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Improvement of the Wash Fastness of Non-metallised Acid Dyes on Conventional and Microfibre Nylon 6,6

S. M. Burkinshaw* & K. D. Maseka

Department of Colour Chemistry and Dyeing,
The University, Leeds LS2 9JT, UK

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ABSTRACT

The adsorption of a commercial syntan on to both conventional and microfibre nylon 6,6 was found to increase with decreasing application pH, indicating that ion–ion interaction contributes to syntan–fibre substantivity. Uptake of the syntan on both types of fibre increased with decreasing liquor ratio, possibly as a result of syntan aggregation, and also increased with increasing application temperature, this being attributable to the higher kinetic energy of the syntan molecules and the greater extent of fibre swelling operative at the higher temperatures. From the finding that uptake of the synthetic tanning agent on to undyed conventional and microfibre nylon 6,6 followed a BET mechanism, it was postulated that adsorption involves the formation of multi-layers and that forces other than ion–ion contribute towards syntan–fibre interaction. This postulate gained support from the observation that although the presence of 1% omf dye on the two types of fibre reduced the extent of syntan uptake, the mechanism of syntan adsorption on to both substrates was unaffected. The finding that syntan uptake was greater on microfibres than conventional fibres was attributed to the greater surface area of microfibres. Despite the greater uptake of the syntan on to dyed microfibre, the wash fastness of syntanned, dyed microfibre was lower than that of its syntanned, dyed conventional decitex counterpart. The effectiveness of the syntan in improving the wash fastness of several non-metallised acid dyes on microfibre was enhanced by the subsequent application, to the syntanned, dyed substrate, of certain cationic agents. The level of wash fastness achieved using this syntan/cationic agent system was considerably higher than that obtained using an aftertreatment with either 4% omf syntan or the full backtan.

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* Corresponding author.

INTRODUCTION

The wash fastness properties of non-metallised acid dyes in medium to heavy depths on polyamide fibres often leave much to be desired.[1–3] The earliest method of improving the wash fastness properties of such dyes on nylon fibres involved the sequential application of tannic acid and potassium antimonyl tartrate to the dyed material.[1–4] The effectiveness of this full backtan process is considered[1,2] to be due to the formation of a sparingly water-soluble, high relative molecular mass (M_r) potassium antimonyl tannate complex situated at the surface of the dyed fibre that reduces diffusion of dye out of the substrate during wet treatments. Despite the excellent improvement in wet fastness of non-metallised acid dyes on nylon afforded by the full backtan aftertreatment, owing to various disadvantages inherent in the process its use has largely been superseded by that of synthetic tanning agents (syntans).[1–3]

The majority of syntans marketed for use as an aftertreatment of dyed polyamide fibres are typically water-soluble, anionic, formaldehyde polycondensates of sulphonated dihydroxydiarylsulphones.[2,5,6] The particular commercial syntan employed in this work, namely Matexil FA-SNX (ICI), is described[7] as a sulphonated high molecular weight product based on phenol sulphone. It has been proposed[2] that syntans are adsorbed at the periphery of the dyed polyamide fibre and that their ability to improve the wash fastness properties of non-metallised acid dyes on nylon fibres is attributable to this peripheral ‘layer’ of syntan molecules reducing the diffusion of dye out of the dyed, treated fibre during washing; ion–ion repulsion effects operating between the anionic syntan and the anionic dye also contribute to reduced dye diffusion. However, the precise mechanism by which syntans improve the wash fastness properties of dyed nylon fibres remains unclear in view of the varied composition of the polycondensates.

Microfibres are a relatively recent introduction,[1,8–11] being a consequence of the trend in recent decades towards finer filament counts. It is generally agreed that the term ‘microfibre’ denotes a yarn comprising filaments of less than 1 decitex per filament (dtexpf).[1] As a consequence of its greater surface area, more dye has to be applied to microfibre to obtain the same visual depth of shade as its dyed conventional decitex counterpart, with the result that for dyeings of the same visual depth, the wash fastness of dyed microfibre is lower than that of dyed conventional fibre.[1]

This paper describes the exhaustion application characteristics of the commercial syntan Matexil FA-SNX on both dyed and undyed, conventional and microfibre nylon 6,6 fabrics, as well as a method for enhancing the effectiveness of the syntan in improving the wash fastness of several dyes on both types of dyed nylon 6,6 fabrics.

EXPERIMENTAL

Materials

Fabrics

Two types of knitted nylon 6,6 fabrics, namely conventional (78F46; 1.69 dtexpf) and microfibre (85F92; 0.92 dtexpf) were supplied by Du Pont Fibres (UK); each type of fibre was scoured prior to use by treatment at 70°C for 1 h in a stirred, aqueous (tap water) solution (50:1 liquor ratio) containing Lenetol B conc. (ICI) (1 g l^{-1}) (a synergistic blend of ethoxylated fatty alcohols[7]) and sodium carbonate (1 g l^{-1}) followed by thorough rinsing in tap water.

Dyes

Commercial samples of Nylomine Blue A-G (CI Acid Blue 25), Nylomine Navy C-2R (CI Acid Blue 113), Nylomine Green C-G (CI Acid Green 27) and Nylomine Orange C-G (CI Acid Orange 67), each kindly supplied by Zeneca Specialties, as well as Nylosan Brilliant Blue N-FL (CI Acid Blue 278), Nylosan Bordeaux N-BL (CI Acid Red 119) and Nylosan Orange N-RL (CI Acid Orange 127), each generously supplied by Sandoz (UK), were used.

Syntan

A commercial sample of Matexil FA-SNX was generously supplied by ICI Surfactants.

Dyeing auxiliaries

Commercial samples of Matexil LA-NS (the sodium salt of highly sulphonated oil/ethylene oxide condensate[7]) and Matexil LC-CWL (ethylene oxide condensate[7]) were kindly supplied by ICI Surfactants.

Cationic agents

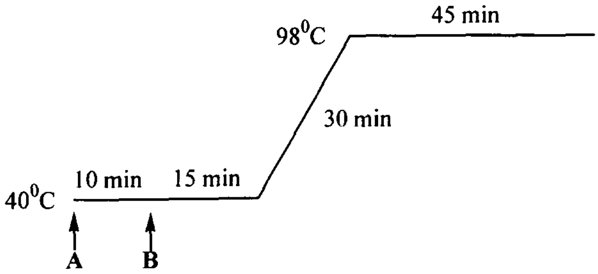
Commercial samples of Matexil FC-ER (low M_r resin[7]), Matexil FC-PN (dicyandiamide condensate[7]) as well as compounds B and B2 (whose composition cannot be disclosed owing to commercial confidentiality) were generously supplied by ICI Surfactants.

All other reagents were of general purpose grade.

Procedures

Dyeing

Samples (2.000 g) of nylon 6,6 fabric were dyed in sealed, stainless steel dyepots of 300 cm^3 capacity housed in a Zeltex Lowboy laboratory-scale



A	fabric	
	HCOOH	1% omf
	NH_4COCH_3	3.5% omf
B	dye	
	Matexil LC-CWL	1% omf
	Matexil LA-NS	1% omf

Fig. 1. Dyeing method.

dyeing machine using a liquor ratio of 50:1; the dyeing method used is shown in Fig. 1. At the end of dyeing, the dyed sample was removed, rinsed thoroughly in tap water and either allowed to dry in the open air or aftertreated.

