

# The Adsorption of a Commercial Stainblocker on Nylon 6.6

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**ABSTRACT:** The adsorption of a commercial stainblocker onto nylon 6.6 fibers of 45 amino end group (AEG), and also 70 AEG, was found to increase with decreasing application pH, indicating that ion–ion interaction contributed to stainblocker–fiber substantivity. Uptake of the stainblocker also increased with increasing application temperature, which is attributable to the higher kinetic energy of the stainblocker molecules and the greater extent of the fiber-swelling operative at the higher temperatures. Adsorption of the stainblocker on to 45 AEG fiber increased with decreasing liquor ratio, possibly as a result of stainblocker aggregation, but in the case of 70 AEG nylon fiber uptake, slightly decreased with decreasing liquor ratio. From the finding that uptake of the stainblocker onto undyed 45 AEG and 70 AEG nylon 6.6 followed a Brunauer–Emmett–Teller mechanism, it was postulated that adsorption involves the formation of multilayers and that forces other than ion–ion contribute toward stainblocker–fiber interaction. This postulate gained support from the observation that although the presence of 1% omf dye on the two types of fiber reduced the extent of stainblocker uptake, the mechanism of stainblocker adsorption onto both substrates was unaffected. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3062–3068, 2000

**Key words:** stainblockers; stain resistance; nylon 6.6; carpets; finishing

## INTRODUCTION

Nylon, one of the most important synthetic fibers, continues to dominate the commercial carpet industry<sup>1</sup> mainly because of the fibers' high resilience, excellent wear characteristics, good dyeability, and acceptable aesthetics. However, one drawback to the fiber has been its lack of resistance to staining<sup>2</sup>; in this context, treatment with *stainblockers* aids the removal of stains from nylon 6.6 carpet fibers.<sup>3</sup>

Stainblockers are, typically, condensates of formaldehyde with phenolsulfonic acids, naphtholsulfonic acids, or sulfonates of dihydroxydiphenylsulfone, or mixtures thereof<sup>2,3</sup>; in addition, nonaromatic sulfonic acid compounds have been claimed as stainblockers.<sup>4</sup> Stainblockers can be

applied to nylon fiber as it is being spun or to nylon carpet after the carpet has been manufactured. Application is usually carried out in conjunction with a fluorohydrocarbon in order to obtain optimum stain resistance and dry soil protection.<sup>2</sup>

Colored food and drink stains, which principally consist of anionic dyes, are substantive toward nylon fibers via ion–ion forces of interaction operating between the anionic groups (e.g.,  $\text{COO}^-$ ,  $\text{SO}_3^-$ ) in the colorant and protonated amino groups in the nylon fibers. It has been proposed<sup>5</sup> that a similar mechanism applies in the case of stainblockers, in that adsorption occurs by virtue of ion–ion forces operating between anionic (e.g., sulfonate) groups in the stainblocker and protonated amino groups in the nylon fiber, resulting in a peripheral layer of stainblocker that restricts diffusion of dyes into the fiber. It has been suggested that ion–ion repulsion effects operating between the residual anionic charges of

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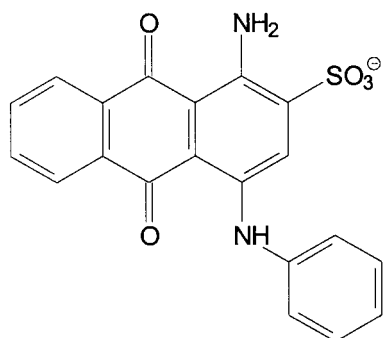


Figure 1 CI Acid Blue 25.

the adsorbed stainblocker and the anionic dyes contribute to reduced dye diffusion.<sup>6</sup> However, the precise mechanism by which stainblockers improve the stain resistance of nylon fibers remains unclear in view of the varied composition of the polycondensates.

This paper describes the exhaustion application characteristics of a typical commercial stainblocker on both dyed and undyed nylon 6.6 fibers in an attempt to ascertain the mechanism by which the stainblocker is adsorbed on the substrate.

