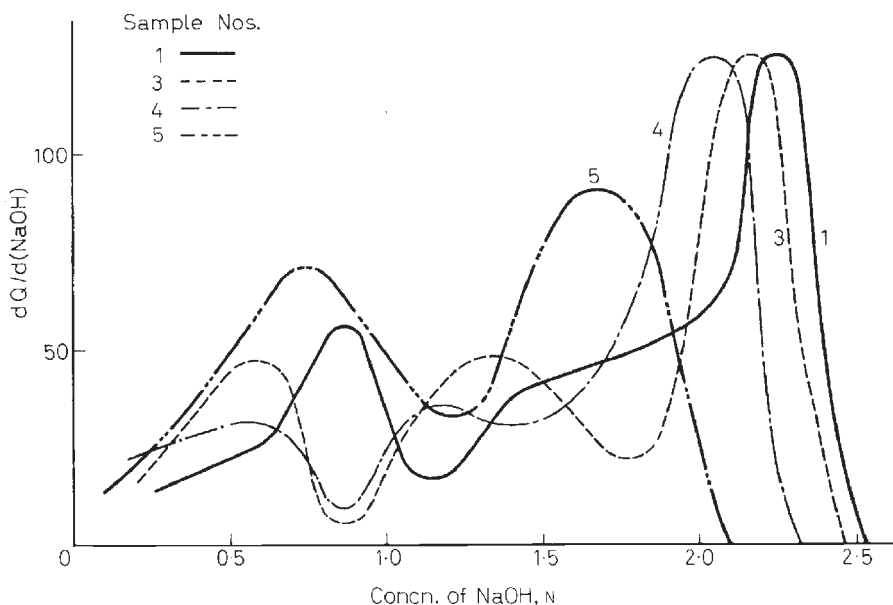


Figure 3. Lateral order distribution curves of test specimens

It is evident that the fibre structures as well as the fibre properties greatly vary with stretching and regeneration conditions. In the following part we would like to introduce another example of how the fibre structures and properties are affected by varying the acid bath condition, keeping the viscose, stretching and regeneration conditions unchanged. Table 2 shows

Table 2. Stained cross section and mechanical properties of test specimens

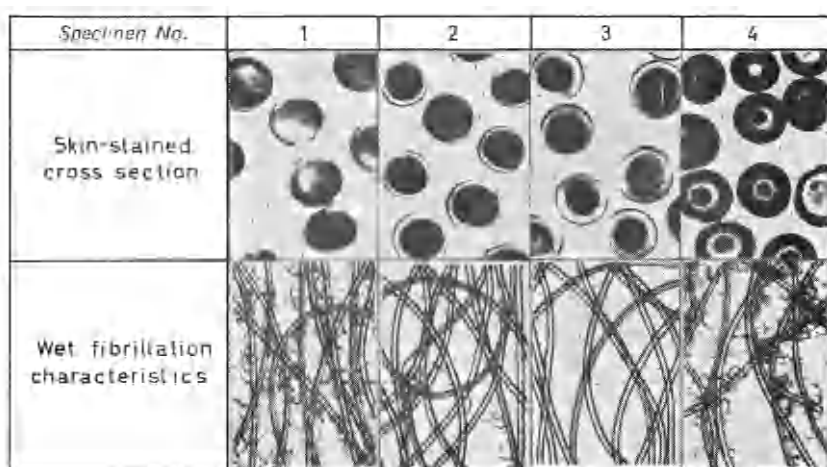
| Specimen                        | 1   | 2   | 3   | 4   |
|---------------------------------|-----|-----|-----|-----|
| Wet tenacity (g/d)              | 3.7 | 3.7 | 3.7 | 3.7 |
| Wet elongation (%)              | 7   | 11  | 14  | 11  |
| Knot tenacity conditioned (g/d) | 1.3 | 2.7 | 3.5 | 1.7 |
| Loop tenacity conditioned (g/d) | 1.1 | 2.3 | 3.0 | 1.4 |
| Degree of dyeing (%)            | 57  | 81  | 87  | 56  |
| Skin-stained cross section      |     |     |     |     |
| Core-stained cross section      |     |     |     |     |

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stained cross section and mechanical properties of these test specimens.

