

PROBLEMS OF POLYNOSIC AND HIGH WET MODULUS FIBRES

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PART I: SPLITTING OF FIBRE

Introduction

Generally speaking, Polynosic type fibres have excellent mechanical and handling characteristics, even after treatment with sodium hydroxide solution, but they have a tendency to split more easily than high wet modulus (HWM) type fibres. On the other hand, the latter have a higher resistance to splitting even though their other properties are comparatively inferior before, and more so after, sodium hydroxide treatment.

Firstly, we examined the tensile physical properties and the splitting characteristics of several types of rayons and cotton, and secondly, examined the relation between the splitting and the fibrillar structure.

Experimental and Results

As samples, we used a regular rayon staple, a high tenacity rayon staple, our experimental HWM rayon staple, our commercial Polynosic rayon staple "Polycot" and a cotton. The tensile physical properties of these samples as given by the Tensilon tensile tester are shown in *Table 1*.

Table 1. Tensile physical properties of the samples

Sample	Tenacity (g/den.)			Elongation (%)			Initial wet modulus at 5% elongation (g/den.)	Water swelling at 20°C by weight (%)
	conditioned	wet	loop	conditioned	wet	loop		
Regular rayon	2.65	1.63	0.75	18.0	20.2	4.4	0.43	95
High tenacity rayon	4.93	3.44	1.09	12.3	16.0	2.3	0.69	76
HWM rayon	4.71	3.31	1.00	15.0	18.3	3.2	0.84	73
Polynosic rayon I	3.75	2.87	0.87	10.8	12.6	2.3	1.02	73
Polynosic rayon II	4.97	3.78	1.11	13.0	14.0	3.0	1.40	72
"Polycot" III	6.03	4.93	1.09	10.8	11.5	2.0	1.92	67
Cotton	3.20	3.66	1.40	9.0	12.2	5.5	1.05	53

As shown in *Table 1*, our Polynosic rayon staple "Polycot" has the highest value of initial wet modulus. It therefore has the highest dimensional stability.

Next, in order to examine the resistance to alkali treatment, we tested the tensile physical properties of these samples after treatment with a 5 per cent (wt/wt) solution of sodium hydroxide for 5 min at 20°C. The results are shown in *Table 2*.

Table 2. Tensile physical properties of the samples after treatment with sodium hydroxide

Sample	Tenacity (g/den.)			Elongation (%)			Initial wet modulus at 5% elongation (g/den.)	Water swelling at 20°C by weight (%)
	conditioned	wet	loop	conditioned	wet	loop		
Regular rayon	1.61	0.87	0.82	33.7	34.5	16.4	0.31	112
High tenacity rayon	2.77	1.90	1.28	45.7	50.6	21.9	0.19	114
HWM rayon	3.74	2.62	1.58	38.6	44.4	16.3	0.33	130
Polynosic rayon I	3.53	2.34	0.96	15.8	16.8	5.1	0.75	80
II	4.45	3.45	0.99	15.6	14.7	3.4	1.03	83
“Polycot” III	5.79	4.57	1.17	12.7	13.2	2.7	1.55	75
Cotton	3.04	3.44	1.69	8.2	11.2	6.7	0.84	56

The change ratio of tensile physical properties of samples are shown in *Table 3*.

Table 3. Change ratios of tensile physical properties of the samples

Sample	Tenacity			Elongation			Initial wet modulus	Water swelling
	conditioned	wet	loop	conditioned	wet	loop		
Regular rayon	0.61	0.53	1.10	1.87	1.71	3.73	0.72	1.18
High tenacity rayon	0.56	0.55	1.18	3.72	3.16	9.52	0.28	1.50
HWM rayon	0.79	0.79	1.58	2.57	2.43	5.10	0.39	1.78
Polynosic rayon I	0.94	0.82	1.10	1.46	1.33	2.22	0.74	1.10
II	0.90	0.91	0.89	1.20	1.05	1.13	0.74	1.15
“Polycot” III	0.96	0.93	1.07	1.18	1.15	1.35	0.81	1.12
Cotton	0.95	0.94	1.21	0.91	0.92	1.22	0.80	1.06

Table 3 shows that, as is well known, both the regular rayon and the high tenacity rayon undergo greater changes as compared to the HWM rayon and Polycot; the last two show better dimensional stability. While comparing the HWM rayon with the Polycot, it can be seen that the former has remarkably less alkali resistance, especially at the initial wet modulus which corresponds to the degree of dimensional stability. However, it has been said that the defects of a Polynosic fibre are its brittleness and its wet fibrillation or splitting.

