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Stain resist treatments for nylon 6,6

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Abstract

A commercial syntan reduced the staining imparted to adjacent nylon 6,6 fabric during washing at 60 °C. The extent of staining decreased with increasing pH of application of the syntan which can be attributed to a corresponding increase in uptake of the syntan. Stain resistance increased with increasing temperature of treatment due to the higher kinetic energy of the syntan molecules and the greater extent of fibre swelling at higher temperatures. The level of staining decreased with decreasing liquor ratio owing to a corresponding increase in the effective concentration of syntan in the treatment bath; increased syntan aggregation in the application of liquor may also have contributed to the greater uptake of the polycondensate at low liquor ratio. The finding that the extent of staining gradually decreased with increasing time of application can be attributed to increased uptake of the syntan. Although the use of a cationic polymer did not enhance the stain resist effectiveness of the syntan, treatment of the adjacent nylon 6,6 with the full backtan markedly reduced the level of staining achieved.
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Keywords: Nylon 6,6; Stain resistance; Acid dyes; Syntans; Full backtan

1. Introduction

Nylon, one of the most widely popular synthetic fibres, enjoys widespread usage in many areas due to its excellent physical properties, good dyeability and pleasant aesthetics; the fibre continues to dominate the commercial carpet industry [1]. However, nylon substrates are susceptible to staining and treatment with a *stainblocker* is used to expedite the removal of stains from nylon carpet yarn. Stainblockers are, typically, formaldehyde polycondensates of sulfonated, substituted phenols, naphthols or dihydroxydiphenyls or mixtures thereof; non-aromatic sulfonic acids are also used [2–4]. They are applied either during carpet fibre spinning or after carpet manufacture. Stainblockers for nylon are designed to be effective primarily against coloured foods and drinks, which usually comprise anionic dyes that are substantive to nylon substrates via electrostatic forces operating between the anionic groups present in the colourant and protonated amino groups in the nylon fibre. In terms of the mechanism by which syntans impart stain resistance to nylon:

- the syntan displays similar adsorption to the anionic stains insofar as the negatively charged sulfonic acid groups of the stainblocker interact with protonated amino groups in the nylon fibre, thereby competing with the anionic colourants for adsorption sites in the fibre;
- syntan molecules adsorbed on or near the surface of nylon provide a negatively charged barrier that repels the anionic colourants from the fibre.

Stainblockers for nylon are closely related to *syntans* (synthetic tanning agents) which are, typically, water-soluble, anionic polycondensates of formaldehyde with arylsulfonates and sulfonates of dihydroxydiaryl sulfones [5] and which are employed widely to improve the wet fastness properties of nylon that has been dyed with anionic (mainly acid) dyes. The adsorption of syntans on dyed nylon occurs by virtue of ion–ion forces of interaction operating between anionic

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(sulfonate) groups in the syntan and the terminal amino groups in the nylon substrate; other forces of interaction, such as H-bonding and ion–dipole forces also will contribute towards syntan–fibre substantivity [5]. It has been shown that the adsorption of large M_r syntans follows a BET mechanism and results in the formation of multilayers of adsorbed syntan molecules at the periphery of dyed nylon [5,6]. The ability of a syntan to improve the wash fastness of acid dyes on nylon can therefore be attributed to this 'layer' of syntan molecules on the fibre surface reducing the extent of dye diffusion from the dyed material during washing.

Thus, similarities exist between the manner of adsorption of syntans and stainblockers on nylon and also, the mechanism by which the two types of compound function.

However, as the extent to which an aftertreatment with a syntan can improve the fastness of dyed nylon often leaves much to be desired, the effectiveness of commercial syntans in improving the wash fastness of both pre-metallised acid dyes [7,8] and non-metallised acid dyes [9,10] on nylon 6,6 can be enhanced by the subsequent application of a polymeric cationic agent to the syntanned, dyed material. It is proposed [5,9] that this two-stage aftertreatment process results in the formation of a large molecular size, low aqueous solubility, complex between the anionic syntan and the cationic compound within the dyed fibre.

