

# HIGH WET MODULUS FIBRES: THEIR STRUCTURE, PROPERTIES AND FABRIC PERFORMANCE

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## INTRODUCTION

When the viscose process was first used its attraction to the textile industry was the fact that it made available relatively cheap continuous filament yarn as an alternative to silk. The original process was developed to give yarns of adequate strength and extensibility so that these could be used on normal knitting and weaving machines to provide high quality products free from discontinuities, broken fibre, etc. and to maintain the great evenness of dyeing so important in the sheer fabrics in which it was first used. It is evident that these qualities similarly form basic requirements of staple fibre and hence the rayon originally marketed as staple fibre used spinning conditions close to those established for continuous filaments textile yarns.

The rise in production of regular rayon staple over the last 30 years is a striking demonstration of the general suitability of the material for the textile industry. However, when the present production is compared with that of cotton it is equally evident that very large sections of the total cotton market are still quite untouched and outside the scope of rayon staple (cf. *Table 1*). The reason for the strength of the cotton demand is by no means explained by the price since although some cotton is cheap, much of it has no price advantage over rayon. Hence we might well ask why rayon, which has a supreme advantage over all other man-made fibres, in being chemically identical to cotton, has not profited more from the advantages inherent in manufactured fibres (such as price stability, control over staple length, denier and quality) and made deeper inroads into the cotton market. The differences in behaviour of rayon and cotton are in two

*Table 1.* World production of certain textile fibres (Figures given are in million lbs.)

|                           | 1950   | 1955   | 1960   | 1961   | 1962   | 1963   | 1964   |
|---------------------------|--------|--------|--------|--------|--------|--------|--------|
| Cotton                    | 14 654 | 20 926 | 22 284 | 21 647 | 22 994 | 24 028 | 24 597 |
| Wool                      | 2330   | 2789   | 3231   | 3279   | 3286   | 3346   | 3340   |
| Polyamide                 | —      | —      | 896    | 1055   | 1347   | 1627   | 1992   |
| Polyester                 | —      | —      | 271    | 333    | 446    | 581    | 745    |
| Acrylics +<br>Modacrylics | —      | —      | 241    | 265    | 369    | 466    | 663    |
| Acetate                   | 591    | 483    | 530    | 565    | 621    | 651    | 747    |
| Viscose filament          | 1456   | 1911   | 2064   | 2035   | 2113   | 2158   | 2287   |
| Viscose staple            | 1496   | 2639   | 3137   | 3314   | 3564   | 3919   | 4222   |

main directions. Firstly, there is the superior performance of cotton in the wet state. In part this is a matter of greater strength under wet, sometimes strongly alkaline conditions but of more importance is the dimensional stability displayed even under severe washing conditions. Secondly, there is the improved handle of cotton fabrics in so far as they are firmer and drape more attractively. Whilst these desirable properties have been known for a long time it is only recently that the exact relations between them and fibre properties have been established. This knowledge has become the key to the development of improved rayons since it is obvious that an understanding of the fibre properties necessary to confer the required fabric properties is essential. Let us, therefore, first consider the relation between fabric and fibre properties bearing in mind the particular requirements of the cotton goods market and then consider just in what directions, and how far rayon has been improved. We can subsequently see what demands are made on the viscose process and its raw materials

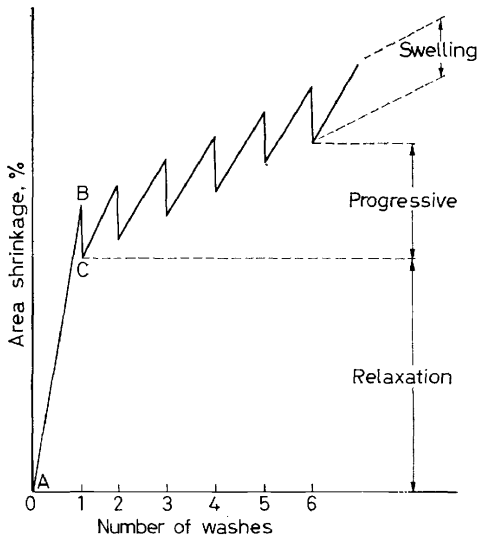
## FABRIC PROPERTIES

### (1) Shrinkage

The most notable deficiency of viscose rayon by comparison with cotton is its shrinkage during washing. Early work on this subject was complicated by the fact that, even for a given fabric, the shrinkage behaviour is complex and depends on the history of the fabric as well as the severity of washing and the conditions of drying. We now recognise three types of shrinkage.

#### (a) *Relaxation shrinkage*

This refers to the relaxation, at the first wash, of strains which have been induced during processing. In *Figure 1* where the area dimension of a fabric undergoing a series of washing and ironing cycles is depicted relaxation



*Figure 1.* The effect of washing on relaxation, swelling and progressive shrinkages

shrinkage is indicated by the change AB. In so far as fabrics are subjected during processing to a given strain (e.g. held to width) there is little one can do to minimize this effect but in so far as fabrics are subjected to given stress, obviously a high modulus (dry or wet as the case may be) is beneficial.