Four shades were produced:

(i) Acid Blue
1% omf CI Acid Blue 25

(ii) Navy Blue
2.5% omf CI Acid Blue 113
0.29% omf CI Acid Orange 67
0.39% omf CI Acid Bue 278

(iii) Maroon
4.94% omf CI Acid Red 119
0.86% omf CI Acid Orange 127

(iv) Green
1.8% omf CI Acid Orange 67
2.24% omf CI Acid Green 27
1.125% omf CI Acid Blue 113

Aftertreatment of dyed samples with the full backtan

This was carried out in sealed, stainless steel dyepots of $300\,cm^3$ capacity housed in a Zeltex Lowboy laboratory-scale dyeing machine. The rinsed sample of dyed nylon 6,6 fabric was treated, using a liquor ratio of 50:1, with tannic acid (2% omf) at pH 2.5 (adjusted using formic acid) for 30 min at 95°C. The tannic acid treated sample was then removed and treated, for 15 min at 95°C, with 2% omf potassium antimonyl tartrate at pH 2.5 (adjusted using formic acid) using a 50:1 liquor ratio. The full backtanned dyeing was then thoroughly rinsed in tap water and allowed to dry in the open air.

Aftertreatment of dyed samples with Matexil FA-SNX

The rinsed sample of dyed nylon 6,6 fabric was treated in sealed stainless steel dyepots of 300 cm^3 capacity housed in a Zeltex Lowboy laboratory-scale dyeing machine, using a liquor ratio of 50:1, with Matexil FA-SNX (2% or 4% omf) at pH 4 (adjusted using formic acid) for 30 min at 80°C. The syntanned dyeing was then thoroughly rinsed in tap water and allowed to dry in the open air.

Aftertreatment of syntanned, dyed samples with cationic agents

This was carried out in sealed, stainless steel dyepots of 300 cm^3 capacity housed in a Zeltex Lowboy laboratory-scale dyeing machine. At the end of the aftertreatment with Matexil FA-SNX (2% omf), the syntanned, dyed material was thoroughly rinsed in tap water and treated, using a liquor ratio of 50:1, with the cationic agent (2% omf) at pH 5 (McIlvaine buffer[12,13]) for 20 min at 50°C. The treated dyeing was then thoroughly rinsed in tap water and allowed to dry in the open air.

Measurement of the rate of syntan uptake on to undyed nylon 6,6 fabric

Effect of pH. McIlvaine buffers,[12,13] prepared using distilled water, were used to achieve the appropriate treatment pH value. Samples (2.000 g) of nylon 6,6 fabric were treated with Matexil FA-SNX (2% omf) at pH values of 2.2, 3, 4, 5, 6 and 7 at 80°C for 1 h using a liquor ratio of 50:1 in partially sealed glass dyepots of 300 cm^3 capacity housed in a Zeltex Vistacolor laboratory-scale dyeing machine. Adsorption rates were determined by continuously monitoring the absorbance of the syntan treatment bath at 264 nm using a 1 mm quartz flow-through cell housed in a Pye–Unicam SP 8600 spectrophotometer; the arrangement of the apparatus used is shown in Fig. 2. The absorbance data obtained were converted to percentage exhaustion values using eqn (1), where A_0 and A_t are the absorbances at times 0 and t, respectively.

$$\frac{A_0 - A_t}{A_0} \times 100 \tag{1}$$

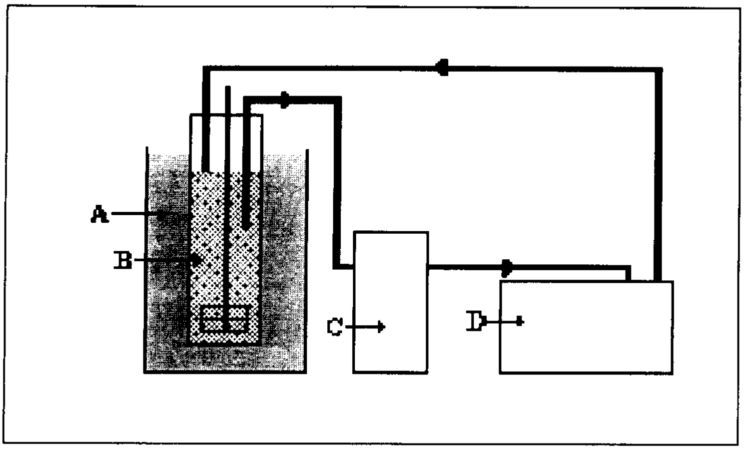


Fig. 2. Schematic representation of apparatus used to continuously monitor the absorbance of treatment liquor where **A** represents the Vistacolor dyeing machine, **B** the dyepot, **C** the peristaltic pump and **D** the spectrophotometer.

Effect of temperature. Samples (2.000 g) of nylon 6,6 fabric were treated with Matexil FA-SNX (2% omf) at pH 5 at both 50°C and 80°C for 1 h using a liquor ratio of 50:1 in partially sealed glass dyepots of 300 cm^3 capacity housed in a Zeltex Vistacolor laboratory-scale dyeing machine. Adsorption rates were determined by continuously monitoring the absorbance of the syntan treatment bath using the equipment and procedure described above, and were converted to percentage exhaustion values as described above.

Effect of liquor ratio. Samples (2.000 g) of nylon 6,6 fabric were treated with Matexil FA-SNX (2% omf) at pH 5 at 95°C for 1 h using liquor ratios of 25:1 and 100:1 in partially sealed glass dyepots of 300 cm^3 capacity housed in a Zeltex Vistacolor laboratory-scale dyeing machine. Adsorption rates were determined by continuously monitoring the absorbance of the syntan treatment bath using the equipment and procedure described above; the absorbance values were converted to percentage exhaustion using the method described above.

Equilibrium adsorption isotherms of the syntan on undyed and dyed nylon 6,6 fabrics

Both undyed and also dyed (CI Acid Blue 25; 1% omf) nylon 6,6 samples (2.000 g) were treated, using a 100:1 liquor ratio, in a series of aqueous acidic (pH 4) solutions of Matexil FA-SNX of various concentrations (1–16 g l^{-1}) at 80°C for 7 h in sealed stainless steel dyepots of 300 cm^3

capacity housed in a Zeltex Polycolor laboratory-scale dyeing machine. At the end of treatment, the concentration of syntan remaining in the treatment liquor was determined by reference to the extinction coefficient of a calibration plot of the syntan at 264 nm (the λ_{max} of the syntan in the medium).

During treatment of the dyed substrates with syntan, dye was desorbed from the fibres. Since both the syntan and the dye absorbed at 264 nm, the absorbance values thus obtained related to the concentration of both syntan and dye in the treatment bath. In order to calculate the actual concentration of syntan in the treatment bath and thus the extent of syntan uptake, it was necessary to subtract, from the combined syntan and dye absorbance value at 264 nm, the absorbance of the dye alone at this wavelength. Before this could be done, however, it was necessary to ensure that there was no interaction between the dye and syntan. Solutions of the dye (0.01 $g\,l^{-1}$) and also of the syntan (0.01 $g\,l^{-1}$) were prepared in pH 4 buffer solution and the absorbance of the two solutions measured at both 620 nm (the λ_{max} of the dye in this medium) and 264 nm using a 1 cm path length quartz cell housed in a Pye–Unicam SP 800 spectrophotometer. A solution was prepared containing dye (0.01 $g\,l^{-1}$) and Matexil FA-SNX (0.01 $g\,l^{-1}$) in pH 4 buffer solution, and the absorbance of the solution was measured at both 264 and 620 nm. It was found that the absorbances at 620 nm of the dye solution and of the dye–syntan solution were identical, and that the absorbance of the dye–syntan solution at 264 nm was the sum of the value of the dye solution and the syntan solution separately at this wavelength. It was thus concluded that no interaction had occurred between the syntan and dye, and that the absorbances of the syntan and dye at 264 nm were additive.