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In order to examine fibrillar splittings of the samples, they were tested by tumbling them with a 5 per cent solution of sodium hydroxide in a mixer rotating at 3000 rev./min for 50 min. The degree of the splitting is shown in *Figure 1*.

The Polycot shows the greatest splitting, the regular rayon and the HWM rayon show slight partial splitting, but the high tenacity rayon is completely

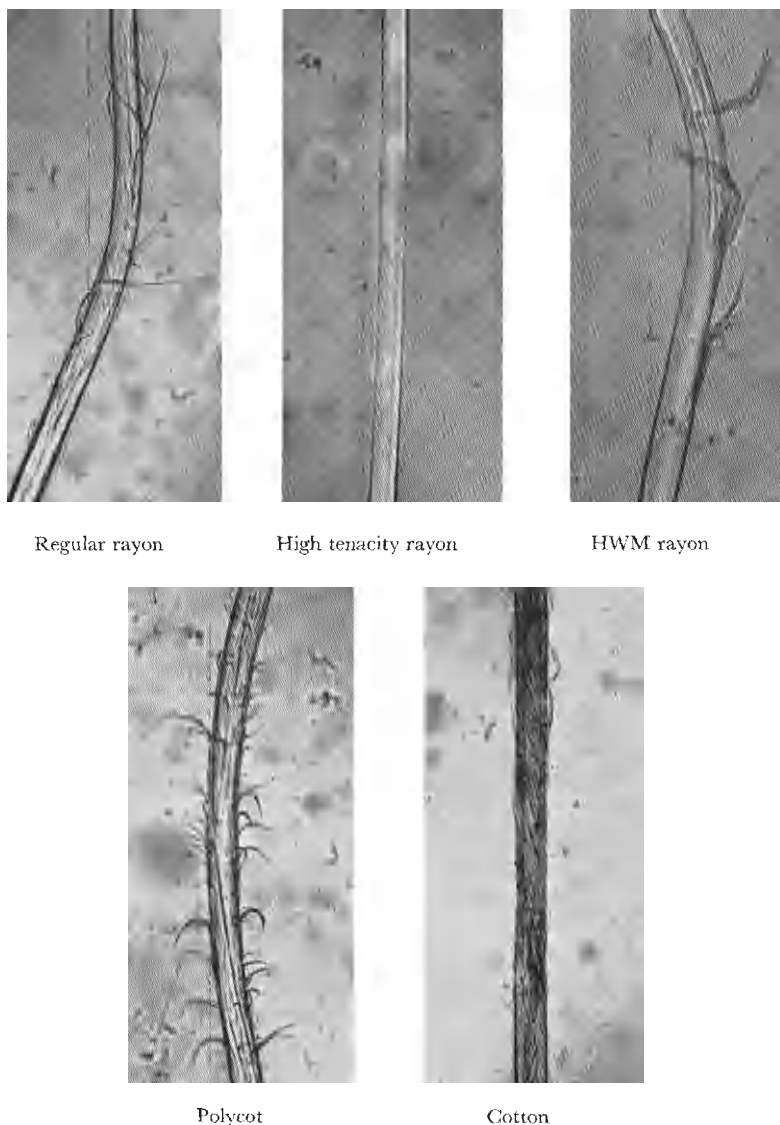


Figure 1. Photomicrographs of splitting of samples (200 \times)

free from splitting. It has been assumed that the splitting phenomena correlate with the fine microfibrillar structure.

Figure 2 shows the results of microscopic observation of these samples after swelling by 3 per cent solution of sodium hydroxide. The photomicrographs of cotton and Polycot show their striking resemblance in fibrillar structure, while that of other rayons show, at least in their core, disordered "mushy" structures with no organized fibrils. Even the regular rayon and the HWM rayon, both without fibrillar structures, show the partial splitting phenomenon.