Syntans were originally introduced as a means of overcoming the inherent disadvantages of the traditional, full backtan aftertreatment [5], namely, the acute toxicity of potassium antimony tartrate, impairment of fabric handle as well as lowering of light fastness and shade change imparted to dyeings. This two-stage aftertreatment comprises the application of tannic acid to the dyed substrate followed by the sequential application of potassium antimony tartrate (tartar emetic). The natural, high M_r gallotannin component behaves as a high M_r acid which binds to the protonated amino-end groups in the nylon substrate and the sequential treatment with tartar emetic results in the formation of a potassium antimony tannate complex that is situated at the surface of the dyed substrate and which provides a physical barrier to the diffusion of dye from the dyed fabric during washing. Previous research reported an aftertreatment of 1:2 pre-metallised acid dyes [11] and non-metallised acid dyes [12] on nylon 6,6 fabric with a modified full backtan system that did not use potassium antimony tartrate. It was found that the extent of wash fastness improvement imparted by the modified full backtan system was greater than that afforded by a commercial syntan and, in addition, backtanning imparted little shade change and harsh handle to dyeings.

A nylon textile can be exposed to a variety of potential stains, in addition to coloured foods and drinks, the most significant of which is vagrant dye generated during domestic laundering. In this latter context, such dyes include those classes that are used to dye nylon as well as dyes that are used on other types of fibre, notably cellulosic fibres. Thus, typically, a domestic wash comprises a cocktail of vagrant anionic dyes that may include acid, mordant, direct and reactive dyes; clearly, other classes of dye (e.g. disperse and sulphur dyes) may be present. As nylon fibres continue to be a regular component of a domestic wash load, their propensity to attract and adsorb vagrant dyes remains problematic. This work describes an attempt to determine the ability of a commercial syntan to resist the staining imparted to undyed nylon by vagrant dye during washing. In addition, it was decided to ascertain whether or not the stain resistance offered by the syntan could be enhanced by the subsequent application of a polymeric cationic agent. The stain resist effectiveness of the syntan, both alone and when used in conjunction with a cationic agent, was compared to that proferred by a modified full backtan.

2. Experimental

All wet treatments were carried out in sealed, stainless steel dyepots of 200 cm^3 capacity, housed in a *Zeltex Polycolor PC 1000* laboratory-scale dyeing machine.

2.1. Materials

Commercial samples of the dyes listed in Table 1 were generously supplied by Crompton & Knowles, UK. Conventional decitex knitted nylon 6,6 fabric (78F68; 1.14 dtex) supplied by Du Pont, UK was used. This was scoured in a solution of 2 g dm^{-3} Na_2CO_3 and 5 g dm^{-3} non-ionic surfactant *Lanapex R* (ICI Surfactants) for 30 min at 60 °C. The fabric was then rinsed thoroughly in tap water and dried in the open air. Commercial samples of the syntan *Fixogene AXF* and the cationic agent *Fixogene CXF* were kindly supplied by Uniqema and commercial samples of *Floctan 1* (high M_r gallotannin) and the complexing agent *Gallofix* were generously provided by Omnichem-Ajinmoto. A sample of potassium antimony tartrate was obtained from Aldrich. All other reagents used were standard laboratory grade.

2.2. Dyeing

The method shown in Fig. 1 was used, employing a liquor ratio of 20:1. Ammonium sulfate was used to provide a pH of 4 for the *Nylanthrene* dyes while McIlvaine buffer [13] was used to achieve a pH of 6 for the *Neutrilan* dyes. At the end of dyeing, the dyed sample was removed, rinsed thoroughly in tap water and allowed to dry in the open air.