To calculate the actual concentration of syntan in the treatment bath, the absorbance of the treatment bath was measured at both 620 nm and at 264 nm. The absorbance value obtained at 620 nm was converted to dye concentration ($g\,l^{-1}$) by reference to the extinction coefficient of a calibration plot of the dye at 620 nm in pH 4 buffer solution. Using eqn (2), the concentration of desorbed dye, as determined at 620 nm (C_{D620}), was converted to the corresponding absorbance value of the dye at 264 nm (A_{D264}) by reference to the extinction coefficient (ϵ_{D264}) of a calibration plot of the dye at 264 nm in pH 4 buffer solution.

$$A_{D264} = \epsilon_{D264} \times C_{D620} \tag{2}$$

The resulting absorbance value of the dye at 264 nm was then subtracted from the absorbance value of the syntan plus dye at this wavelength (A_{SD264}) to yield the absorbance of the syntan alone at 264 nm (A_{S264}), using eqn (3).

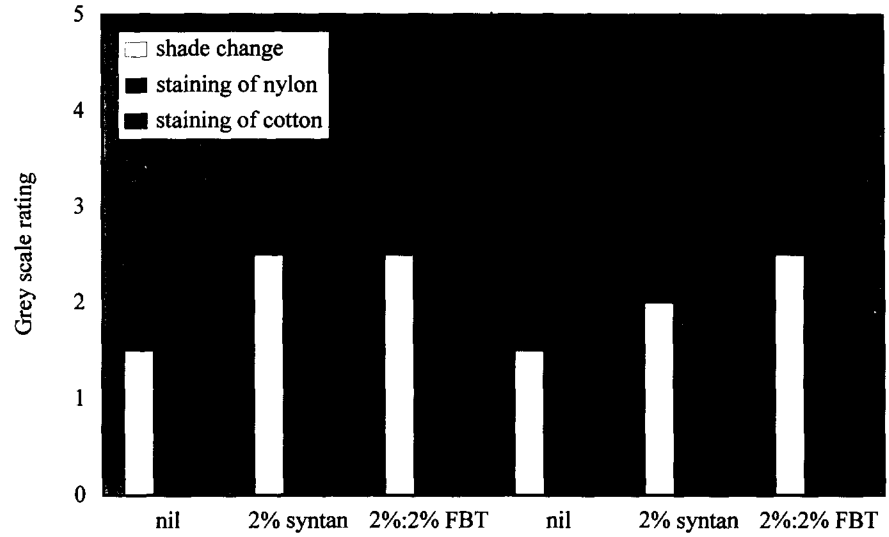


Fig. 3. Wash fastness of 1% omf CI Acid Blue 25 dyeings.

$$A_{S264} = A_{SD264} - A_{D264} \tag{3}$$

The concentration of syntan adsorbed onto the substrate was then calculated using eqn (4).

$$C = C_0 - (A_{S264}/\epsilon_{S264}) \tag{4}$$

where C is the concentration of syntan adsorbed on to the fibre and C_0 the concentration of syntan in the treatment bath at time $t = 0$.

Fastness determination

The fastness of dyed samples to the ISO C06/C2 wash test and the ISO B02 light test was determined using the standard methods.[14]

RESULTS AND DISCUSSION

Figure 3 shows that the fastness to the ISO C06/C2 wash test of CI Acid Blue 25 (1% omf) on both conventional decitex and microfibre nylon 6,6 fabrics left much to be desired; clearly, the fastness of the microfibre dyeing was lower than that of its dyed conventional decitex counterpart. Figure 3 also shows the extent to which aftertreatment with 2% omf Matexil FA-SNX and also 2%:2% omf tannic acid:potassium antimonyl tartrate (the full backtan) enhanced the wash fastness of the dyeings on both fibre types; it is apparent that aftertreatment was less effective in the case of the dyed microfibre. As complete dyebath exhaustion had been achieved on both types of fibre, the results displayed in Fig. 3 are comparative, and therefore show that although the same amount of dye was present on conventional and micro nylon fibres, the extent of dye loss that occurred during washing was greater from the dyed microfibre. This finding warranted investigation and, as the use of the full backtan aftertreatment has been largely superseded by that of syntans, a study was made of the adsorption characteristics of the syntan on both types of substrate to determine whether the observed lower effectiveness of the syntan aftertreatment of dyed microfibre (Fig. 3) was due to a difference in the mechanism by which the syntan was adsorbed on to conventional and microfibre nylon 6,6 fabrics.

Figures 4 and 5 clearly show that both the rate and extent of adsorption of Matexil FA-SNX onto conventional and microfibre nylon 6,6 increased with decreasing application pH. These findings concur with those[15] for the adsorption of another commercial syntan, Cibatex PA (Ciba–Geigy), on conventional nylon 6,6 fibres, and also with those[13,16,17] for the adsorption of several commercial syntans on wool. The results in Figures 4 and 5 indicate that ion–ion interaction, operating between the protonated amino end groups in the nylon fibre, and presumably sulphonic acid groups in the anionic syntan, contributes towards syntan–fibre substantivity.

Figures 6 and 7 show that both the rate and extent of uptake of the syntan on conventional and microfibre nylon 6,6 increased with decreasing liquor ratio; these findings agree with those obtained for the adsorption of several syntans on wool[13,16,17] and, as previously suggested,[13,16,17] can be attributed to a corresponding increase in the effective concentration of syntan in the treatment bath that accompanies a reduction in liquor ratio. Although no information is provided concerning the chemical composition and relative molecular mass (M_r) of Matexil FA-SNX, it can be suggested that aggregation of the syntan will occur in solution by virtue of both polar and non-polar forces operating between the large molecular size syntan molecules. Thus, as proposed earlier,[13,16,17] the increased effective concentration of syntan that accompanied a decrease in liquor ratio can be expected to increase the degree of syntan aggregation in solution, which in turn can be considered to result in greater uptake of the tanning agent.

Figures 8 and 9 demonstrate that both the rate and extent of adsorption of the syntan on to conventional and microfibre nylon 6,6 increased with increasing application temperature; these results concur with those obtained

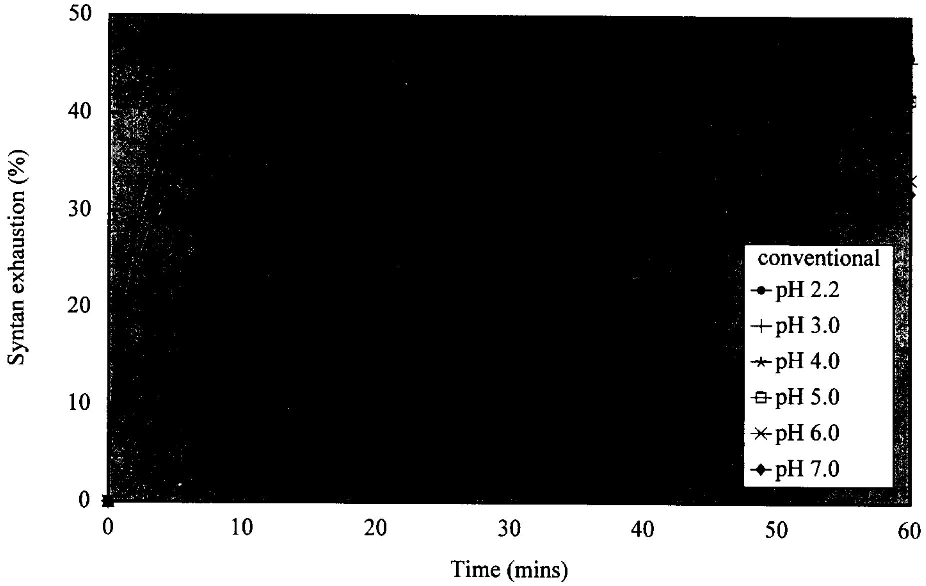


Fig. 4. Effect of pH on syntan uptake on to conventional fibre (2% omf; 50:1 liquor ratio; 80°C).