(b) *Swelling shrinkage*

This refers to the change to BC (*Figure 1*), viz. the difference in dimension between the loose dried and the ironed states. The mechanism of this behaviour was studied in detail by Collins<sup>1</sup>. If a yarn swells when wetted out this either leads to a longer path of the yarns around each other or to a more shrunken fabric. Collins showed that usually the latter occurs. It is evident that the lower the water imbibition and the less the swelling of yarn, the smaller will be this type of shrinkage. In the case of cotton, this type of shrinkage is not great, partly because of the low water imbibition, and partly because of the large amount of free space in the yarn into which the fibre can swell. Rayon with its higher water imbibition and round section (giving leaner yarns) shows greater shrinkage. However, because, of the reversible nature of this effect this is the least important of the three types.

(c) *Progressive shrinkage*

This is sometimes called felting shrinkage because of the way in which in extreme cases of this behaviour are often accompanied by movement of the fibre out of the yarn to give a felted structure on the surface of the fabric. The "boardy" feel and poor appearance resulting from this type of shrinkage adds to the detrimental nature of this effect and hence this type of shrinkage is most important. Certainly it is one in which rayon shows particular deficiencies. Of the three types of shrinkage it is the least understood. However, its dependence on filament denier, yarn twist and detailed fabric construction together with its sensitivity to washing conditions all suggest that it is associated with the movement of filaments within the yarns rather than of yarns as a whole. This is further substantiated by the observation of the felting effect described above. From this point of view it is not surprising that increasing the wet modulus of a fibre decreases the effect since this will reduce the relative motion of the fibres one to the other. Certainly the advantages of an increased wet modulus are experimental fact. This general picture is reinforced by the fact that although cotton yarns have much higher moduli than would be expected from their filament moduli (due to an extraordinarily efficient "conversion" of filament to yarn moduli) as far as progressive shrinkage is concerned cotton behaves as might be expected from its *filament* modulus rather than its *yarn* modulus.

In view of the foregoing, therefore, whilst it is helpful for a viscose rayon to have a high dry and wet modulus to help reduce relaxation shrinkage and whilst a low water imbibition reduces swelling shrinkage, a more important requirement for fibres contending for the cotton goods market is to have a high wet modulus to reduce progressive shrinkage.

## (2) **Wet strength and resistance to soda treatment**

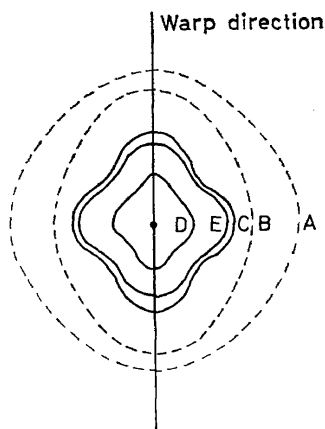
Allied to a high wet modulus is the property of high wet strength. Whilst the dry strength of cotton and regular rayon are comparable, the wet strength of rayon at about 1.5 g/den. is only about 50 per cent of that of

cotton. In some instances this is not of crucial importance but in some wet processing operations there is the distinct risk of rayon splitting and tearing and the finisher who is accustomed to being able to handle cotton very roughly will obviously see the tenderness of rayon a handicap.

Closely connected with this property is the behaviour of fibres in aqueous sodium hydroxide. Mercerizing treatment is common in the cotton industry and whilst the necessity for it is much less frequent in the case of rayon nevertheless benefits in handle are still to be obtained by such techniques and hence resistance to alkaline conditions is important. Further blends with cotton will usually need to be able to stand a full mercerising treatment.

### (3) Fabric handle

This term is used to embrace the whole of the subjective tactile judgement of a fabric. Haworth and Oliver<sup>2</sup> have shown that there are three physical fabric parameters that form the basis of these judgements and these are thickness (or bulk), stiffness, and smoothness. All of these, particularly the last two are strongly dependent on fabric construction but fibre properties do make significant contributions. Firstly, there is the direct effect of fibre stiffness as measured by the bending modulus. Secondly, there is the more important contribution to bulk and stiffness arising from fibre cross-section. Thus cotton is flattened in cross-section and this results in more bulky yarns which are both stiffer in themselves and which also give an increase in fabric bulk. Further yarn-yarn interaction is greater as their bulk and surface area increase and consequently bending of the fabric does not take place so readily—thus fabric stiffness is increased. A further feature of cotton fabrics emphasised by Cooper<sup>3</sup> is that allied to the increased stiffness is a directional effect whereby stiffness changes for varying angles to the warp (or weft) axis. *Figure 2* displays the change of fabric flexural rigidity at various angles to the fibre axis and it is seen that rayon displays an overall smaller rigidity notably at directions diagonal to the fabric axis. *Figure 3* shows the differences between



*Figure 2.* Variation of stiffness with direction. The relative flexural rigidities of U 1009-type fabrics [A–B, Cotton fabrics; C, 3 denier “Fibro”; D, 1½ denier “Fibro”; E, 1½ denier “Vincel”]

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rayon and others when subjected to a shearing action. Cotton is much more resistant. These effects are all believed to be due to differences in yarn-yarn interaction and are believed to be a further important physical difference responsible for the contrasting subjective assessments of handle of cotton and rayon fabrics.