## EXPERIMENTAL

### Fabrics

Two types of knitted nylon 6.6 fabric, namely, of 45 m-eq · kg<sup>-1</sup> AEG (78f68; 1.15 dtexpf) and 70 m-eq · kg<sup>-1</sup> AEG (78f68; 1.15 dtexpf), were kindly supplied by Du Pont Nylon (UK). Each type of fabric was scoured prior to use by treatment at 70°C for 30 min in a pilot-scale winch dyeing machine using a liquor ratio of 50:1, in a bath containing 1 gL<sup>-1</sup> *Sandozin NIE* (Clariant) and 2 gL<sup>-1</sup> sodium carbonate followed by thorough warm water and cold water rinsing.

### Dyes

A commercial sample of *Nylomine Blue A-G* (CI Acid Blue 25) (Figure 1) was kindly supplied by Zeneca Colours.

### Stainblocker

A sample of a commercial stainblocker was generously supplied by Du Pont (UK). Owing to commercial confidence, no details of the stainblocker can be divulged.

### Dyeing Auxiliaries

Commercial samples of *Matexil LA-NS* and *Matexil LC-CWL* were kindly supplied by ICI Surfactants; *Sandozin NIE* was provided by Clariant (UK).

All other reagents were of general purpose grade.

### Dyeing

Samples (2 g) of nylon 6.6 fabric were dyed with CI Acid Blue 25 (1% omf) in sealed, stainless steel dye pots of 300 cm<sup>3</sup> capacity housed in a Zeltex Polycolor laboratory-scale dyeing machine using a liquor ratio of 50:1; the dyeing method used is shown in Figure 2. At the end of dyeing, the dyed sample was removed, rinsed thoroughly in tap water, and allowed to dry in the open air.

### Effect of pH on the Rate of Stainblocker Adsorption

McIlvaine buffers,<sup>7,8</sup> prepared using distilled water, were used to achieve the appropriate treatment pH value. Samples (2 g) of nylon 6.6 fabric were treated with the stainblocker (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 dye pots of 300 cm<sup>3</sup> capacity housed in a Zeltex Vistacolor laboratory-scale dyeing machine. Adsorption rates were determined by continuously monitoring the absorbance of the stainblocker treatment bath at 262 nm using a 1 mm quartz

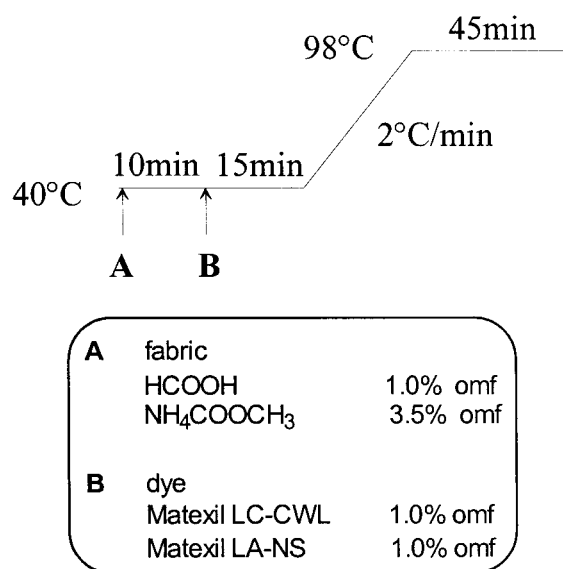
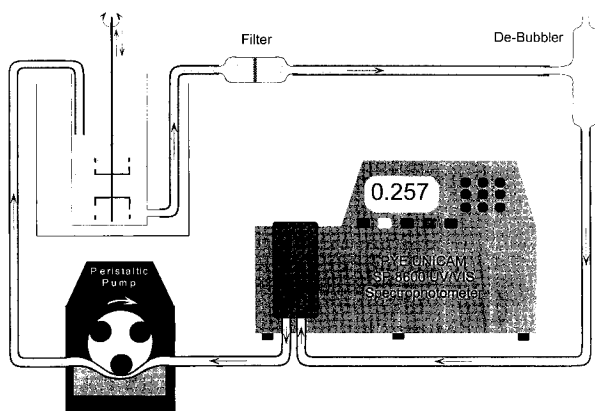


Figure 2 Dyeing method.



**Figure 3** Arrangement of the apparatus used to continuously monitor the absorbance of treatment liquor.

flow-through cell housed in a Pye-Unicam SP 8600 spectrophotometer; the arrangement of the apparatus used is shown in Figure 3. The absorbance data were converted to percentage exhaustion (%*E*) values using

$$\%E = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where  $A_0$  and  $A_t$  are the absorbencies at time 0 and  $t$ , respectively.