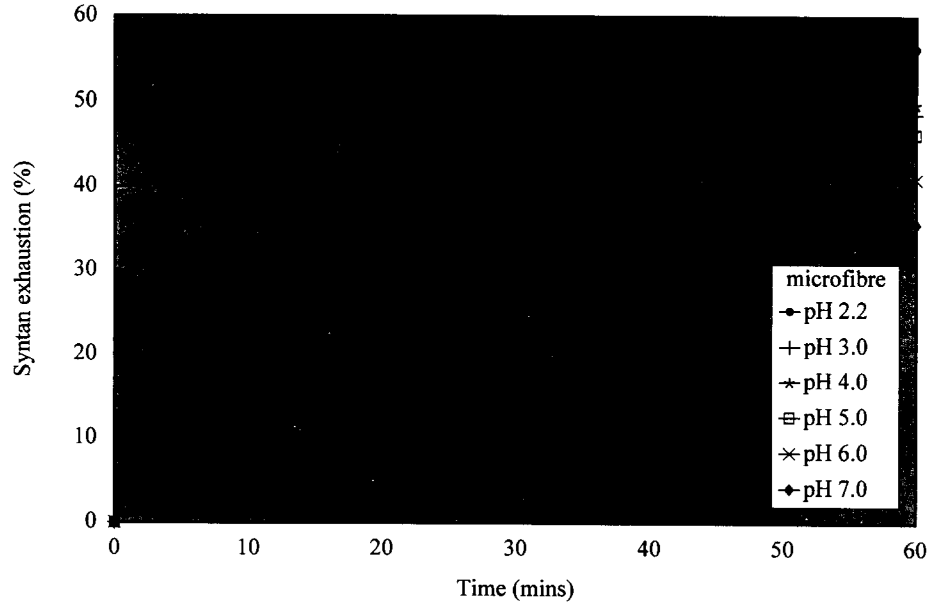


Fig. 5. Effect of pH on syntan uptake on to micro fibre (2% omf; 50:1 liquor ratio; 80°C).

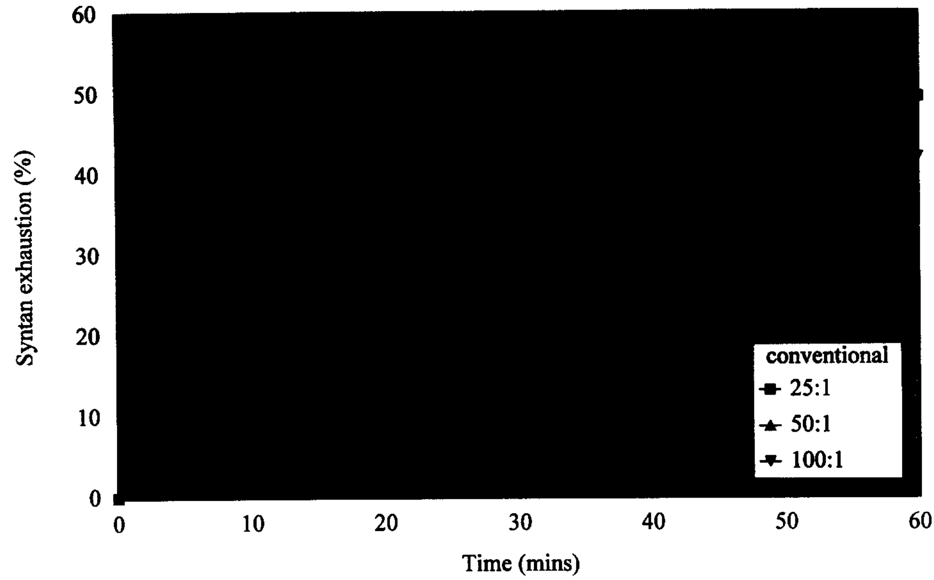


Fig. 6. Effect of liquor ratio on syntan uptake on to conventional fibre (2% omf; pH 5; 95°C).

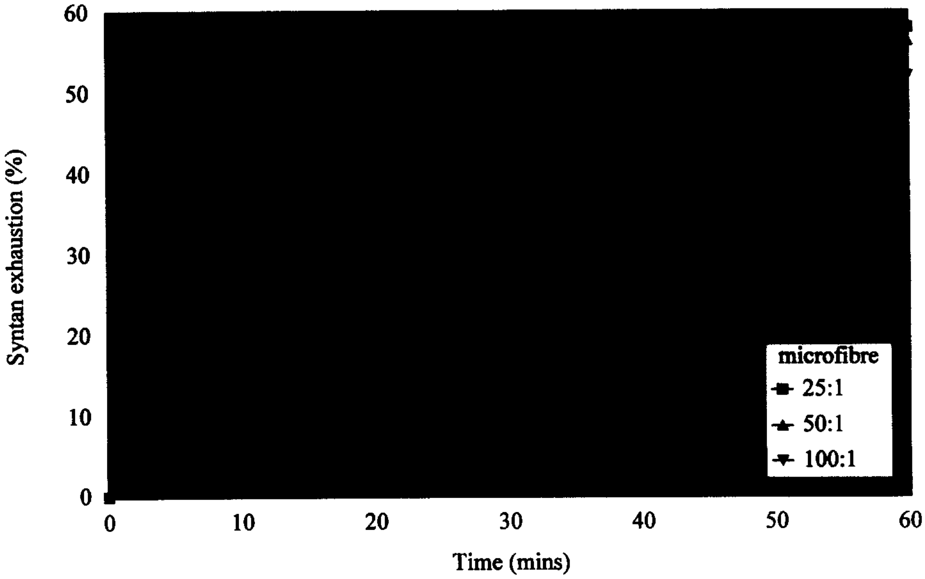


Fig. 7. Effect of liquor ratio on syntan uptake on to micro fibre (2% omf; pH 5; 95°C).

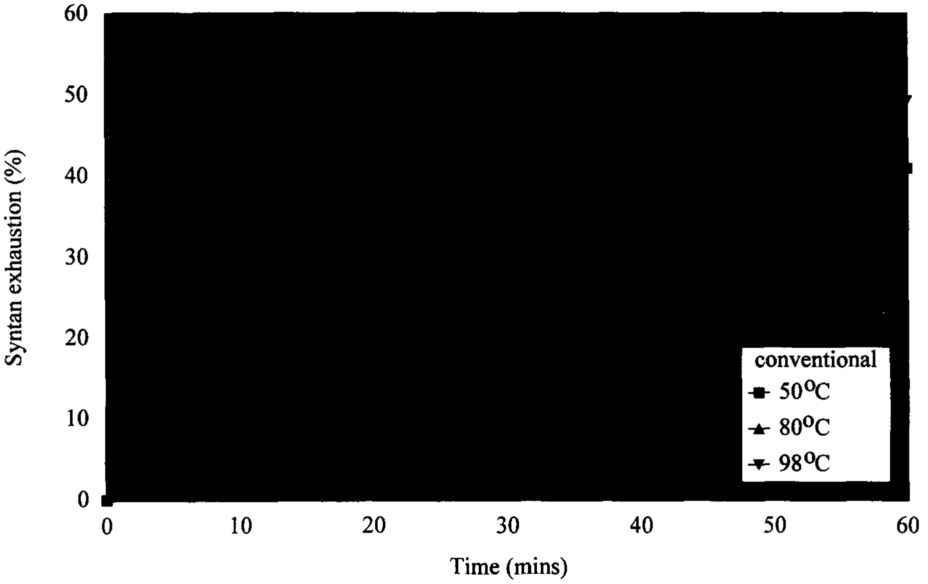


Fig. 8. Effect of temperature on syntan uptake on to conventional fibre (2% omf; 50:1 liquor ratio; pH 5).