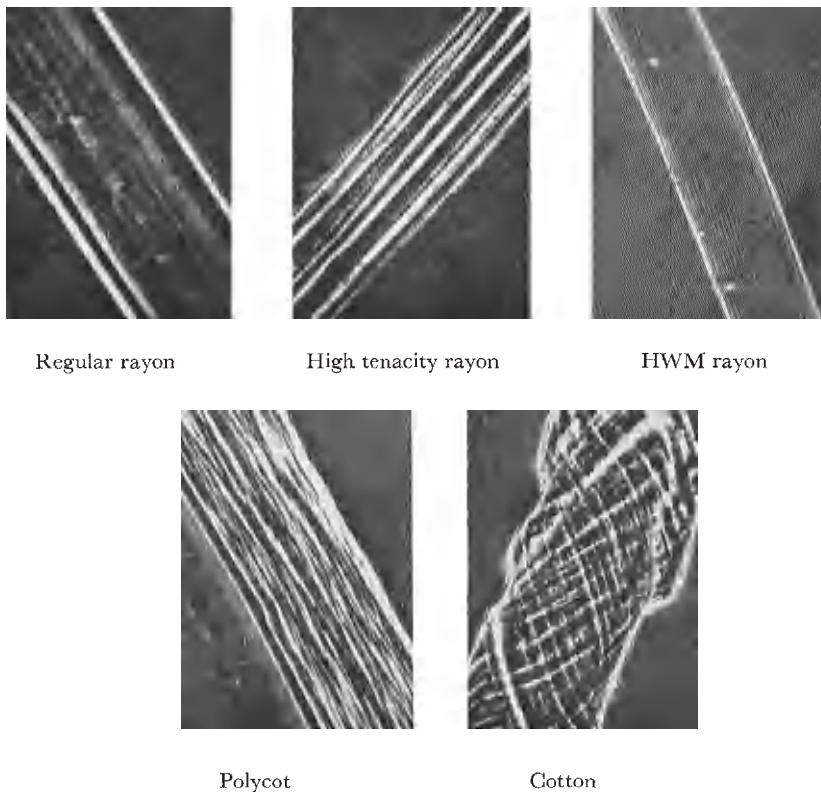


Figure 2. Photomicrographs showing fibrillar structure (900 \times)

In order to ascertain the relationship between splitting and fibrillar structure, we carried out the splitting test with the several experimental Polynosic-type viscose fibres having the fibrillar structures resulting from various spinning bath conditions obtained by changing the concentrations of sulphuric acid and sodium sulphate while keeping the zinc sulphate concentration constant at 0.1 g/l. The results are shown in Figure 3. It can be seen from Figure 3 that whereas all the experimental fibres have a fine fibrillar structure, no splitting occurs with some. The splitting or no splitting zones are shown in Figure 4. From this it appears that the splitting phenomenon is not dependent on the degree of fibrillar structure.