The difference in the exhaustion of the stainblocker on 45 AEG and 70 AEG fibers (% $\Delta E$ ) was calculated using

$$\% \Delta E = (\%E \text{ obtained on 70 AEG fibre} - \%E \text{ obtained on 45 AEG fibre}) \quad (2)$$

### Effect of Temperature on the Rate of Stainblocker Adsorption

Samples (2 g) of nylon 6.6 fabric were treated with the stainblocker (2% omf) at pH 5 at 50, 80, and 98°C for 1 h using a liquor ratio of 50:1 in partially sealed glass dyepots of 300 cm<sup>3</sup> capacity housed in a Zeltex Vistacolor laboratory-scale dyeing machine. Adsorption rates were determined by continuously monitoring the absorbance of the stainblocker treatment bath using the equipment and procedure described above, and were converted to percentage exhaustion values as described above.

### Effect of Liquor Ratio on the Rate of Stainblocker Adsorption

Samples (2 g) of nylon 6.6 fabric were treated with the stainblocker (2% omf) at pH 5, at 95°C for 1 h

using liquor ratios of 25:1, 50:1, and 100:1 in partially sealed glass dyepots of 300 cm<sup>3</sup> capacity housed in a Zeltex Vistacolor laboratory-scale dyeing machine. Adsorption rates were determined by continuously monitoring the absorbance of the stainblocker 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 Stainblocker on Undyed and Dyed Nylon 6.6 Fabrics

Both undyed and dyed (CI Acid Blue 25; 1% omf) nylon 6.6 samples (2g) were treated, using a 100:1 liquor ratio, in a series of aqueous, acidic (pH 4) solutions of the stainblocker of various concentrations (1–16 gL<sup>-1</sup>) at 80°C for 12 h in sealed, stainless steel dyepots of 300 cm<sup>3</sup> capacity housed in a Zeltex Polycolor laboratory-scale dyeing machine. At the end of treatment, the concentration of stainblocker remaining in the treatment liquor was determined by reference to the extinction coefficient of a calibration plot of the stainblocker at 262 nm (the  $\lambda_{\text{max}}$  of the stainblocker in the medium).

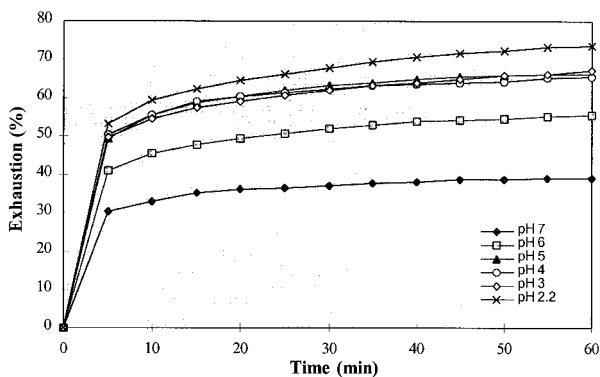
During treatment of the dyed substrates with stainblocker, dye was desorbed from the fibers. Since both the stainblocker and the dye adsorbed at 262 nm, the absorbance values thus obtained related to the concentration of both stainblocker and dye in the treatment bath.

In order to calculate the actual concentration of stainblocker in the treatment bath and thus the extent of stainblocker uptake, the technique described by Burkinshaw and Maseka<sup>9</sup> was followed.

## RESULTS AND DISCUSSION

Stainblockers that are used on nylon fibers are, in essence, very similar or even identical to syntans that are used to improve the wet fastness properties of anionic dyes on the substrate. Thus, it was anticipated that the exhaustion behavior of the conventional stainblocker used in this work would resemble that of typical syntans.

Figures 4 and 5 clearly show that both the rate and extent of adsorption of the stainblocker on to both 45 AEG and 70 AEG nylon 6.6 increased with decreasing application pH. These findings concur with those<sup>9,10</sup> obtained for the adsorption of two