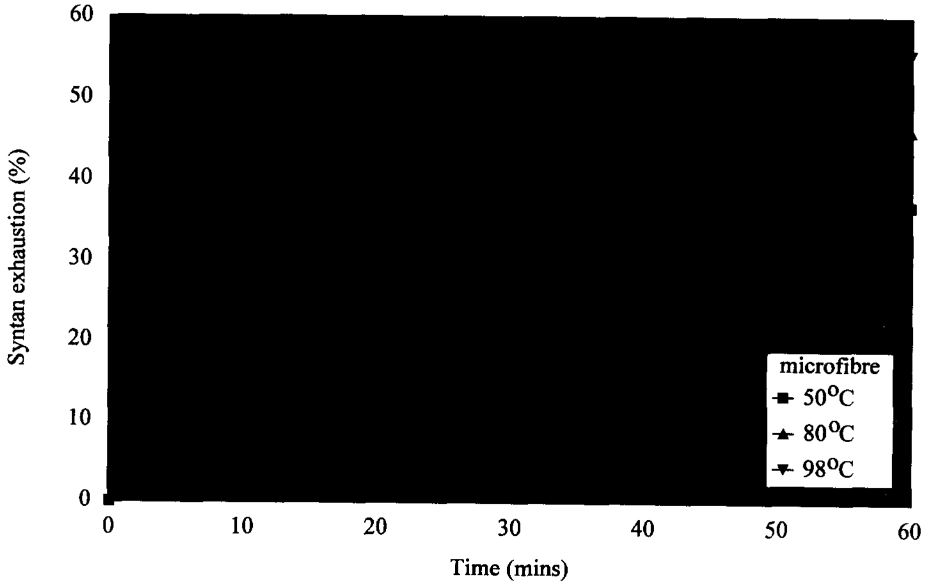


Fig. 9. Effect of temperature on syntan uptake on to micro fibre (2% omf; 50:1 liquor ratio; pH 5).

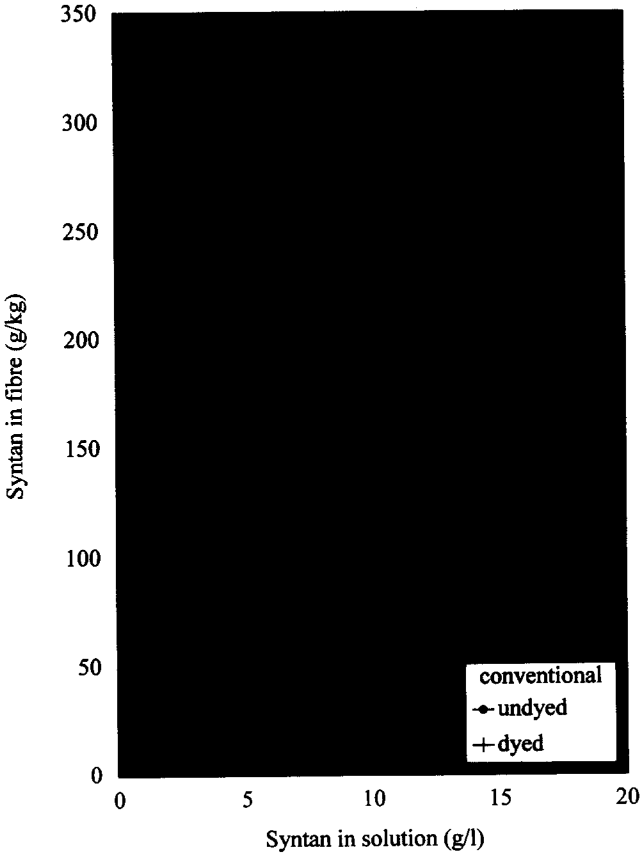


Fig. 10. Adsorption isotherm for syntan uptake on to conventional fibre (pH 4; 100:1 liquor ratio; 80°C).

for the adsorption of several syntans on wool[13,16,17] and, as previously suggested,[13,16,17] can be attributed to the higher kinetic energy of the syntan molecules and their consequent greater diffusional power within the substrate, together with the higher extent of fibre swelling that accompanies an increase in application temperature. Inspection of Figs 4–9 reveals that both the rate and extent of syntan uptake were greater on microfibres at each of the six pH values, the three liquor ratios and the three temperatures employed; this finding can be attributed to the greater surface area of this type of fibre.

The equilibrium isotherms of the syntan on undyed conventional (Fig. 10) and undyed microfibre (Fig. 11) nylon 6,6 show that adsorption on to both types of fibre followed a BET mechanism, which implies that uptake involves the formation of multilayers of adsorbed syntan molecules. Although these

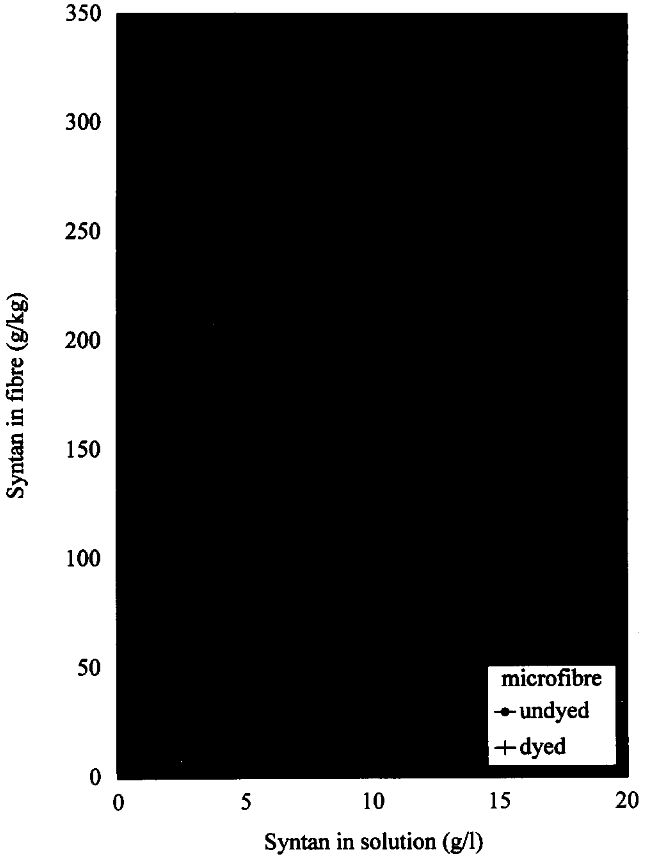


Fig. 11. Adsorption isotherm for syntan uptake on to micro fibre (pH 4; 100:1 liquor ratio; 80°C).