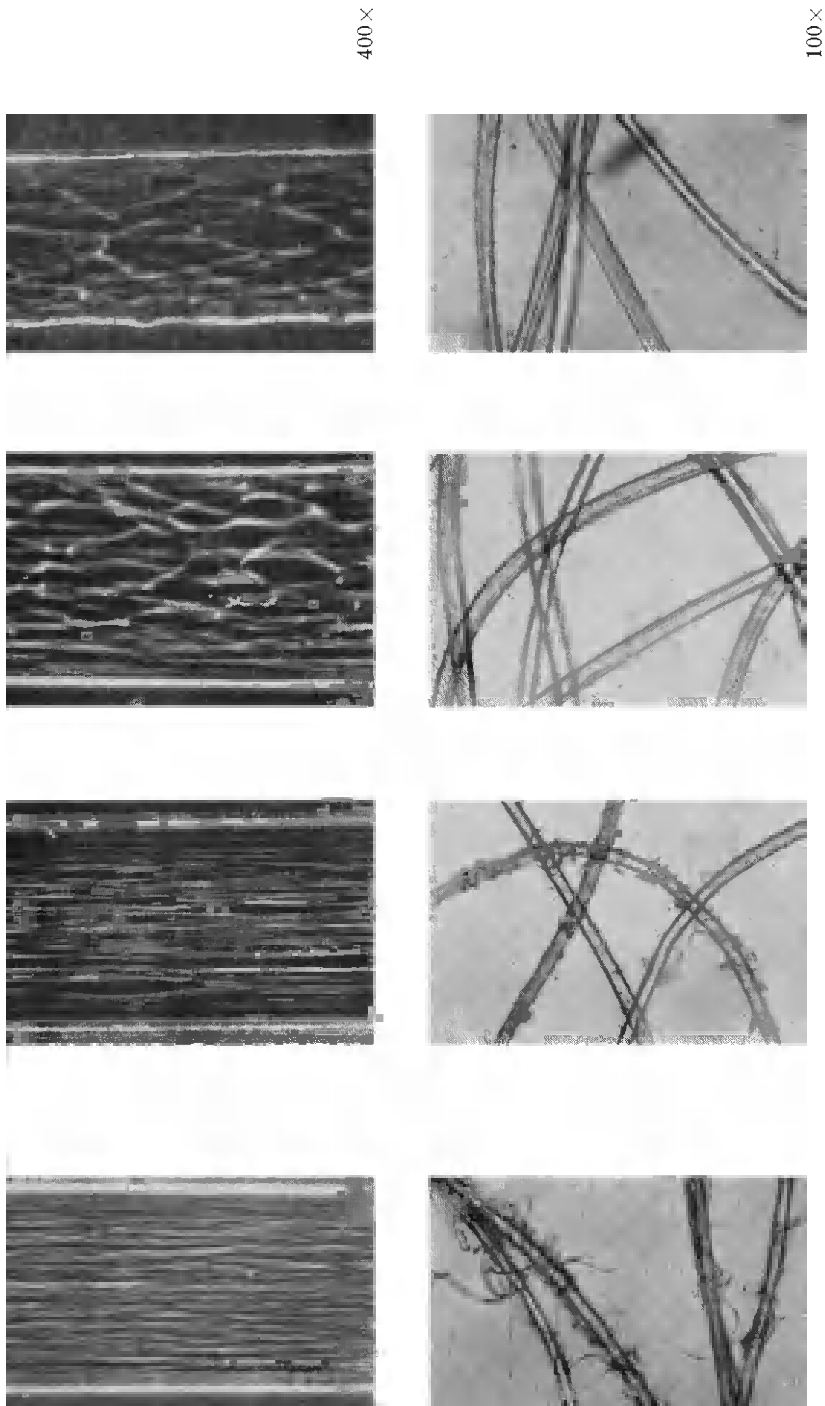


Figure 3. Photomicrographs showing fibrillar structure and splitting of the experimental fibres

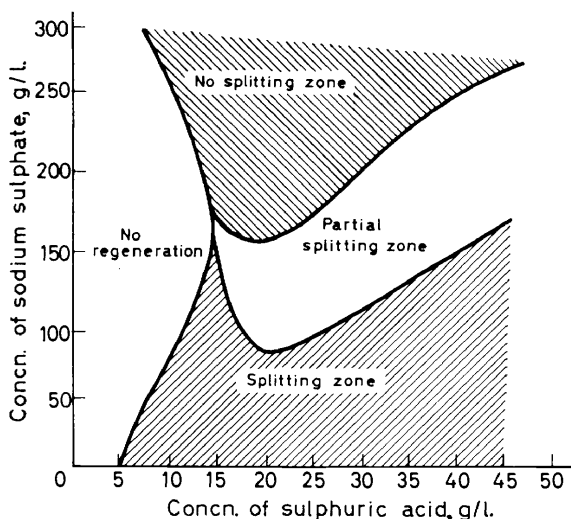


Figure 4. Relation of splitting to spinning bath condition

To find out whether this splitting might be dependent on the lateral affinities between the fibrils, and in particular, whether the existence or not of voids has a bearing on the problem, we investigated the voids in these samples by electron microscope. Cross-sections of these samples shown in *Figure 5* indicate that the Polycot has many voids as also the high tenacity rayon even though the latter is completely free from splitting.