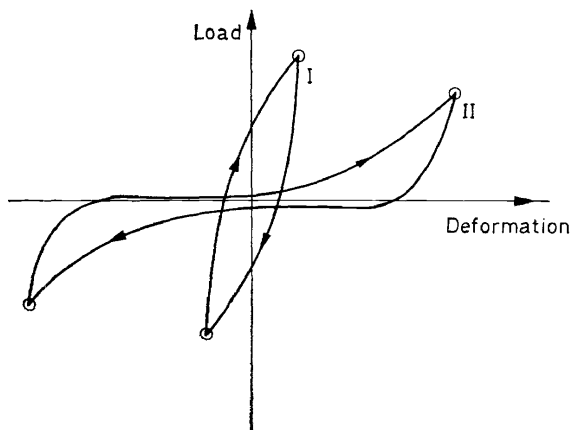


Figure 3. Resistance to shearing deformations. Typical cyclic diagrams for U 1009-type fabrics [I, Typical cotton; II, "Fibro" or "Vincel"; O, buckling point]

## FIBRE PROPERTIES

Let us now consider how far we have gone towards meeting the level of fibre properties demanded by the level of fabric performance which the textile industry expects. Firstly, it is evident that the variety of end uses, the variety of fabric constructions and the variety of blends of fibres available mean that an established minimum level of fibre performance is impossible to define.

Table 2. HWM-fibres

| Classification                            | High strength                   | Standard   | High elongation          | Cotton | Rayon staple |
|---|---------------------------------|--|--------------------------|--------|--------------|
| Fibres represented                        | { Super Polyflox<br>Junlon, W63 | { Z54, Vincel<br>Polyflox, Koplon<br>Polyno, Polycot,<br>Tufcel<br>Zantrel | { Superfaser<br>Fibre 40 | Uppers | —            |
| Tenacity (g/den.)<br>air-dry              | 4.6-5.2                         | 3.2-4.0  | 3.8-4.8                  | 3.6    | 2.5          |
| wet                                       | 3.4-4.0                         | 2.0-3.0  | 2.4-3.4                  | 4.0    | 1.4          |
| Extensibility (%)<br>air-dry              | 6-10                            | 8-12   | 12-14                    | 9      | 18           |
| wet                                       | 8-14                            | 9-16   | 16-20                    | 10     | 22           |
| Wet modulus<br>(g/den.) per<br>100% extn. |                                 |  |                          |        |              |
| at 2% extn.                               | 15-25                           | 10-18  | 6-9                      | 12     | 4            |
| at 5% extn.                               | 25-40                           | 14-28  | 10-13                    | 18     | 5            |
| Water imbibition                          | 65-75                           | 55-70  | 65-75                    | 40-50  | 90-100       |

In trying to develop fibres suitable for this market many different combinations of properties have been chosen and offered to the textile industry. For convenience we may classify them into three main types (*Table 2* and *Figure 4*). Firstly, the standard high modulus or Polynosic fibres are seen

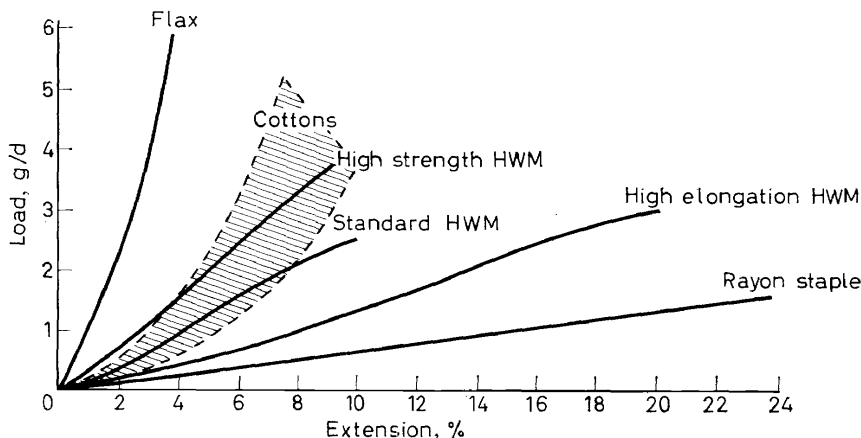


Figure 4. Wet stress-strain curves for various fabrics

to give a compromise of properties such that with wet moduli at about 20 g/den. per 100 per cent extension, they offer stability to shrinkage equal to that of cotton. Added to this they have sufficiently improved tensile properties to give good dry and wet performance either alone or in blend with cotton. Thus in the latter case the similarity of extensibility of the rayon and cotton eliminates the minimum of strength in blends of regular rayon with cotton. Further, blends are possible in which wet and dry strengths are identical.