Table 1
Dyes used

Commercial name	C.I. generic name	Dye type
Neutrilan Black M-RX	C.I. Acid Black 194	Pre-metallised acid dyes
Neutrilan Black M-RL	C.I. Acid Black 172	
Neutrilan Navy M-BR	C.I. Acid Blue 193	
Neutrilan Orange S-R	C.I. Acid Orange 144	
Neutrilan Red K-2G	C.I. Acid Red 278	
Nylanthrene Blue C-GLF	C.I. Acid Blue 281	Non-metallised acid dyes
Nylanthrene Navy C-WG	C.I. Acid Blue 345	
Nylanthrene Red C-3BR	C.I. Acid Red 151	
Nylanthrene Orange C-SLF	C.I. Acid Orange 116	
Nylanthrene Blue B-2RF	C.I. Acid Blue 62	
Nylanthrene Yellow B-4RK	C.I. Acid Yellow 219:1	

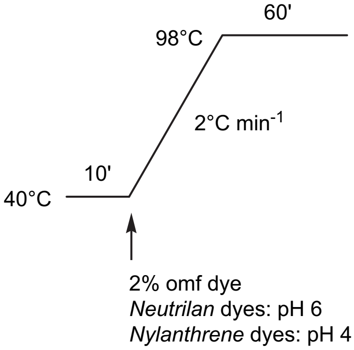

Fig. 1. Dyeing method.

2.3. Syntan treatment

The method shown in Fig. 2 was used. To assess the effect of the application pH of the syntan on stainblocking efficiency, undyed nylon 6,6 fabric was treated with 2% omf syntan at 98 °C at pH 2.6, 3, 4, 5 and 6 using McIlvaine buffer; a liquor ratio of 20:1 was used. The effect of temperature of syntan application on stain resistance was determined by applying 2% omf syntan at 50, 60, 70, 80, 90 and 98 °C using a pH of 5 and a 10:1 liquor ratio. The effect of liquor ratio on stainblocking was assessed by applying 2% omf syntan at pH 5 and 98 °C using various liquor ratios (10:1, 20:1, 30:1 and 50:1) while the duration of syntan application was also varied (10, 20, 30 and 60 min) at pH 5, using a 10:1 liquor ratio at 98 °C.

At the end of each treatment, the syntanned samples were removed, rinsed in tap water and allowed to dry in the open air.

2.4. Syntan/cation treatment

Undyed nylon 6,6 samples were treated with 2% omf syntan at pH 5 at 98 °C, using a 10:1 liquor ratio and then subsequently treated with 2% omf cationic polymer (Fig. 3) using a 10:1 liquor ratio. At the end of the treatment, the samples were removed, rinsed thoroughly in tap water and allowed to air dry.

2.5. Full backtan treatment

The method in Fig. 4 was used, employing a 20:1 liquor ratio; the application pH (pH 3.5) was adjusted using acetic acid. The backtanned samples were removed, rinsed thoroughly in tap water and allowed to air dry.

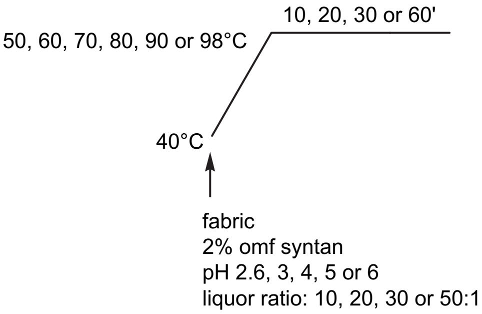

Fig. 2. Syntanning method.

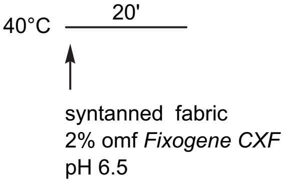

Fig. 3. Cationic agent treatment.