As neither the greater fibrillar structure of the fibre nor the existence of voids now appears to cause the splitting, we have turned our attention to the possible effects on splitting caused by the surface layer state of the fibre.

These experiments are still in progress and so far no definite conclusions have emerged.

PART II: DYEING OF POLYNOSIC FIBRE

Introduction

The hue resulting from the dyeing of a Polynosic fibre treated with a direct dyestuff is less brilliant than that of a regular rayon. This means that the dyeing of a Polynosic fibre, whether staple or filament, gives a broader spectral reflectance curve in the visible region, when measured by a colorimeter, than does that of regular rayon. The difference in brilliancy occurs more remarkably in the dyeing of filament than that of staple.

This phenomenon arises partly from the different optical character of the dyeing caused by difference in fibre cross-section and the degree of the dyestuff's orientation in the fibre, i.e. whether or not the dyestuff is orientated along the fibre's axis.

In this paper, firstly, the colour difference in dyeing hue is estimated by the Kubelka-Munk K/S function¹ and the excitation purity pe according to the standard colorimetric reference system CIE^{2, 3} and secondly, the optical character of the fibre in question is analysed by a spectrophotometer.

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Regular rayon



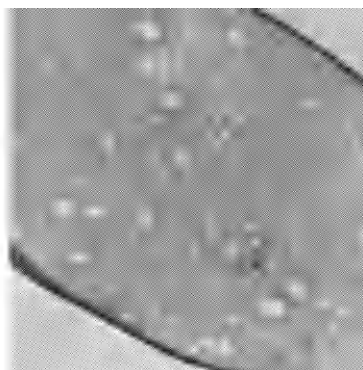
High tenacity rayon



HWM rayon



Polycot



Cotton

Figure 5. Electron photomicrographs showing the cross-section of samples

Experimental

As samples, we used 33-filament, 75-denier regular rayon yarn and 33-filament, 75-denier Polynosic yarn.

These samples were first scoured for 120 min, at 95°C in a bath containing a 0.3 per cent (wt/wt) solution of sodium fatty alcohol sulphate salt and a 0.05 per cent (wt/wt) solution of sodium carbonate. They were then removed from the bath, squeezed and dried.

After that, they were dyed for 10 h at 80°C in a bath containing the dyestuff C.I. Direct Blue 1 together with 0.5 per cent sodium sulphate as an assistant agent. The former has a size of $31\text{\AA} \times 13\text{\AA}$ and was obtained by thrice purifying commercial dye by the Robinson and Mill's method⁴. The concentration of the dyestuff in the bath was varied from 0.1 per cent owf (on the weight of fibre) to 5 per cent owf.

The quantity of the dyestuff absorbed in the fibre, which corresponds to the dye quantity at equilibrium in this dyeing condition, was determined after extraction from the fibre by a 25 per cent (wt/wt) aqueous pyridine solution by colorimetric measurement using a Type EPU-2A Hitachi spectrophotometer.

In addition, the spectral reflection factor curve in the visible region for each sample was measured by a Type RC-III Shimazu colorimeter.

In order to express the luminous concentration, we used the Kubelka-Munk K/S function which corresponds to it and is given by equation (1)

$$K/S = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (1)$$

where K is the absorption coefficient and S is the diffusion coefficient. R_∞ is the reflection factor of an infinitely thick layer and can be read on the spectral reflectance curve in the visible region recorded by the Shimazu colorimeter.

To express colour brilliancy, we used the excitation purity pe , which was determined as follows. The spectral reflection factor R_λ in the visible region was first measured by the Shimazu colorimeter and then the tristimulus values X , Y and Z were calculated by the equations (2), (3) and (4)

$$X = K \int_{380}^{700} P_\lambda R_\lambda \bar{x}_\lambda d\lambda \quad (2)$$

$$Y = K \int_{380}^{700} P_\lambda R_\lambda \bar{y}_\lambda d\lambda \quad (3)$$

$$Z = K \int_{380}^{700} P_\lambda R_\lambda \bar{z}_\lambda d\lambda \quad (4)$$

where K is $1 / \int_{380}^{700} P_\lambda \bar{y}_\lambda d\lambda$, P is the energy distribution of the light source, and \bar{x}_λ , \bar{y}_λ , and \bar{z}_λ are distribution coefficients.