By contrast with these fibres, the high extensibility intermediate modulus fibres have properties biased to give improved blending performance with high extensibility synthetics such as polyesters and with the combination of both high tenacity and extensibility, i.e. with a high work of rupture, they give a bonus with respect to abrasion resistance. On their own they will show markedly improved shrinkage behaviour over regular rayon but will need further stabilising by blending with other staple fibres or by after treatment if the highest resistance to shrinkage is required.

At the other extreme are the very high modulus fibres which offer a washing performance superior to cotton and whose very high tensile strength makes adequate compensation, in terms of abrasion resistance and blending properties, for the low extensibility.

For the rest of this paper all three types of fibres will be referred to collectively as HWM-fibres.

In addition to an improved modulus and a higher ratio wet/dry tenacity all the fibres have significantly lower water imbibition than regular rayon and it is evident therefore that the main improvement in properties that they offer is indeed in wet properties. To this may be added a considerable increase in strength under alkaline conditions to the extent that whilst full cotton

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mercerization cannot usually be applied a treatment at about 7 per cent sodium hydroxide is possible that gives an improvement in handle, in appearance, in dyeing properties and in their ability to take resin treatment. The increased resistance to sodium hydroxide is indicated in *Table 3* where

*Table 3.* Resistance of fabrics to 5 per cent sodium hydroxide

| <i>Fibre</i>                 | <i>Tension fibre withstands<br/>in 5% NaOH<br/>(g/den.)</i> |
|------------------------------|---|
| Regular staple               | 0.2   |
| Standard HWM-fibre           | 0.5   |
| High extensibility HWM-fibre | 1.2   |
| High strength HWM-fibre      | 1.3   |

the tensions to which fibre can be loaded and still survive treatment with 5 per cent sodium hydroxide at 20°C are given.

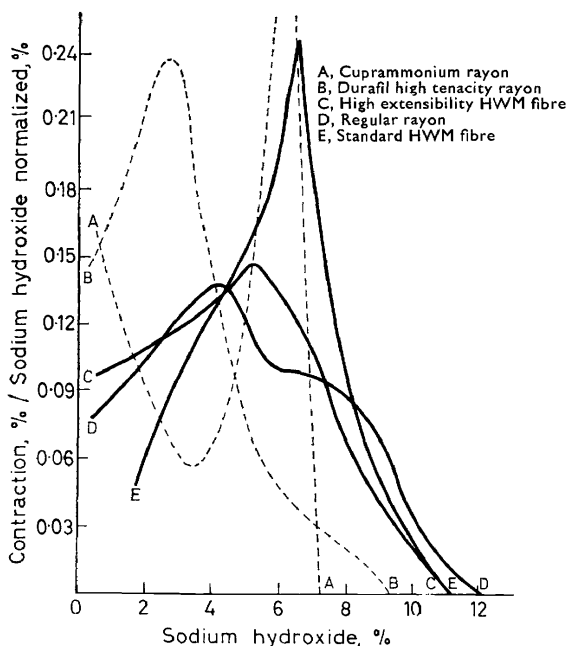
It will be evident from the discussion of fabric properties that we have only travelled part way towards providing a really satisfactory fibre for the cotton goods market. Thus with regard to handle improvements relatively little has been achieved. Certainly there is the possibility of soda treatment mentioned above but as far as untreated fabrics are concerned it is only the high strength, high modulus group of fibres which are significantly stiffer than regular rayon. In the case of these the resultant fabrics are detectably firmer in handle. However, the real need is for a more bulky yarn and it must be admitted that the round cross-section of the Polynosic fibres makes this target very difficult to attain. In other end uses the production of crimped fibre provides an answer to this problem but of course the inevitably low modulus of such a fibre precludes such a solution in the case of this type of fibre. One answer to the problem is to blend rayon with a very low density fibre such as polypropylene. Ten or twenty per cent of the latter greatly increases yarn bulk and fabric stiffness. An alternative solution is to emulate cotton and make fibres of flattened cross-section. Again marked changes in handle can occur but usually flat filament rayon has only been produced at the expense of tensile properties. Hence a commercially satisfactory solution is still awaited.