In the case of Specimen No. 1, the acid bath contains no zinc sulphate. In No. 2, the acid bath contains a very small amount of zinc sulphate and its content increases towards Specimen No. 4. Fibre No. 1 gives very little core-stainable layer in the surface part and Nos. 2 and 3 have a clear core-stainable layer in the outer region. On the other hand, fibre No. 4 shows skin-stainable layer in the outer part.

Furthermore in *Table 2*, it is again clearly seen that the mechanical properties of the fibre largely vary according to the skin-core structure. In wet fibrillation properties shown in *Figure 4* it is confirmed that the fibres having a thicker core-stainable layer in the outer part are hard to fibrillate.



*Figure 4.* Photomicrographs: stained cross section and wet fibrillation characteristics

From these examples, fibres having a thick core-stainable layer in the outer region appear to be superior in all respects, for example, mechanical properties, fibrillation behaviour, alkali resistance, dyeability, etc.

It is very interesting to note that these fibres, after the improvement of their defects like the brittleness and the fibrillation, still maintain such features as the high crystallinity and the alkali resistance which are the characteristics of Polynsic fibres.

### INNER STRUCTURE OF HIPOLAN S

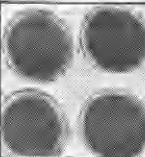
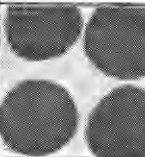

The possibility has thus been found for manufacturing the new fibres in which some of the general shortcomings of Polynsic fibres can be improved and which possess the merits of both the Polynsic and the HWM-type of fibres. Hipolan S is a unique Polynsic fibre which has been recently commercialized on this principle.

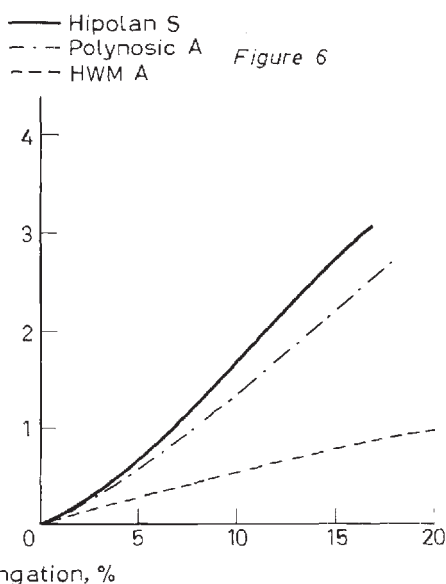
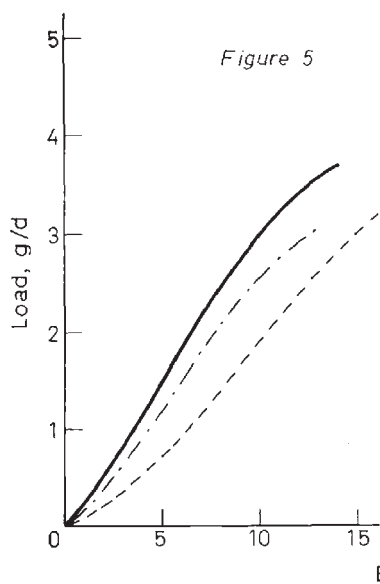
Further analysis has been carried out in detail on the fibre structures of the commercial Hipolan S product. In this case, a standard Japanese commercial Polynsic Fibre A which is completely skin stainable and a foreign

HWM fibre A were selected for comparison. *Table 3* shows the mechanical properties and stained cross section of these three fibres.