results agree with those obtained for the adsorption of various syntans on wool,[13,16,17] they disagree with those obtained[18] for the adsorption of both Cibatex PA and a novel sulphonated novolac syntan on to nylon 6, each of which was found to follow a Freundlich mechanism. This disagreement between the Freundlich mechanism proposed by Cook & Guthrie[18] and the BET mechanism obtained both by Burkinshaw & Nikolaides[13,16,17] and the present authors can be attributed to differences in the concentration ranges employed by the different workers. In the case of the adsorption isotherms of various syntans on wool,[13,16,17] a concentration range of between 0.5 and 14 g l^{-1} was used and concentrations of between 1 and 16 g l^{-1} were employed in the present work; in contrast, the concentration range used by Cook & Guthrie for each of the two syntans employed in their study was 0.05–0.25 g l^{-1}. Thus, it can be postulated that the Freundlich isotherms obtained by Cook & Guthrie may, owing to the low concentration of syntan used, constitute the initial region of BET isotherms. Nevertheless, the results shown in Figs 10 and 11, together with the previous findings of Cook & Guthrie[18] and also Burkinshaw & Nikolaides,[13,16,17] clearly indicate that syntan adsorption on to undyed nylon and wool fibres does not occur simply by virtue of ion–ion interaction operating between the anionic syntan molecules and specific sites (namely the protonated amino groups) in each fibre. Therefore other forces of interaction, for example hydrogen bonding and ion–dipole as well as hydrophobic interaction operating between the aromatic centres in the syntan molecules and hydrophobic regions of the fibre, contribute towards syntan–fibre interaction. In view of the BET adsorption mechanism obtained in the present work (Figs 10 and 11), such forces can also be considered to contribute towards multi-layer adsorption of the syntan, which will also contribute towards syntan–fibre substantivity. Figures 10 and 11 also show that the extent of uptake of the syntan on to microfibre nylon was greater than that obtained on conventional fibre; this finding concurs with those described above for the effects of temperature, liquor ratio and pH on uptake of the syntan and, as previously mentioned, can be attributed to the greater surface area of the microfibre substrate.

An attempt was made to further determine the influence that ion–ion interaction makes towards syntan adsorption; since it is widely held[3] that the adsorption of a small molecular size anionic dye (such as CI Acid Blue 25) on to nylon 6,6 is confined to the amino end groups within the polymer, then the presence of the dye should markedly affect the adsorption of the syntan if uptake of the tanning agent occurred mainly by virtue of ion–ion forces of interaction at the terminal amino groups in the substrate. Figures 10 and 11 clearly show that the presence of 1% omf of the dye on the substrate reduced the extent of adsorption of Matexil FA-SNX on to both conventional and microfibre nylon 6,6. However, it is also clear that adsorption of the syntan on to each type of dyed nylon 6,6 fibre occurred by a BET mechanism, and therefore that the presence of the dye did not affect the mechanism of adsorption of the syntan. These findings support the earlier proposal that uptake of the syntan does not occur primarily by virtue of ion–ion forces of interaction, and therefore that other polar and non-polar forces contribute towards syntan–fibre substantivity. Further support for the proposal that adsorption of syntans on nylon 6,6 occurs by a combination of ion–ion forces together with both polar and non-polar forces of interaction was demonstrated[17] by the finding that Cibatex PA was adsorbed on to basic-dyeable nylon 6,6, and also on to acid-dyeing nylon 6,6, the latter fibre having been chemically modified such that all available amino end groups were replaced with sulphonic acid groups, to an extent that was not substantially different to that secured on regular acid-dyeing nylon 6,6 fibre.

Thus, it can be concluded that the uptake of Matexil FA-SNX onto microfibre nylon 6,6 differs from that onto its conventional decitex counterpart insofar as uptake of the tanning agent occurs at a faster rate and to a greater extent on microfibre, this being attributable to the greater surface area of the latter substrate. However, the mechanism of adsorption of the syntan was identical for both types of fibre, namely that in addition to ion–ion interaction, other forces contribute to syntan–fibre substantivity, giving rise to a BET adsorption mechanism; this latter finding is not unexpected, as both the microfibre and conventional nylon 6,6 fibres employed in the study comprised the same polymer.

Returning to the wash fastness results (Fig. 3), which revealed that although the same amount of CI Acid Blue 25 was present on dyed conventional and micro nylon fibres, the extent of dye loss that occurred during washing was greater from the dyed microfibre, it can now be postulated that the observed lower effectiveness of the syntan aftertreatment on dyed microfibre was not due to a difference in the mechanism by which the syntan was adsorbed on to the microfibre fabric. Indeed, as the uptake of the syntan was greater on dyed microfibre than on dyed conventional fibre (Figs 10 and 11), the observed lower effectiveness of the syntan aftertreatment on dyed microfibre can be attributed to the greater surface area of the microfibre, this resulting in a greater surface area from which dye loss can occur.

An attempt was made to enhance the effectiveness of Matexil FA-SNX. The full backtan process comprises the sequential application of tannic acid and potassium antimonyl tartrate to the dyed material; in this sequential process, the potassium antimonyl tartrate insolubilises the anionic water-soluble tannic acid, resulting in the formation of a large M_r, sparingly water-soluble, potassium antimonyl tannate complex situated at the surface of the dyed fibre which reduces diffusion of dye out of the substrate during wet treatments. Matexil FA-SNX and other syntans marketed for use as an aftertreatment of dyed polyamide fibres are typically water-soluble anionic formaldehyde polycondensates of sulphonated dihydroxydiarylsulphones. Thus, by analogy with the full backtan process, the effectiveness of the syntan aftertreatment of dyed nylon might be enhanced if it were possible to subsequently treat syntanned, dyed nylon and form a sparingly water-soluble high M_r complex on the dyed nylon; as the syntan is strongly anionic, then a suitable cationic compound should be capable of forming such a complex. Hence, various cationic compounds were used in conjunction with the syntan, and their abilities to enhance the effectiveness of the tanning agent were assessed; in this context, the results presented represent only a

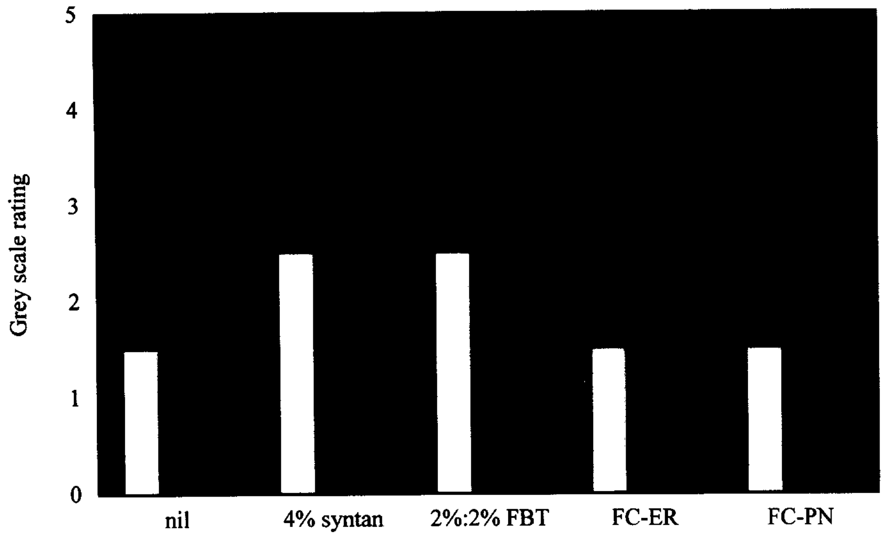


Fig. 12. Wash fastness results for 1% omf dyeings of CI Acid Blue 25 (legend as for Fig. 3).

small fraction of the work that was carried out using this particular approach.