2.6. Wash testing/staining

The ISO 105:C06/C2 wash test protocol was followed except that a piece of undyed nylon 6,6 was used as adjacent material instead of multifibre strip [14]. The undyed material was either untreated or had been treated with the syntan, syntan/cation or the full backtan, prior to use. At the end of wash testing, the dry, stained adjacent nylon 6,6 fabric was measured using an *X-rite* spectrophotometer interfaced to a PC using D_{65} illumination, 10° standard observer with specular component excluded and UV component included. The weighted *K*/*S* values were recorded; samples were folded so as to realise a total of four thicknesses of fabric.

3. Results and discussion

This work attempts to determine the ability of a commercial syntan, syntan/cation and full backtan to resist staining imparted by vagrant dye during washing. Although nylon can be dyed using several classes of anionic dye (acid, mordant, direct and reactive), acid dyes (both non-metallised and pre-metallised types) predominate. However, as the level of wash fastness displayed by members of this dye class on nylon 6,6 (especially the non-metallised representatives) can often be quite poor, it was decided to use nylon 6,6 which had been dyed with both non-metallised and pre-metallised acid dyes as the source of the vagrant dye; the dyes used (Table 1) were chosen arbitrarily.

3.1. Effect of application pH of syntan

Samples of undyed nylon 6,6 were treated with the syntan at different pH values (pH 2.6, 3, 4, 5 and 6) at 98 °C for

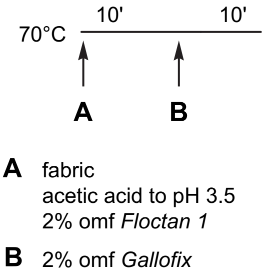

Fig. 4. Full backtan treatment.

30 min using a 20:1 liquor ratio; the syntanned samples were then washed at 60 °C in conjunction with dyed nylon. The extent of staining of the undyed nylon 6,6 by vagrant dye that occurred during washing was determined by measuring the *K/S* of the stained adjacent material. Fig. 5 reveals that, for each dye used, the extent of staining was reduced by the use of the syntan, at each of the five pH values used. This finding can be explained in terms of the mechanism by which syntans are adsorbed onto nylon. Under acidic conditions, as used in this work, the uptake of syntans occurs primarily by electrostatic interaction between the anionic sulfonate groups in the syntan and the protonated amino groups in the nylon; other forces of interaction, such as H-bonding and ion–dipole forces also will contribute towards syntan–fibre substantivity [5]. It has been shown that the adsorption of large M_r syntans follows a BET mechanism and results in the formation of multilayers of adsorbed syntan molecules at the periphery of dyed nylon [5,6]. Thus, it seems reasonable to propose that under the acidic conditions employed, the syntan was adsorbed on to the undyed nylon, probably at the periphery of the fibres and resisted uptake of vagrant anionic dye molecules.

Fig. 5 shows that the extent of staining of adjacent nylon 6,6 decreased with increasing pH of application of the syntan. This result was not unexpected, as the uptake of syntans onto nylon 6,6 has been shown to increase with decreasing pH over the range pH 2–7 [6,15]. This finding agrees with the observation [16] that the adsorption of a commercial stainblocker on nylon 6,6 increased with decreasing application pH over the range pH 2.2–7 due to correspondingly greater amino-end groups which result in ion–ion interaction, operating between protonated amino-end groups in the nylon fibre and sulfonate groups in the anionic stainblocker. However, Fig. 5 also shows that the extent of staining was lowest when the syntan had been applied at pH 5. This can be explained in terms of the particular nature of the interaction between the fibre and the syntan used in this work. At pH 2.6, strong ion–ion forces of interaction will operate between the protonated amino groups in the substrate and the anionic syntan. Under such conditions, the large molecular size syntan molecules will be adsorbed rapidly at the fibre surface forming a 'layer' of adsorbed syntan that reduces the extent of diffusion of syntan within the fibre; in turn, this will limit the extent of syntan adsorption and result in the syntan being confined mostly to the outer surface of the fibre. As the pH of application increases (pH 3–5), the strength of the electrostatic forces between the syntan and fibre will decrease, enabling greater diffusion of the syntan to occur within the fibre and, therefore, greater syntan uptake to occur. Thus, accordingly, the extent of staining should decrease over the pH range 2.6–5, which was indeed the case (Fig. 5). At pH 6, however, the magnitude of the ion–ion forces operating between the syntan and fibre will be smaller than at any of the lower pH values used (i.e. pH 2.6–5) resulting in lower syntan uptake and, therefore, lower stain resistance, as was observed (Fig. 5).