## FIBRE STRUCTURE

Long before the significance of HWM-fibres was fully realized it was appreciated that a very wide spectrum of physical properties was attainable from cellulose and this gave the impetus to structural investigations aimed at elucidating the origin of these differences. Thus in the case of HWM-fibres X-ray, density and accessibility measurements have demonstrated the greater extent of crystallization and also the increased lateral order in those regions fringing the crystallized areas. This order extends even to the non-crystalline regions as is shown by the high level of orientation measured optically. (The latter reflects the ordering of both crystalline and non-crystalline regions and its value relative to that taken from X-ray spots, which correspond to crystalline region only, indicates the alignment of the

non-crystalline regions). The increased orientation of the non-crystalline regions is perhaps the most important structural feature of HWM-fibres since it is the reason both for the high modulus and low extensibility and also for the greatly reduced sensitivity to water.

Here also lies the reason for the greatly increased resistance to soda. Indeed the behaviour of fibres in soda provides a very useful technique to characterize fibres structurally. Thus if a fibre or continuous filament yarn is suspended under a very slight tension in soda of progressively increasing concentration, and the length to which it shrinks measured at each concentration, a differential curve of the rate of change of length with soda may be constructed. Such curves for various fibres are given in *Figure 5*. It will



*Figure 5.* Effect on shrinkage of various fabrics after treatment with different concentrations of sodium hydroxide

be seen that in the case of Durafil, shrinkage takes place at low soda concentrations indicating the low energy of the intermolecular restraining forces, whilst for high modulus fibres a much higher degree of swelling is required before relaxation of orientation can occur. Thus here we have a very simple and diagnostic technique to indicate the changes in lateral order in the range of cellulose fibres. The dependence of soda swelling behaviour on supra molecular structure has been stressed because it is believed that, in terms of the soda stability demanded in fabrics it is the most relevant. Thus certainly in the final stages of dissolution (e.g. in making measurements of yarn solubility in soda) cellulose D.P. becomes



dominant but of course it is much lower degrees of swelling that are of interest with regard to the soda stability of fabrics.

### HIGH MODULUS SPINNING PROCESSES

Whilst it is generally agreed that the commercial development of HWM-fibres arose from the spinning of Toramomen by Tachikawa the structural study of fibres referred to in the above section makes it clear that fibres with similar structures had been spun much earlier. Thus the properties of Lillienfeld rayon leave one in no doubt that it should be classed with the high strength, high modulus fibres. The small weights in which it has been spun are however an apt reminder of the acute dependence of commercial success of a fibre on its cost of production. Similarly the two bath processes<sup>4</sup> described in the patent literature (e.g. Fibre G) obviously produce a similar type of fibre. To these we may add highly stretched saponified acetate fibres such as Fortisan and possibly fibres produced by the ammonium sulphate or the cuprammonium processes.

These various processes are mentioned to stress the point that whilst the route to textile yarn and to tyre yarn is a fairly unique one that to HWM-fibres can be most varied. Further, whilst some routes may be readily seen to offer little hope of commercial success there still remains a variety of feasible yet widely different processes, which lead to the production of fibres with a different balance between the major properties of tenacity, extensibility and initial modulus and also to differences in secondary properties. Here then is the reason why the present situation with regard to the merits of different types of HWM-fibres is in such an indeterminate state. Thus on the one hand the textile requirements are not unambiguously defined whilst on the other hand no overriding advantage is offered by any particular route to this general pattern of properties.

Let us try to see what these processes have in common by working back through the viscose spinning process and not indicating an order of importance. Firstly, they all need a relatively large amount of work applied to the fibre during stretching to orient the whole structure. This is reflected in a high stretch, a high stretching tension, or both. (Because of this high stretching tension and the crimp free nature of the fibre and the round cross-section all of which lead to the close packing of the fibre in the tow, there are frequently problems of achieving suitably opened product with this type of fibre).

Secondly, in order for this stretch to be effective throughout the whole structure of the fibre it is necessary for it to be applied whilst the degree of substitution by xanthate groups is still relatively high. In this way the fibre is maintained in a fairly swollen state so that all the molecules may move relatively to one another in order that more complete orientation of the structure can be achieved. This difference in the mechanism of stretching is further indicated by a greatly reduced tendency to relax once the stress is removed. In tyre yarns and in regular rayons the structure is largely established before stretching and the filaments display a marked tendency to return to the pre-stretch condition but in HWM-fibres the structure before stretch is less well determined and the relaxing tendency is less. It follows of

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course from this state of affairs, that stretching plays a bigger role in determining the structure of high modulus fibres than is the case in tyre yarns. This is certainly reflected in an increased dependence of gel swelling, water imbibition, dye affinity and moisture regain on stretch (*Table 4*).