Emphasis should be placed particularly on the wet tenacity, the wet modulus, the knot tenacity and the loop tenacity. *Figure 5* gives load-elongation

*Table 3.* Mechanical properties and stained cross section of commercial Polynosic fibres

|                                       | <i>Hipolan S</i>  | <i>Polynosic A</i>  | <i>HWM A</i>  |
|---------------------------------------|---|---|---|
| <u>Untreated</u>                      |   |   |   |
| Denier                                | 1.2   | 1.2   | 1.25  |
| Conditioned tenacity (g/d)            | 4.7   | 4.0   | 4.3   |
| Wet tenacity (g/d)                    | 3.7   | 3.1   | 3.2   |
| Conditioned elongation (%)            | 12  | 11  | 14  |
| Wet elongation (%)                    | 14  | 14  | 16  |
| Knot tenacity conditioned (g/d)       | 2.4   | 1.5   | 1.9   |
| Loop tenacity conditioned (g/d)       | 2.0   | 1.3   | 1.6   |
| Wet modulus at 5% elongation (g/d)    | 1.5   | 1.3   | 0.7   |
| Wet elongation under 0.5 g/d load (%) | 2.0   | 2.1   | 3.5   |
| <u>After treatment with 5% NaOH</u>   |   |   |   |
| Wet tenacity (g/d)                    | 3.3   | 2.7   | 2.0   |
| Wet elongation under 0.5 g/d load (%) | 3.5   | 3.5   | 9.0   |
| Skin-stained cross section            |  |  |  |



*Figure 5.* Load-elongation curves in wet state

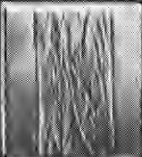





*Figure 6.* Load-elongation curves in wet state after treatment with 5 per cent sodium hydroxide

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curves of these fibres in wet state and *Figure 6* shows that of after treatment with a 5 per cent sodium hydroxide solution. Hipolan S shows highest wet modulus. It is evident that the HWM-fibre shows low resistance to 5 per cent sodium hydroxide solution, while the resistance of Hipolan Sand Polynosic A are at a higher level.

*Table 4* shows some of the structural data of these fibres. Polynosic A has the highest degree of polymerization, and HWM A has the lowest.

*Table 4.* Structural characteristics of commercial Polynosic fibres

|  | <i>Hipolan S</i>   | <i>Polynosic A</i>   | <i>HWM A</i>   |
|--|--|--|--|
| Degree of polymerization                   | 460  | 580  | 390  |
| Degree of orientation (x-ray method) (%)   | 93   | 93   | 91   |
| Degree of crystallinity (x-ray method) (%) | 48   | 48   | 45   |
| Moisture regain (%)                        | 12.6   | 12.5   | 13.5   |
| Water retention (%)                        | 68   | 70   | 69   |
| Degree of dyeing (%)                       | 67   | 38   | 23   |
| Alkali imbibition in 6% NaOH (%)           | 360  | 400  | 600  |
| Fibrillar structure                        |   |   |   |
| Wet fibrillation characteristics           |  |  |  |

Hipolan S is characterized by its relatively low degree of polymerization for a Polynosic type fibre. In spite of the relatively low degree of polymerization, Hipolan S has excellent mechanical properties and alkali resistance. This has great advantage from the manufacturing point of view.

Hipolan S and Polynosic A show a high level of crystallinity and orientation. Furthermore Hipolan S gives the lowest imbibition in 6 per cent alkali. As was already mentioned, HWM A does not show a high fibrillar structure, while Polynosic A has a high fibrillar structure throughout the entire fibre. Hipolan S possesses a high fibrillar structure only in its inner part. Hipolan S and HWM A are by far superior in wet fibrillation performance compared with Polynosic A. In order to clarify the relation between the inner structure of the fibre and fibre performance such as mechanical properties and fibrillation behaviour, the radial-wise distribution of the structural characteristics has been examined. In this study, the peeling-off method making use of topochemical nitration which was proposed by Okajima *et al.*<sup>4</sup> has been applied.

*Figure 7* shows the radial-wise dye absorption equilibrium of Hipolan S and Polynosic A with a direct dyestuff. (Japanol Brilliant Blue 6BKX.)

With Hipolan S, the outer core-stainable region shows a higher level of dye absorption, while the inner skin-stainable region shows a lower value. With Polynosic A the whole structure is uniform except that there is a very thin outer layer of a higher dye absorption.