From the obtained tristimulus values X , Y and Z the chromaticity coordinates (x, y) were calculated by the following equations (5) and (6) and chromaticity values were plotted on the diagram.

$$x = \frac{X}{X + Y + Z} \quad (5)$$

$$y = \frac{Y}{X + Y + Z} \quad (6)$$

The excitation purity pe is defined as the percentage ratio of the length between the chromaticity coordinate of the light source (here C light was used, so $x = 0.3101$, $y = 0.3163$) and the chromaticity value obtained, and that between the chromaticity coordinate of the light source and the point where the extrapolated line intersects the spectral locus.

In order to express the optical anisotropic property of the dyestuff in the fibre, i.e. the degree of orientation of the dyestuff molecule in the fibre, we used the value of dichroism D^5 , which was determined as follows.

A fibre was wound around a 9 mm square glass block and was then dipped for 10 h at room temperature in a 10 mm square glass cell containing trisecyl phosphate. Then by the Shimazu spectrophotometer transmittance intensities of light parallel and perpendicular to the fibre axis ($I_{||}$ and I_{\perp} in an undyed fibre, $I'_{||}$ and I'_{\perp} in a dyed fibre) were respectively measured. Using these values, parallel and perpendicular optical densities $K_{||}$ and K_{\perp} were calculated by equations (7) and (8), and then the value of dichroism D was calculated by equation (9)

$$K_{||} = -\log \frac{I'_{||}}{I_{||}} \quad (7)$$

$$K_{\perp} = -\log \frac{I'_{\perp}}{I_{\perp}} \quad (8)$$

$$D = \frac{K_{||} - K_{\perp}}{K_{||} + 2K_{\perp}} \quad (9)$$

Results

The relationships between the Kubelka–Munk K/S function at the maximum absorption wavelength of the dyestuff and the dyestuff concentration D_{ϕ} in the fibres, shown in Figure 6, indicate that as the concentration of the dyestuff on the fibres increases so does the K. M. function K/S .

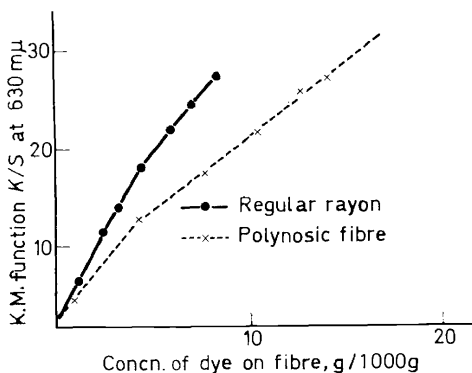


Figure 6. Relation between dye concentration and K/S function

The relationships between the excitation purity pe and the dyestuff concentration and the Kubelka-Munk K/S function are shown in *Figures 7 and 8*.

As can be seen from *Figures 6-8*, the dyeing of the Polynosic fibre gave results inferior to that of the regular rayon in both the luminous concentration K/S and excitation purity pe . In our view the less brilliancy of the dyed

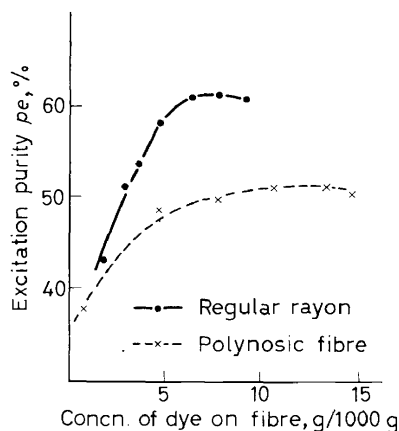


Figure 7. Relation between dye concentration and pe

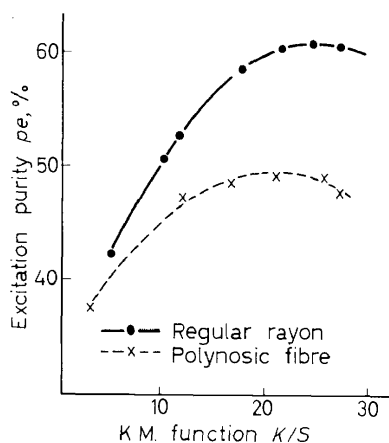


Figure 8. Relation between K/S and pe

Polynosic fibre as compared to the regular rayon is due to the difference between the fibre's cross-section and the dye orientation in the fibre.