*Table 4.* Effect of stretch on water imbibition, gel swelling, moisture regain and dye affinity for a standard high modulus fibres and for a super tyre yarn

| Stretch (%) | Gel swelling <sup>a</sup> (%) | Water imbibition <sup>b</sup> (%) | Dye affinity <sup>c</sup> (%) | Moisture regain <sup>d</sup> (%) |
|-------------|-------------------------------|-----------------------------------|-------------------------------|----------------------------------|
|             |                               | HIGH MODULUS                      |                               |                                  |
| 0           | 340                           | 123                               | 80                            | 13.5                             |
| 20          |                               | 102                               |                               |                                  |
| 40          | 180                           | 86                                |                               |                                  |
| 60          | 180                           | 75                                |                               |                                  |
| 80          |                               | 71                                | 23                            | 11.8                             |
| 90          | 80                            |                                   |                               |                                  |
|             |                               | TYRE YARN                         |                               |                                  |
| 2           | 90                            | 77                                | 91                            | 14.5                             |
| 20          |                               | 72                                | 89                            | 14.5                             |
| 40          | 80                            | 68                                | 78                            | 14.5                             |
| 60          | 80                            | 63                                | 58                            | 14.3                             |
| 80          |                               | 61                                | 44                            | 14.2                             |
| 100         | 80                            | 58                                | 58                            | 14.2                             |

<sup>a</sup> Per cent water imbibed by never dried yarn.

<sup>b</sup> Per cent water imbibed by dried yarn.

<sup>c</sup> Per cent exhaustion of dye bath under standard conditions.

<sup>d</sup> Per cent moisture uptake at 60% RH; 25°C.

Since there is a certain emphasis on stretching at a high degree of xanthate substitution it is not necessarily advantageous to stretch through hot acid because, although this gives increased molecular mobility, it also results in rapid decomposition of cellulose xanthate. However, if the highest strength and modulus is required then fixation is essential during stretch and before even the modest relaxing tendency of these fibres can operate.

Many different techniques are possible to preserve the swollen nature of the gel until the fibre is ready for stretching. Indeed it is here that the variety of the various processes shows itself. The most common feature is to use a relatively low bath temperature so that coagulation and regeneration proceed slowly. The reduction of acid concentration and of spin bath immersion are further obvious directions in which to move. Modifiers also, in the presence of zinc, have a retarding effect and so for that matter has zinc itself. (Here, however, there is a certain difficulty since the vigorous coagulating action of zinc which of course forms the cornerstone of tyre yarn processes must be avoided). It should be added that the sodium sulphate concentration is usually low. Thus the rapid increase in extensibility occurring at sodium sulphate concentrations above the level corresponding to the acid salt NaHSO<sub>4</sub> leads to this being the useful limit of salt concentration in HWM-processes.

A more vigorous retardant—at least to the regeneration of xanthate—is

formaldehyde. This readily reacts with xanthate groups under acid conditions to give a stable ester whose formation leads to a labile gel which can be readily stretched to a very great extent. Such is the stability of the methylol ester formed that formaldehyde in a viscose spin-bath will over-ride the effect of other components such as zinc ions and will always lead to the formation of relatively low extensibility yarns. This stability does of course bring its own difficulties in that vigorous conditions are required to achieve complete xanthate fixation. A further disadvantage in the use of formaldehyde is the formation of noxious sulphur compounds and also, of course, its cost.

An alternative technique to reduce the rate of regeneration is to use buffer baths but these are of less importance. Finally in the case of Lillienfeld rayon, advantage is taken of the very slow rate of regeneration of cellulose xanthate in concentrated acid, and of the plasticizing action of sulphuric acid at high concentration.

Before leaving the subject of the slow coagulation rate it is worth mentioning that it is this which is responsible for the round section of the fibre. Thus under slowly coagulating conditions the whole cross-section of the filament shrinks evenly and the crenulations which come from the rapid fixation of the outer annulus of the fibre are avoided. It is evident therefore that at the present state of knowledge HWM-fibres are inevitably round and therefore the yarns lean.

A third common feature of these processes is that they normally operate at a slower spinning speed than that used for regular rayon. It is fortunate that the high stretches employed result in a reduced velocity in the bath or else even lower speeds would be required to avoid damage to the tender gel and to achieve the very best properties.

A fourth feature is that these processes operate with viscose of higher viscosity than that used for regular rayon. In part this follows from the fact that since the coagulation power of the bath is low a high viscose viscosity serves to give the gel the necessary coherence to secure good spinning performance. Thus the more slowly the shrinkage of the filament is achieved the more necessary is a high viscosity viscose likely to be, and vice versa. In addition to this may be added the minor benefits which result from higher D.P. in terms of effecting a greater degree of orientation and of strength from a given stretch.