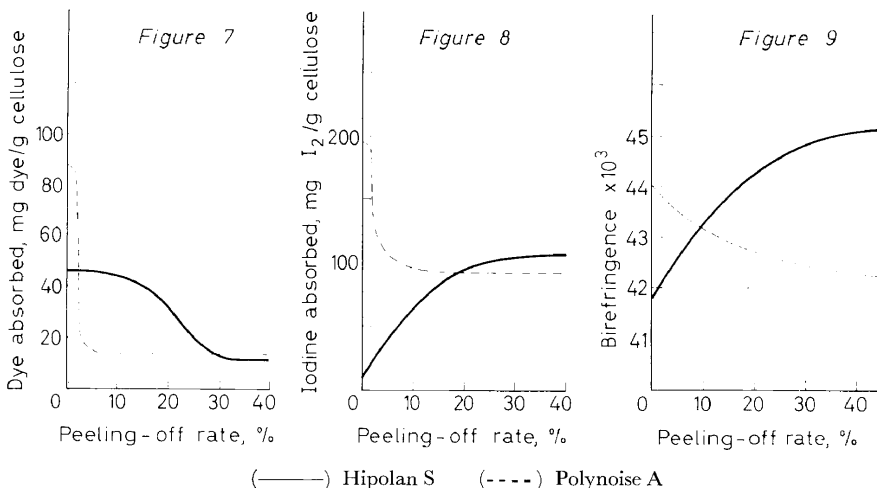


Figure 7. Radial-wise distribution of dye absorption  
 Figure 8. Radial-wise distribution of iodine absorption  
 Figure 9. Birefringence of peeled-off specimens

Figure 8 presents the radial-wise iodine absorption distribution of Hipolan S and Polynosic A. In Polynosic A a very thin outer layer of high iodine absorption is also observed, while the inner layer shows relatively low and uniform iodine absorption similar to the case with the dye absorption. This very thin outer layer of high absorption power of dyestuff and iodine would be equivalent to the so-called cuticle layer reported by Nakai<sup>5</sup> in his study of Shintoramomen.

On the other hand, Hipolan S shows a low iodine absorption in the outer layer and a high absorption in the inner region. Judging from these facts, the cuticle layer of Polynosic A is rather porous and relatively low crystalline while the outer layer of Hipolan S is porous but highly crystalline. This is one of the most outstanding characteristics of Hipolan S compared with the other Polynosics. Figure 9 shows the birefringence of peeled-off specimens of Hipolan S and Polynosic A.

It is clearly seen from Figure 9 that the molecular orientation of Hipolan S is lower in the outer part of the fibre than in the inner part. In contrast to this, Polynosic A shows a higher orientation in the outer layer. From these observations, it has been ascertained that in Hipolan S, the outer layer has a higher degree of crystallinity and lower orientation than in the inner region. In the case of Polynosic A, except for the cuticle layer the degree of crystallinity and orientation is nearly uniform. The improved brittleness and fibrillation tendency and the higher wet modulus and alkali resistance of Hipolan S are certainly based on this specific radial-wise structure. In particular, the low orientation of Hipolan S in the outer layer contribute to its high loop tenacity and hinder fibrillation of the fibre surface. In

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contrast to Hipolan S, HWM A has an outer layer which resembles the skin of the ordinary rayon. The skin layer of the HWM fibre has no high fibrillar structure and its toughness is higher than the core layer.

It is interesting to investigate the fibre-forming mechanism of Hipolan S. The work is in progress in our laboratory. In this paper we would like to point out only the resemblance between the outer layer of Hipolan S and that of the viscose rayon when treated with a swelling agent as reported by Yurugi<sup>6</sup>, Kato<sup>7</sup> and others. So it is believed at present that the specific radial-wise structure of Hipolan S is formed through a kind of swelling effect during the course of the spinning process.