Cationic agents are widely used as an aftertreatment to improve the wash fastness of direct dyes on cellulosic fibres. The mechanism by which such agents function can be considered to be due to the cationic agent forming a complex with the adsorbed direct dye, the large M_r and low aqueous solubility of this complex resulting in enhanced wash fastness. Initially, an assessment was made of the ability of two such cationic agents, namely Matexil FC-PN and Matexil FC-ER, to improve the wash fastness of CI Acid Blue 25 on microfibre nylon 6,6. Figure 12 shows the fastness to the ISO C06/C2 wash test obtained for microfibre nylon 6,6 fabric which had been dyed using 1% omf CI Acid Blue 25 and aftertreated with 2% omf of each of the two cationic compounds; the wash fastness achieved for the untreated dyeing, as well as those secured by means of an aftertreatment with 4% omf Matexil FA-SNX and also the full backtan (2% tannic acid:2% potassium antimonyl tartrate), are also displayed. Clearly, neither of the cationic agents used improved the wash fastness of the dyeing.

Figure 13 shows the wash fastness (ISO C06/C2) of dyed (1% omf CI Acid Blue 25) microfibre which had been aftertreated, firstly with 2% omf Matexil FA-SNX and subsequently treated with 2% omf of Matexil FC-PN, Matexil FC-ER, compound B or compound B2; the wash fastness

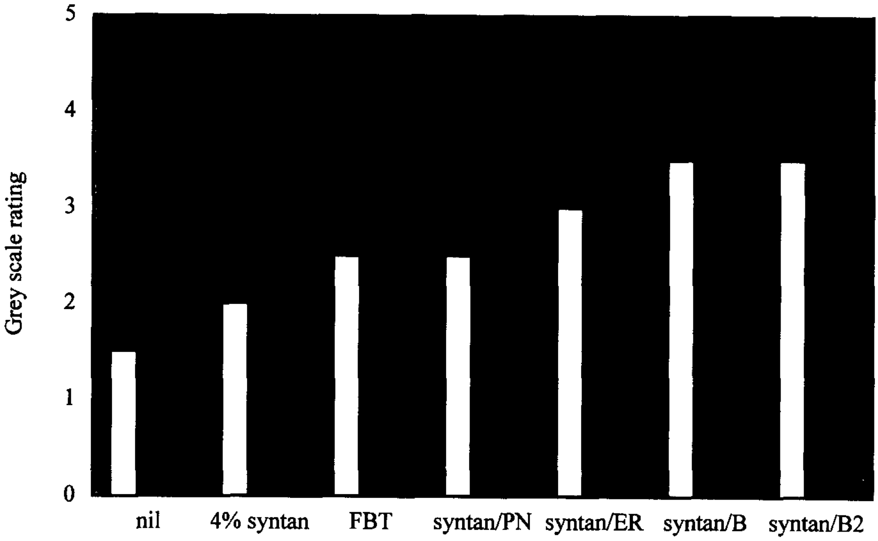


Fig. 13. Wash fastness results for 1% omf dyeings of CI Acid Blue 25 (legend as for Fig. 3).

achieved for the untreated dyeing as well as those obtained using an aftertreatment of 4% omf Matexil FA-SNX, and also the full backtan (2% tannic acid:2% potassium antimonyl tartrate), are also shown. When the wash fastness achieved using a 4% Matexil FA-SNX aftertreatment is compared with that obtained using each of the four sequential syntan/cationic agent aftertreatments, it is evident that the subsequent application to the syntanned dyed fibre of each of the four cationic agents resulted in a marked increase in wash fastness. Indeed, as Fig. 13 shows, the subsequent application of Matexil FC-ER, compound B and also compound B2 to the syntanned dyeing imparted levels of wash fastness that were not only some 0.5–1.5 points higher than those achieved using 4% omf syntan alone, but were also between 0.5 and 1 points higher than those imparted by the full backtan aftertreatment. The extent of the difference in wash fastness between that achieved using the syntan alone and that imparted by the syntan/compound B and syntan/compound B2 aftertreatments corresponded to 75% in terms of shade change and staining of adjacent nylon, and 33% in terms of cotton staining. In contrast, while the level of wash fastness achieved using the syntan/Matexil FC-PN aftertreatment was higher than that obtained using the syntan alone, the extent of the improvement of fastness imparted by the syntan/Matexil FC-PN aftertreatment was not higher than that achieved using the full backtan. In this latter context, although many different types of cationic compounds were examined with regard to their effects on

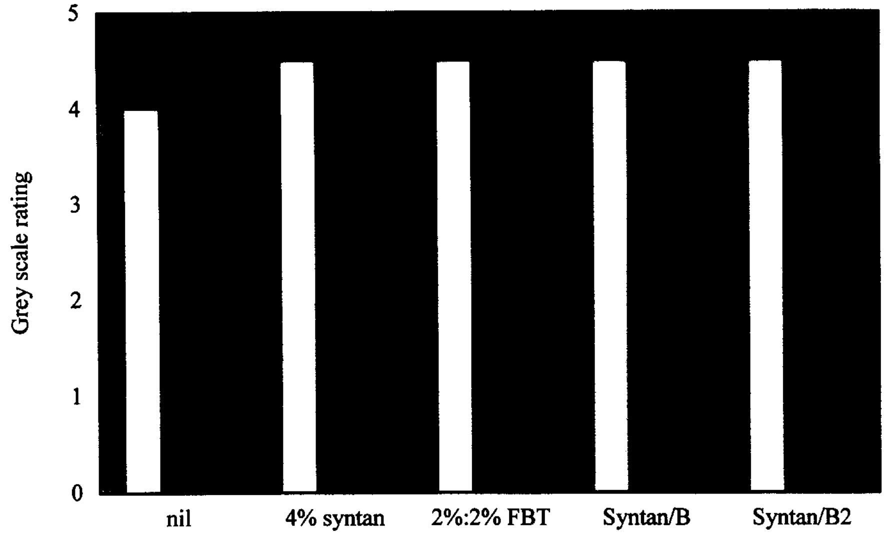


Fig. 14. Wash fastness results for navy blue dyeing (legend as for Fig. 3).

syntanned dyed nylon, while many yielded dyeings of higher wash fastness than that secured using the syntan alone, only relatively few gave results that were markedly superior to that imparted by the full backtan aftertreatment.

The effectiveness of the sequential syntan/cationic agent aftertreatment was further examined using three commercial trichromat dyeings. Figures 14–16 show the ISO C06/C2 wash fastness of navy blue, maroon and green dyeings, respectively, of microfibre nylon 6,6. For each of the three dyeings, the full backtan aftertreatment was generally less effective than the syntan alone in improving wash fastness; however, both the syntan/compound B and syntan/compound B2 aftertreatments imparted levels of fastness that were considerably higher than those achieved using either the syntan alone or the full backtan. While aftertreatment with the two syntan/cationic agent systems did not enhance the level of shade change achieved when compared with those obtained for the syntan alone and for the full backtan aftertreatments, the extent of the enhanced wash fastness obtained using the syntan/compound B and syntan/compound B2 aftertreatments was, when compared with that secured using the syntan alone, between 0.5 and 1.5 points higher in terms of staining of adjacent nylon, 0.5 points higher in terms of cotton staining, and between 1 and 2 points higher in terms of staining of adjacent nylon, and 1.5 points higher in terms of cotton staining, when compared with the level of fastness achieved using the full backtan.