A further viscose feature is the level of xanthate substitution. A high level will inevitably lead to a higher level at stretch and in order to effect the highest stretches and to produce the yarns of highest modulus viscoses of high salt figure are often used. However, the use of suitably retarding conditions may make this unnecessary and certainly the use of large amounts of carbon disulphide in viscose making to raise the  $\gamma$ -number at stretch by a few units seems an extravagance. More important than the degree of polymerization or the degree of substitution, however, is the actual cellulose concentration. Regular rayon is usually spun from viscose relatively concentrated in cellulose whilst substantially more dilute ones are used for high modulus fibres. It is tempting to think that low viscose cellulose concentrations have a direct effect in leading to lower concentrations of cellulose in the gel. However, since tyre yarns also benefit from low cellulose concentrations

it may be that in both cases it is increased control over the process of structure formation that is important and that it is the reduced speed at which it takes place in more dilute solutions which is advantageous. Certainly, however, the use of viscoses of lower cellulose and higher viscosity obviously demand higher cellulose D.P. in the viscose and consequently in the pulp.

### PULP

Pulp properties of particular interest to manufacturers of HWM-fibre are average cellulose D.P. (i.e. pulp viscosity) distribution of D.P. (i.e.  $\alpha$ -content, etc.), unreactive material (i.e. cellulosic and non-cellulosic), colour and cost.

The viscosity requirements are of course determined by viscose cellulose concentration and viscosity and viscose by the need to achieve sufficient pre-ripening time to preserve adequate flexibility in the viscose making process. Thus a viscosity of about 20 c/s (1 per cent cuprammonium Tappi T-206) for prehydrolysed sulphate pulps and around 35 c/s for sulphite pulps are the ranges of interest to viscose manufacturers; this difference reflecting of course the difference in depolymerization characteristics. It seems unlikely that the viscosity requirements will change greatly in the near future but the increased technical difficulty of using high viscosity viscose and the need for economy which, in a small way can come from higher cellulose concentrations suggests that the pulp viscosity demanded in the future is likely to be lower rather than higher.

The original production of HWM-fibre with its accent on preserving the supramolecular cellulose structure present in cotton led to the use of high viscosity high  $\alpha$ -cotton pulps. Even when a move was made from cotton to wood pulps it was still the high  $\alpha$ -cellulose pulps of high D.P. which were needed to give the required viscose viscosity. Further to this was the fact that it was obvious that the very large increases in tensile properties sought (e.g. 100 per cent in wet tenacity) would be most readily obtained by using the best available pulp. These were therefore used in the development of all the types of HWM-fibres. Now whilst it is true that the strongest of the HWM-fibres are the most sensitive to pulp D.P. distribution it is also true that in the case of the standard HWM-fibres even a modest loss in tenacity and extensibility may be intolerable in view of the minimum level of properties required.

So far the viscose industry has had relatively little success in using low  $\alpha$ -pulps for HWM-fibres and hence one is tempted to define what sort of pulp is required. Perhaps it should first be said that since the  $\gamma$ -cellulose does not reach the final product, in quantity, and since fibres made experimentally using hemi-free steeping liquor still display a sharp dependence of tenacity on pulp quality then the  $\gamma$ -cellulose is relatively unimportant. (This statement demands qualification due to extra costs incurred in removing hemi-cellulose from steep liquor and arising from reduced yield in production processes but it forms a basis for discussing the relationship between pulp quality and fibre tensile properties). If now the  $\gamma$ -cellulose content of the pulp is neglected then the magnitude of the effect of pulp quality on tenacity becomes most striking. Thus for  $\beta$ -contents within the region of 1-3 per cent tenacity and extensibility losses of around 12 per cent can be observed. In part the figure needs qualifications due to the production of

non  $\alpha$ -cellulose in pre-ripening and also since often for lower quality pulps less stretch can be applied. However, if allowance is made for these factors it is still obvious that the per cent loss in tenacity is greater than the per cent of non  $\alpha$ -material in the fibre. Thus this loss in tenacity is much more than simply one of the  $\beta$ -cellulose merely failing to contribute to the fibre strength. Either the small quantity of  $\beta$ -cellulose does much positive harm to the fibre structure and thus gives rise to a disproportionate drop in tensile properties or the effect is spread over a much greater range of cellulose D.P. than that classified as  $\beta$ -cellulose—or both effects are operative. In fact one might suspect that with rising D.P. there are effects which range from the positive disruption of the structure to much more minor tensile effects.

Such an argument suggests that  $\beta$ -cellulose primarily and the short chain length  $\alpha$ -cellulose to a lesser extent are the cause of the poor tensile properties obtained from lower  $\alpha$ -pulps and it is a reduction of such material that will help viscose manufacturers most in making acceptable high wet modulus fibres. This view is reinforced by the sizable changes which also occur in water imbibition when high modulus fibres are spun from low  $\alpha$ -pulps. This also suggests that the change in structure is relatively extensive and not confined merely to the development of a few weak points. It is therefore believed that low D.P.  $\alpha$ -cellulose is a significant factor in the strength of high modulus fibres and apart from the importance of this fact it raises the question of the extent to which the further characteristics of pulp in the low D.P. region of  $\alpha$ -cellulose would help us in specifying more exactly what is required.