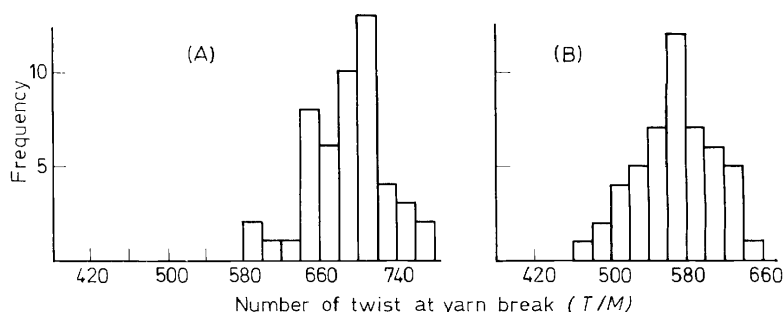
### FABRIC PERFORMANCE OF HIPOLAN S

As can be expected from the mechanical properties of the fibre, Hipolan S offers good processability during the spinning and the weaving, particularly it has an advantage of processing the fine count yarn of good uniformity and high strength. *Table 5* shows typical values of the spun yarn properties of Hipolan S, Polynosic A and HWM A.

*Table 5.* Mechanical properties of spun yarn from Polynosic fibres

|                            | <i>Hipolan S</i> | <i>Polynosic A</i> | <i>HWM A</i> |
|----------------------------|------------------|--------------------|--------------|
| Count (s)                  | 60               | 60                 | 60           |
| Lea strength (lb)          | 52               | 44                 | 48           |
| Lea elongation (%)         | 5.9              | 5.0                | 6.4          |
| Single yarn strength (g)   | 229              | 187                | 188          |
| Single yarn elongation (%) | 7.7              | 6.1                | 8.7          |
| Unevenness                 |                  |                    |              |
| U percentage (%)           | 13.1             | 14.5               | 15.2         |

*Figure 10* shows the distribution of twist resistance of spun yarns, an indication of the number of twists to cause yarn break. This is a basic measure required particularly for evaluating the suitability of yarn for producing fabrics of high twisted yarn. In *Figure 10*, (A) is an example of Hipolan S, and (B) an example of the completely skin-type Polynosic fibre. It is clear that the higher twist resistance is available with Hipolan S, taking advantage of its non-brittle character.



*Figure 10.* Distribution of twist resistance of spun yarns [(A), an example of Hipolan S; (B), an example of the completely skin type Polynosic fibre]

Figure 11 shows the various properties of a 100 per cent Polynosic broadcloth, scoured, mercerized, dyed, and resin finished. In Figure 11, (A) is an example of Hipolan S, and (B), an example of a completely skin-type Polynosic fibre. From this Table, it is evident that Hipolan S gives substantially good resistance to flex abrasion.

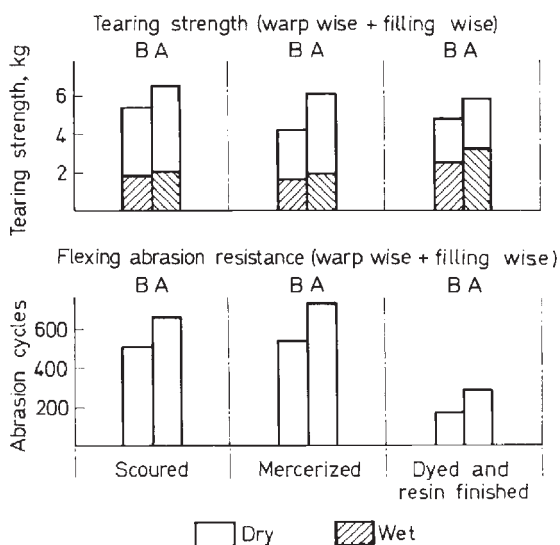


Figure 11. Mechanical properties of Polynosics fabrics

Figure 12 shows a photomicrograph of the fuzz on scoured and dyed Polynosic fabrics. In the case of highly oriented Polynosic, the fabric surface becomes fuzzy through an appreciable fibrillation and the dyed fabric looks rather whitish. In the case of Polynosic A, the same phenomenon is observed, although to a lesser extent. Such troubles can be avoided to some extent by adopting proper dyeing and finishing conditions, but this would