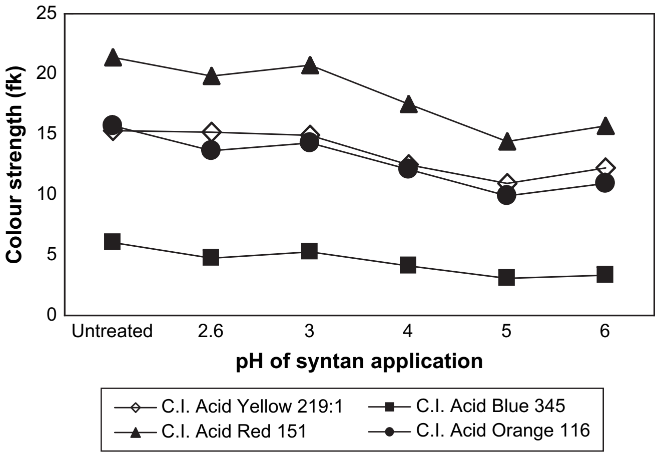

Fig. 5. Effect of pH on staining.

As pH 5 had been found to provide minimum staining, this pH was employed to study the effects of temperature, liquor ratio and duration of syntan treatment on staining, as described below.

3.2. Effect of temperature of syntan application

Undyed nylon fabrics were treated with the syntan at different temperatures (50, 60, 70, 80, 90 and 98 °C) using a pH of 5 for 30 min using a 20:1 liquor ratio. Fig. 6 shows that the extent of staining achieved, for each of the four dyes, decreased with increasing application temperature. Previous work [6] showed that both the rate and extent of uptake of a syntan on nylon 6,6 increased with increasing application temperature, this being attributed to the higher kinetic energy of the syntan molecules and their consequent greater diffusional rate within the substrate, together with higher fibre swelling that accompanied an increase in application temperature. Thus, the decrease in staining that accompanied an increase in syntan application temperature (Fig. 6) can be attributed to an increase in syntan uptake over the temperature range studied.

As 98 °C had been found to provide minimum staining, this temperature was employed to study the effects of liquor ratio and duration of syntan treatment on staining, as described below.

3.3. Effect of liquor ratio of syntan application

Undyed nylon fabrics were treated with the syntan at 98 °C using a pH of 5 for 30 min at different liquor ratios (10:1, 20:1,

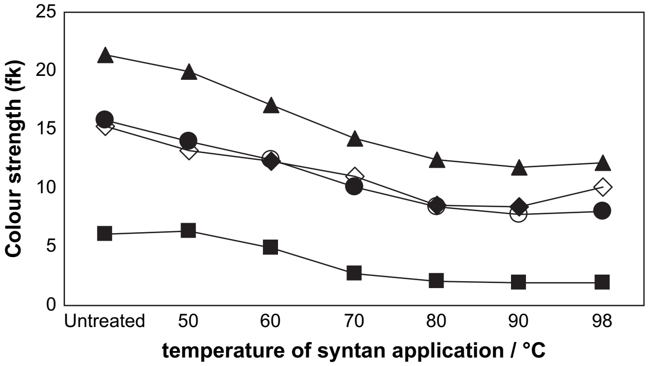

Fig. 6. Effect of temperature on staining.

30:1 and 50:1). Fig. 7 shows that the extent of staining imparted by the four acid dyes during washing increased with increasing liquor ratio; the lowest extent of staining was achieved when treatment has been carried out at a liquor ratio of 10:1. The results shown in Fig. 7 can be attributed to a corresponding increase in the effective concentration of syntan in the treatment bath that accompanied a decrease in liquor ratio. Such an increase in syntan concentration at low liquor ratio may also increase the degree of syntan aggregation in the application liquor which can be assumed to result in greater uptake of the polycondensate.