The situation with regard to dissolving quality is not so straightforward. The first high modulus fibres used viscoses of very high  $\gamma$ -value and this of course necessitated the use of large proportions of carbon disulphide. Under these circumstances changes in those aspects of dissolving quality influenced by the amounts of carbon disulphide used may be possible and in this way certain pulp deficiencies tolerated. Thus apart from exclusion due to price, certain prehydrolysed sulphate pulps are quite unusable for regular staple production due to their poor performance under "lean" viscose making conditions. These pulps are, however, quite suitable (technically) for high modulus fibres using higher amounts of carbon disulphide. Whilst this situation gives more latitude with regard to dissolving quality there are several factors which work oppositely. Firstly, the higher viscosity of the viscose employed means that the mechanical efficiency of xanthate dissolving deteriorates unless special equipment is used. Secondly, the higher viscosity in itself reduces filter life and this demands lower viscose blockage constants if filtration cost is not to be increased. Thirdly, it should be mentioned that those high modulus processes based on baths containing zinc will normally show substantial benefits in properties from using small spinnerette holes. This could result in unusually severe demands on viscose quality which will become particularly important if the highest tenacity levels are sought.

The effect of pulp colour in the resultant fibre requires comment. As long as high  $\alpha$ -pulps were used only for tyre yarn colour was unimportant but obviously HWM-fibres are more demanding and current prehydrolysed sulphate pulps give rather poorly coloured products unless fairly vigorous

bleaching is undertaken. The present large weight of HWM-fibres going into cotton blending probably alleviates this difficulty at this moment but the greater ease of providing lower  $\alpha$ -cellulose pulps of better colour is an added advantage which will come when these qualities can be used.

Finally, I should attempt to put the cost of pulp into perspective. For those HWM-fibres offering high tenacity and extensibility it is likely that production facilities will have been made available for the introduction and elimination of auxiliary chemicals such as zinc, modifiers, formaldehyde, etc. Having made provisions for the use of these chemicals and having also of course a process responsive to their presence it may be possible to balance off the relative benefits, or otherwise, of say, pulp quality against those of other chemicals. In this way a better balance of cost and properties may be possible and this could enable cheaper pulps to be used, though probably not normal grade pulps. Hence for these fibres at the moment we can at least envisage some extra pulp cost and substantial extra chemical costs. For the simpler, cheaper HWM processes the possibility of balancing of the effects of various grades of pulp against the use of other chemicals in the process is very remote, particularly when one remembers that the *difference* in cost between a normal grade and a top grade pulp is comparable to the *total* cost of any of the *individual* other chemicals.

The whole of the first part of this paper was directed to establishing the basis on which the viscose rayon market could be expanded into that of cotton goods. It is evident that the prize to be gained is very great but only so far as high modulus fibres can be sold as commodity fibres at a competitive price. The full expansion in this field will only come when HWM-fibres can be offered at a price close to that now ruling for regular staple. It is evident therefore that the use of premium grades of pulp at 20–30 per cent higher price than that of grades suitable for regular rayon is prohibitive and that between pulp manufacturers and rayon producers we must find out how to use a lower priced pulp, since only by the use of pulps priced no more than marginally above those used for regular staple is the full potential market to be exploited.

#### END USES

Fabric made 100 per cent in HWM-fibres forms only a minor part of the total usage. The most successful developments in this field have been in knitted underwear and outerwear garments. In these the soft silky handle is attractive and in the former the superior washing performance of HWM-interlock fabrics has given them a significant advantage over cotton.

Blends with cotton are probably the biggest single outlet at the moment. With medium grade cottons it is the ability to import a combed cotton look that is important whilst with cheaper cottons it is the ability of the HWM-fibre to upgrade shorter staple that is attractive. Blends with polyester are also important, with respect to both the standard and the high extensibility HWM-fibres. In the case of the former the moduli for the two fibres are identical over the low extension range important to fabric properties. For the latter the moduli are comparable over the whole stress-strain curve and this makes the high extensibility HWM-fibre particularly suitable for this blend.

Much less well developed is the possibility of blending HWM-fibres with wool. Here it is observed that a shrinkage reduction in direct relations to the wet modulus of the blend fibre is obtained and hence the use of minor proportions of the very high modulus fibres can give very great improvement in fabric behaviour.

It will be evident from the above that we are only just beginning to explore the possibilities of these fibres and that further substantial increases in production are to be expected in the next few years.

*The author is indebted to many colleagues in Courtaulds Ltd. who have made available their work for this paper, and to Dr. N. S. Wooding for his helpful advice on many of the subjects covered. He wishes to thank the Directors of Courtaulds Ltd. for permission to publish this paper.*

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