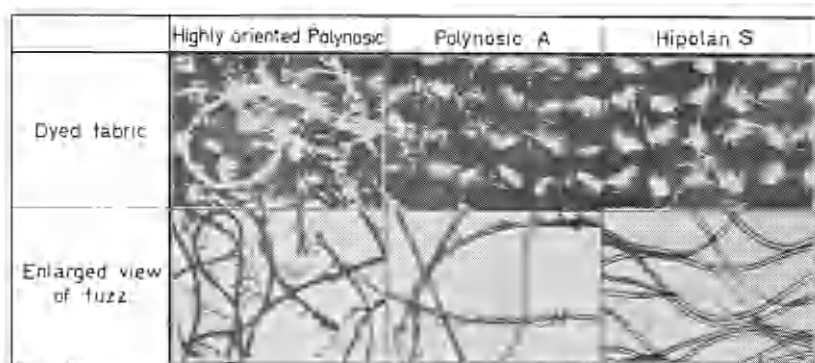


Figure 12. Photomicrographs: Fibrillation characteristics of dyed fabrics

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require very special control throughout these processes. In the case of Hipolan S, however, wide dyeing and other processing conditions can be employed because of its non-fibrillating property.

### FURTHER IMPROVEMENTS IN HIPOLAN S

As mentioned so far, Hipolan S is considered to be an extremely well-balanced Polynosic fibre. Further work is in progress to design a fibre with better Polynosic properties but still preserving the non-brittle, non-fibrillating characteristics.

Some of the results are now being evaluated on a pilot plant scale under the designation HP 411.

Table 6 shows the skin-stained cross-section and mechanical properties of this HP 411 and a highly oriented Polynosic fibre with a skin-stainable outer layer. HP 411 has a core-stainable outer layer similar to Hipolan S. HP 411 has appreciably high tenacity and modulus, as well as a high loop tenacity.

Table 6. Mechanical properties and stained cross section of highly oriented Polynosic fibres

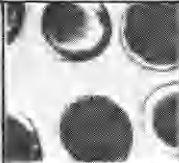

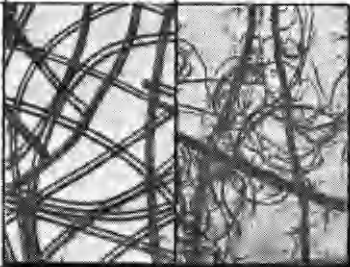
|                                       | HP 411  | Highly oriented Polynosic A   |
|---------------------------------------|---|---|
| <u>Untreated</u>                      |   |   |
| Denier                                | 1.1   | 1.3   |
| Tenacity conditioned (g/d)            | 6.2   | 6.4   |
| Wet tenacity (g/d)                    | 5.8   | 6.1   |
| Elongation conditioned (%)            | 9   | 8   |
| Wet elongation (%)                    | 9   | 8   |
| Knot tenacity conditioned (g/d)       | 2.9   | 2.4   |
| Loop tenacity conditioned (g/d)       | 2.4   | 1.9   |
| Wet modulus at 5% elongation (%)      | 3.2   | 3.5   |
| Wet elongation under 0.5 g/d load (%) | 1.3   | 1.1   |
| <u>After treatment with 5% NaOH</u>   |   |   |
| Tenacity wet (g/d)                    | 5.3   | 5.4   |
| Wet elongation under 0.5 g/d load (%) | 2.5   | 2.4   |
| Skin-stained cross section            |  |  |

Table 7 shows the fine structure characteristics of these fibres. HP 411 has a particularly high alkali resistance due to its high crystallinity. Furthermore, HP 411 offers an extremely good dyeability in spite of its high orientation and high crystallinity. HP 411 exhibits very little fibrillation on the fibre surface, while the highly oriented Polynosic A shows marked development of fibrillation.

It is assumed at present that such features as non-brittleness, good dyeability, resistance to fibrillation of HP 411, in spite of its high tenacity, modulus, crystallinity and orientation, are based upon the radial-wise special structure which approximates that of Hipolan S.