As a 10:1 liquor ratio had been found to provide minimum staining, this was employed to study the effects of duration of syntan treatment on staining, as described below.

3.4. *Effect of treatment time of syntan application*

The effect applying the syntan at 98 °C using a pH of 5 and a liquor ratio of 10:1 for different treatment times (10, 20, 30 and 60 min) on staining of adjacent nylon 6,6 is shown in Fig. 8. It is clear that the extent of staining gradually decreased with increasing time of application which can be attributed to an increase in the extent of uptake of the syntan that accompanied an increase in duration of treatment.

3.5. *Effectiveness of syntan/cation treatment and the full backtan*

Fig. 9 shows the extent of staining of adjacent nylon 6,6 imparted by eight acid dyes from which it is clear that in the case of untreated, adjacent nylon 6,6, high levels of staining were achieved for C.I. Acid Blue 281 and C.I. Acid Blue 62. It is evident that the syntan reduced, very effectively, the extent of staining of each of the eight dyes.

As mentioned, the effectiveness of commercial syntans in improving the wash fastness of both pre-metallised acid dyes [7,8] and non-metallised acid dyes [9,10] on nylon 6,6 can be enhanced by the subsequent application of a polymeric cationic agent to the syntanned, dyed material. It is considered [5,9] that when the syntan/cation treatment is used as an aftertreatment of dyed nylon, the two-stage process results in the formation of a large molecular size, low aqueous solubility, complex of the anionic syntan and the cationic compound at the periphery of the dyed fibre. From this, it follows that the presence of such a syntan/cation complex at the fibre surface may enhance the effectiveness of the syntan in resisting staining. However, Fig. 9 shows that the use of the cationic polymer did not enhance the stain resist effectiveness of the syntan; this can be explained in terms of the mechanism by which the syntan imparts stain resistance to the nylon substrate. The results described above for the effects of pH, temperature, liquor ratio and treatment time on the effectiveness of the syntan to resist staining imply that optimum stain resistance was achieved when adsorption of the large M_r polycondensate resulted in the formation of a 'layer' of adsorbed syntan molecules at the periphery of the nylon. Assuming that the application of the syntan to the nylon fibre resulted in a 'layer' of syntan molecules at the fibre surface, the subsequent application of the cationic polymer made no contribution to this peripheral 'layer' of molecules that resist staining.

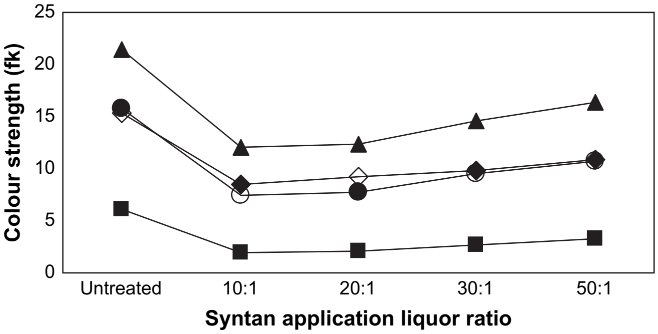

Fig. 7. Effect of liquor ratio on staining.

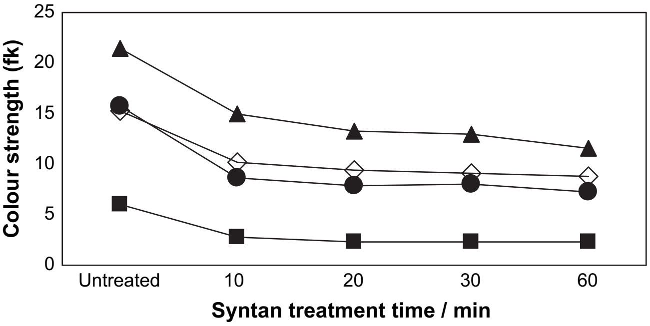

Fig. 8. Effect of treatment time on staining.