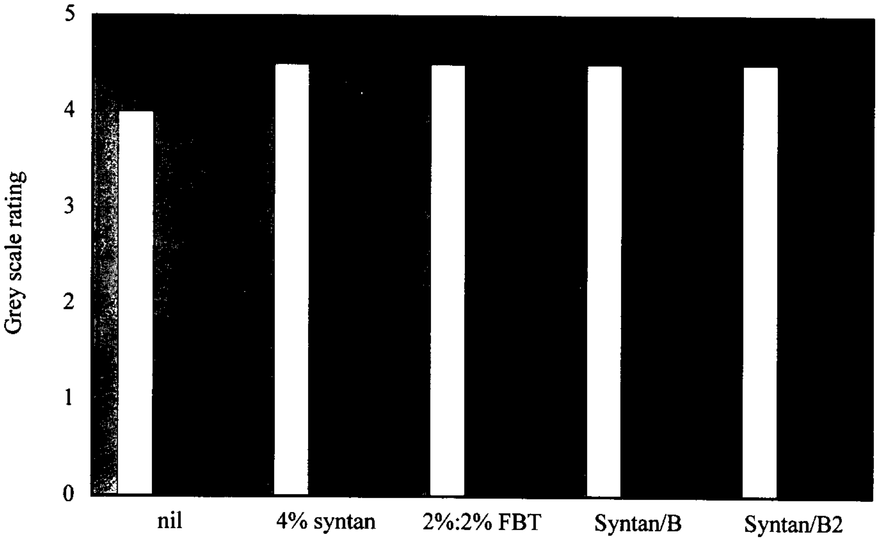


Fig. 15. Wash fastness results for maroon dyeing (legend as for Fig. 3).

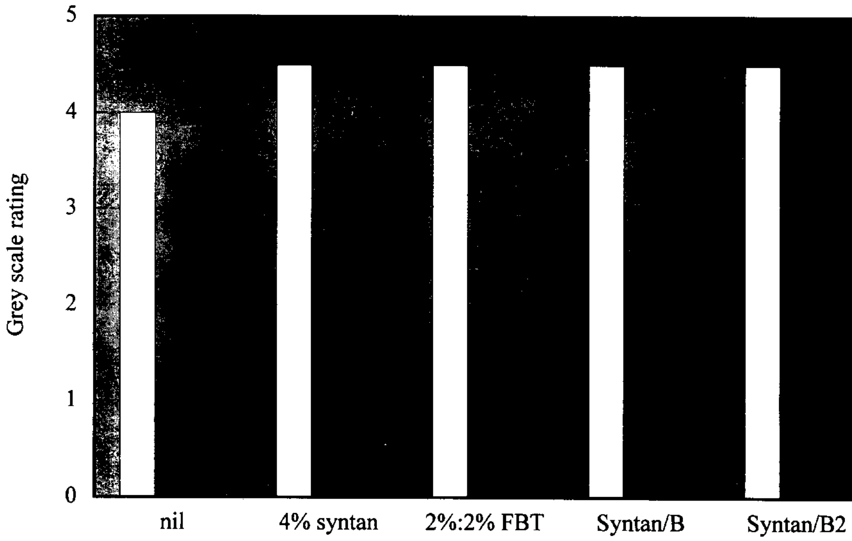


Fig. 16. Wash fastness results for green dyeing (legend as for Fig. 3).

The results displayed in Figs 13–16 clearly demonstrate that the subsequent application of certain cationic agents to syntanned dyed nylon 6,6 microfibre markedly enhanced the effectiveness of the syntan in improving the wash fastness of several non-metallised acid dyes. This enhanced effectiveness can be attributed to the formation of a large M_r, sparinglysoluble, syntan/cationic agent complex. As it is considered that syntans are adsorbed at the periphery of dyed polyamide fibre, it seems reasonable to propose that the syntan/cationic agent complex will also be situated at the periphery of the dyed substrate; consequently, the ability of the complex to improve the wash fastness properties of non-metallised acid dyes on nylon 6,6 fabric can be attributed to this peripheral 'layer' of the complex reducing the diffusion of dye out of the dyed, treated fibre during washing.

The light fastness (ISO B02) of microfibre which had been dyed with the three commercial shades, and either untreated or variously-aftertreated, is shown in Fig. 17, from which it is evident that although each of the four aftertreatments used reduced the light fastness of the maroon dyeing, none of the aftertreatments affected the fastness to light of the navy blue and green dyeings. In the case of the maroon dyeing, the greatest reduction in light fastness (2.5 points) was imparted by the full backtan, the remaining aftertreatments each lowering the light fastness by 1.5 points. The observed reduction in light fastness of the maroon dyeing imparted by the syntan alone, as well as the more marked reduction of light fastness that resulted from aftertreatment with the full backtan, were not surprising in view of the well-known deleterious effect that such aftertreatments can have on the light fastness of some nylon dyeings. Figure 17 also shows that the subsequent application of compound B, and also of compound B2, to the syntanned dyeings had no effect on the light fastness of the syntanned substrate.

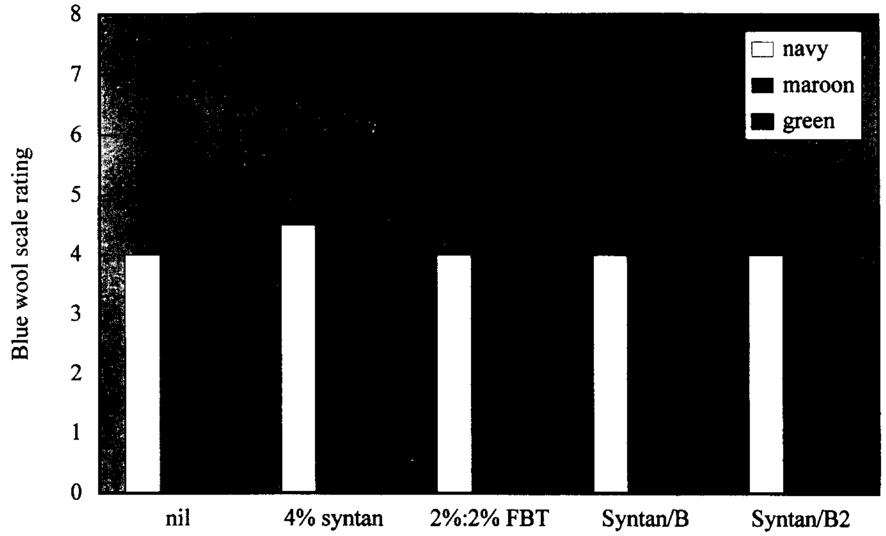


Fig. 17. Light fastness of dyeings.

CONCLUSIONS

The mechanism of adsorption of the syntan on to both conventional and microfibre nylon 6,6 fabrics is identical and, as it involves the formation of multi-layers, forces other than ion–ion contribute towards syntan–fibre substantivity. The greater extent of uptake of the syntan on microfibre than on conventional fibre can be attributed to the greater surface area of the microfibre. The finding that the wash fastness of syntanned dyed microfibre was lower than that of its syntanned dyed conventional decitex counterpart can also be attributed to the greater surface area of the microfibre. The enhanced effectiveness of the syntan in improving the wash fastness of several non-metallised acid dyes on microfibre, which was achieved by the subsequent application to the syntanned dyed substrate of certain cationic agents, can be attributed to the formation of a low-solubility, large M_r, syntan/cationic agent complex, which is probably situated at the periphery of the dyed nylon.

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