Table 7. Structural characteristics of highly oriented Polynosic fibres

|   | HP 411  | Highly oriented Polynosic A |
|---|---|-----------------------------|
| Degree of polymerization                  | 460   | 460                         |
| Degree of orientation (x-ray method)(%)   | 94  | 95                          |
| Degree of crystallinity (x-ray method)(%) | 50  | 51                          |
| Moisture regain(%)                        | 12.0  | 11.8                        |
| Water retention(%)                        | 56  | 63                          |
| Degree of dyeing (%)                      | 67  | 18                          |
| Alkali imbibition in 6% NaOH (%)          | 234   | 213                         |
| Wet fibrillation characteristics          |  |                             |

## CONCLUSIONS

As described so far, the brittleness and fibrillation properties of Polynosic fibres can be improved by converting the outer layer of the fibre which possesses high orientation, high crystallinity and a high fibrillar structure to that of slightly lower orientation and a low fibrillar structure. By achieving this effect Polynosic fibres can be obtained which have various advantages inherent to a HWM-fibre.

Such a fibre structure can only be attained through careful selection of a combination of conditions—viscose, acid bath, stretching, regeneration, etc. Polynosic fibres having such a structure will exhibit a marked well-balanced character which approaches the direction of an ideal fibre.

The present Polynosic fibres, when used in blend with cotton and synthetic fibres, will provide excellent hand in the fabrics, but 100 per cent Polynosic fabrics are still not satisfactory enough to cover the entire field of applications in consideration.

It is difficult to improve the fabric hand merely by means of modifying the inner structure of the fibre. It has been found that morphological modifications of a fibre such as the form of the cross section of the fibre and impartment of high crimp are more effective for improving the fabric hand.

A high crimp Polynosic fibre is also now being developed on a pilot

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plant stage. This newly developed Polynosic fibre, when used in 100 per cent form for woven fabrics and knitted goods brings about a cotton-like hand and a high degree of bulk.

Figure 13 shows the stained cross section and longitudinal view of this highly crimped Polynosic fibre. It is noted that in this specific heterogeneous structure, the radial-wise structure is similar to that of Hipolan S, i.e. there is a distinct core-stainable layer outside the skin part of the fibre.

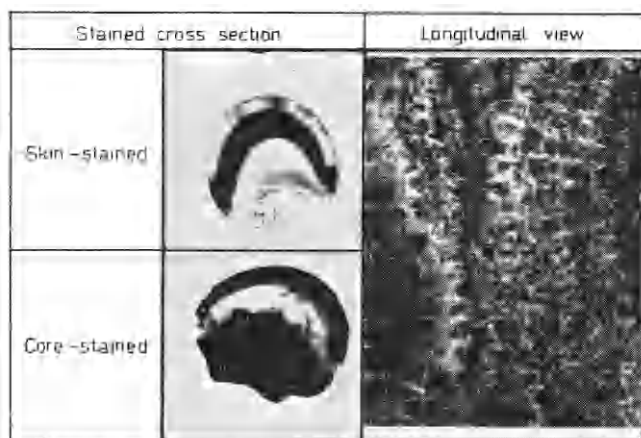


Figure 13. Photomicrographs of high crimp Polynosic fibre

In conclusion, our direction of future improvements in Polynosic fibres will be aimed at developing a fibre more suitable for a high degree of wash and wear processes, such as "permanent press" treatment, by modifying its inner structure and also at expanding the end-use field by further modifications of the morphological structure of the fibre.

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### References

- <sup>1</sup> K. Kato. *Textile Res. J.* **22**, 803 (1957).
- <sup>2</sup> JIS (Japanesic Industrial Standard), L 1015.
- <sup>3</sup> H. Maeda. *J. Soc. Text. Cellulose Ind. Japan* **12**, 6 (1956).
- <sup>4</sup> S. Okajima, S. Hayama, and K. Watanabe. *Bull. Chem. Soc. Japan* **26**, 322 (1953).
- <sup>5</sup> A. Nakai. *Bull. Chem. Soc. Japan* **32**, 1037 (1959).
- <sup>6</sup> T. Yurugi. *J. Soc. Text. Cellulose Ind. Japan* **12**, 96 (1956).
- <sup>7</sup> K. Kato. *J. Soc. Text. Cellulose Ind. Japan* **14**, 678 (1958).