It is well known that the full backtan is more effective than syntans in improving the wash fastness of acid dyes on nylon [5]. In this context, it was therefore not surprising to find that treatment of the adjacent nylon 6,6 with the full backtan reduced the level of staining achieved for each of the eight dyes (Fig. 9), especially in the cases of C.I. Acid Blue 281 and C.I. Acid Blue 62 and that the extent of stain resistance imparted by the full backtan was considerably greater than that afforded by treatment with the syntan and the syntan/cation system. It is well known that, in the case of the aftertreatment of acid dyes on nylon, this two-stage treatment of tannic acid and, in this case, the complexing agent *Gallofix*, results in the formation of a large molecular size, low water-solubility complex that is situated at the surface of the dyed substrate and which provides a physical barrier to the diffusion of dye from the dyed fabric during washing. From the results presented in Fig. 9 it appears that this particular complex is also very effective in resisting the adsorption of vagrant dyes during washing.

4. Conclusions

Under the acidic application conditions used, the syntan reduced the extent of staining imparted to adjacent nylon 6,6 fabric during washing at 60 °C. It is proposed that the syntan was adsorbed onto the undyed nylon, probably at the periphery

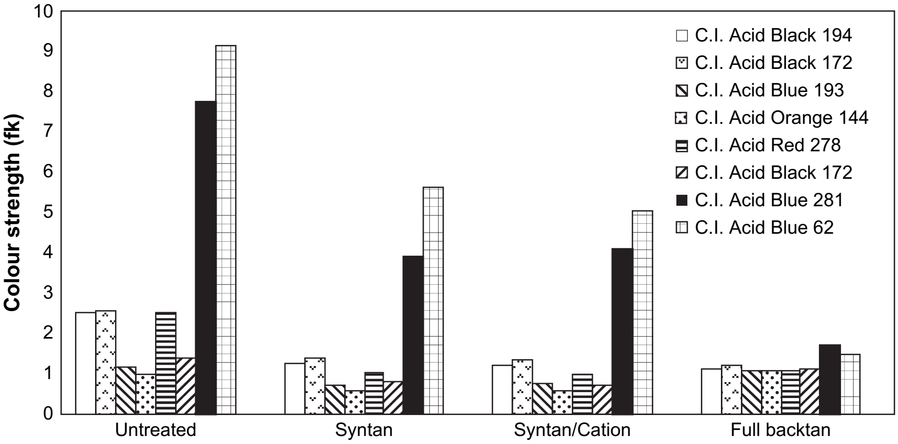

Fig. 9.

of the fibres and resisted uptake of vagrant anionic dye molecules. The extent of staining of adjacent nylon 6,6 decreased with increasing pH of application of the syntan in the range pH 2.6–5, which can be attributed to a corresponding increase in uptake of the syntan. The finding that staining was lowest when the syntan had been applied at pH 5 may be due to the particular nature of the interaction between the fibre and the syntan used in this work. The effectiveness of the stain resistance increased with increasing temperature of treatment due to the higher kinetic energy of the syntan molecules and the greater extent of fibre swelling at higher temperatures. The extent of staining decreased with decreasing liquor ratio owing to a corresponding increase in the effective concentration of syntan in the treatment bath; increased syntan aggregation in the application liquor may also have contributed to greater uptake of the polycondensate at low liquor ratio. The finding that the extent of staining gradually decreased with increasing time of application can be attributed to increased uptake of the syntan.

Although the use of the syntan in conjunction with a cationic polymer did not enhance the stain resist effectiveness of the syntan, in contrast, treatment of the adjacent nylon 6,6 with the full backtan markedly reduced the level of staining achieved, especially in the cases of C.I. Acid Blue 281 and C.I. Acid Blue 62.

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