In order to ascertain the effect of the cross-section (one of the causes just mentioned) on light transmittance through the fibre, the transmittance values were measured after the fibres had been steeped for 15 h in liquids of various refractive indices, prepared by mixing tricresylphosphate ($n =$

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1.552) and butyl stearate ($n = 1.442$) in different concentrations. The results are shown in *Figure 9*.

At the point at which the fibres and liquids have the same refractive indices (as influences in the light transmittance due to fibre cross-section shape are excluded), the light transmittance is maximum. Maximum transmittance values between the Polynosic fibre and the regular rayon are not so different. At other points, whether at increasing or decreasing values of refractive indices of the liquids, the influence of the fibrous shape appears and the regular rayon transmits remarkably less light than does the Polynosic fibre.

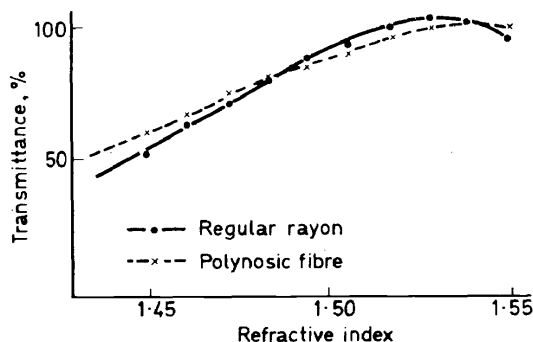


Figure 9. Relation between refractive index and transmittance of light

It seems reasonable to assume that regular rayon has a more irregular refraction than the Polynosic fibre because the former has an irregular serrate cross-section whereas the latter has a round one. The same phenomena would be expected to occur, when the light enters into or comes out of the fibre and thus the regular rayon reflects more light than the Polynosic fibre.

In addition to the previously mentioned phenomena, the Polynosic fibre has a higher molecular orientation than the regular rayon, so when it is treated with a direct dyestuff which is absorbed with its long axis parallel to the cellulose molecular chain, it would be expected that the dyestuff in the Polynosic fibre would show a stronger optical anisotropic property than would that of the regular rayon.

Table 4 shows the values of dichroism D with crystallinity α and orientation factor f obtained by the x-ray method, and the birefringence Δn by the polarization microscopic method.

Table 4. Comparison of the properties of the regular rayon and the Polynosic fibre

	Dichroism D	Crystallinity $\alpha(\%)$	Orientation factor $f(\%)$	Birefringence Δn
Regular rayon	0.244	38	83	0.0200
Polynosic fibre	0.577	45	88	0.0371

As shown in *Table 4*, the birefringence Δn of the Polynosic fibre is higher than that of the regular rayon. Still more attention should be given to the fact that the dyeing of the Polynosic fibre shows a value of dichroism D which is more than twice as high. In other words it shows a strong optical anisotropy.

Accordingly, with the dyeing of the Polynosic fibre, light which has a plane of vibration perpendicular to the fibre axis mostly comes out without being absorbed and this means that the degree of reflectance near the maximum absorption wavelength of the dyestuff is larger.

For these reasons, the spectral reflectance curve in the visible region with the Polynosic fibre treated with the direct dyestuff is broader than that of the regular rayon and the excitation purity pe of the former, obtained from the chromaticity diagram, is lower in value; i.e. the hue of the former looks less brilliant than that of the latter.

In order to confirm this hypothesis, we investigated the dyeings of experimental fibres having different cellulose molecular orientations.

The physical properties of these experimental fibres are given in *Table 5*.

Table 5. Physical properties of experimental fibres

Sample	Tenacity (g/den.)		Elongation (%)		Birefringence	Dichroism
	conditioned	wet	conditioned	wet	Δn	D
I	2.10	1.07	9.4	10.8	0.0206	0.175
II	2.63	1.54	8.2	9.8	0.0320	0.419
III	3.16	1.89	7.8	7.9	0.0371	0.577

These samples were treated by the method mentioned already and then measured. The results are given in *Figure 10*, which shows that as the cellulose molecular orientation decreases, the excitation purity pe increases.

From this experiment, it would be expected that the brilliancy of the

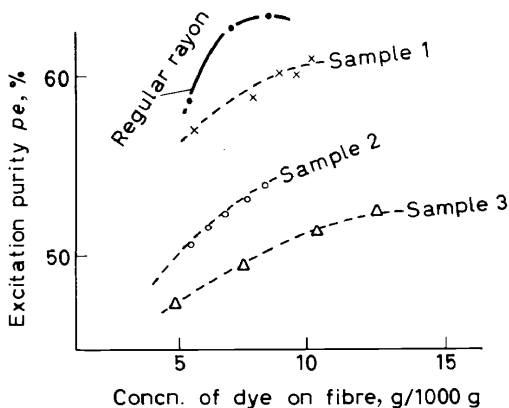


Figure 10. Relation between dye concentration and pe of experimental fibres

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directly dyed Polynosic fibre could be improved by reducing the orientation of dyestuff in the fibre. For this purpose we have developed, after much research, a new process of after treatment with some agents which are effective in reducing the parallel absorption of the dyestuff along the cellulose molecular chain. For example, the brilliancy of the dyed Polynosic fibre was improved by treatment with suitable agents. The results are shown in *Figures 11, 12 and 13*.

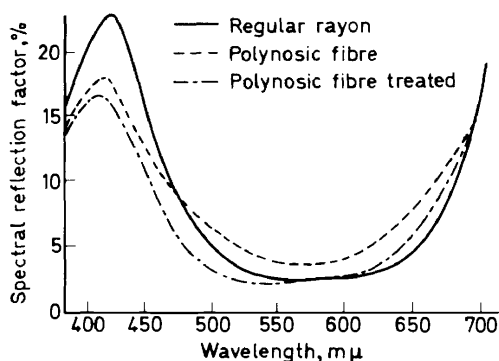


Figure 11. Spectral reflection factor changes associated with agent treatment of Polynosic fibre

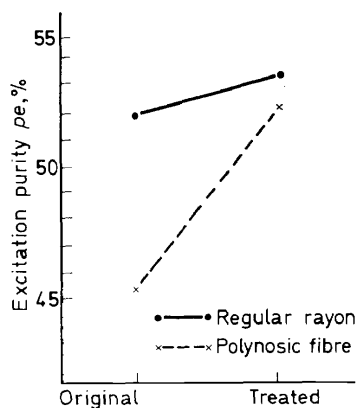


Figure 12. Effect of treatment with agent on pe

Figure 11 shows that the spectral reflectance curve becomes sharper after the fibre has been treated with this agent and thus the brilliancy is increased.

Figures 12 and 13 show the change in the excitation purity pe and K/S function after this treatment. It can be seen from these Figures that the K/S function, which corresponds to the luminous concentration is also increased. It is generally known that treatment with agents decreases the light fastness of dyeing⁶, but we have discovered such agents improve the brilliancy of the dyeing without decreasing the light fastness.

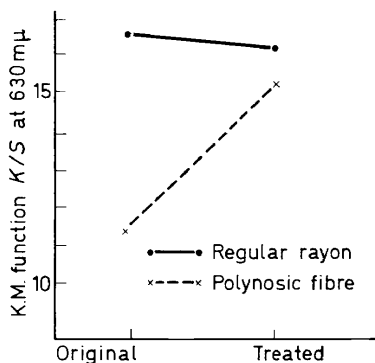


Figure 13. Effect of treatment with agent on K/S

Conclusions

The Polynosic fibre tends to have less brilliancy than regular rayon when it is treated with a direct dyestuff, i.e. the dyeing of the former is inferior to that of the latter in both luminous concentration K/S and excitation purity pe .

This is due to the influence of fibre cross-section and the high orientation of the dyestuff in the fibre.

However, by treatment with agents which are effective in reducing the parallel absorption of the dyestuff along the cellulose molecular chain, we can improve the dyeing hue of the Polynosic fibre.

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