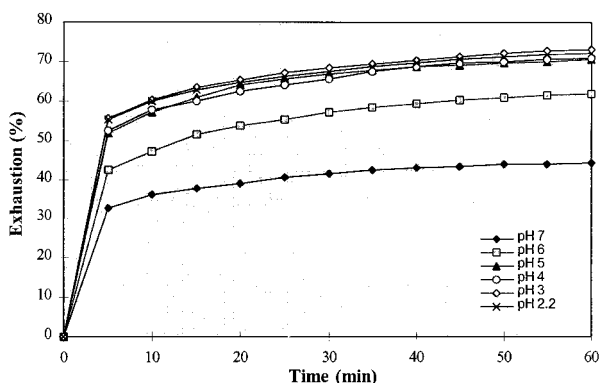


**Figure 4** Effect of pH on stainblocker uptake on to 45 AEG nylon 6.6 (2% omf; 50:1 liquor ratio; 80°C).

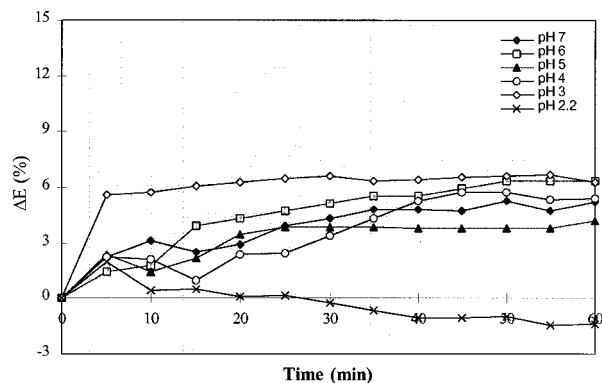
commercial syntans on nylon 6.6 fibers. The results in Figures 4 and 5 indicate that ion-ion interaction, operating between protonated amino end groups in the nylon fiber and, presumably, sulfonate groups in the anionic stainblocker, contributes toward stainblocker-fiber substantivity.

A comparison of Figures 4 and 5 reveals that both the rate and extent of stainblocker adsorption were greater on the 70 AEG nylon substrate. This difference in the exhaustion of the stainblocker on the two types of fiber is shown in Figure 6. The finding that stainblocker uptake was higher on the higher AEG type nylon adds weight to the above postulate that ion-ion forces operating between protonated amino end groups in the fiber and, for example, sulfonate groups in the stainblocker, contribute to stainblocker-fiber substantivity.

However, Figures 4-6 show that the uptake of the stainblocker on to the 70 AEG fiber was not much greater than that on to 45 AEG fiber, espe-



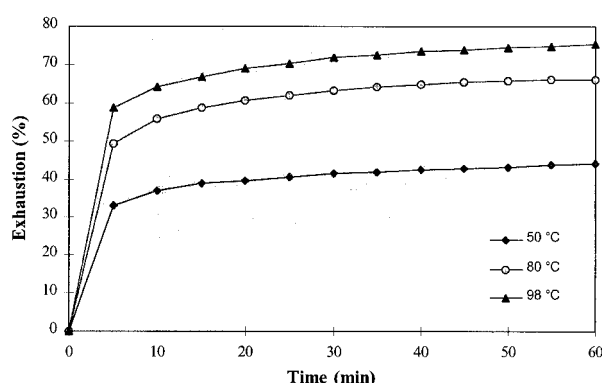
**Figure 5** Effect of pH on stainblocker uptake on to 70 AEG nylon 6.6 (2% omf; 50:1 liquor ratio; 80°C).



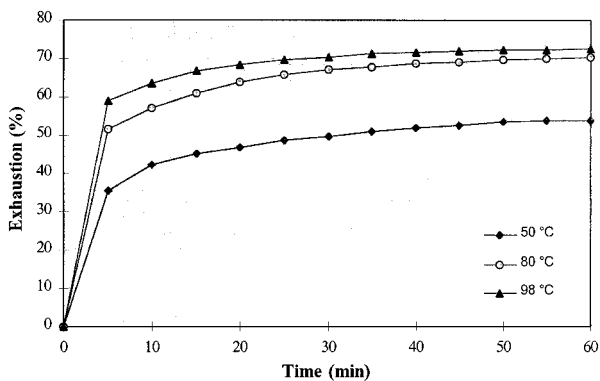
**Figure 6** Difference in exhaustion of stainblocker on to 45 and 70 AEG nylon 6.6 fiber.

cially when it is considered that the increase in AEG from 45 to 70 m-eq · kg<sup>-1</sup> represents an increase of 55%. Indeed, Figure 6 shows that despite this major increase in AEG content from 45 to 70 m-eq · kg<sup>-1</sup>, the corresponding difference in stainblocker uptake on the two types of fiber was comparatively very small and clearly, not of the order of 55%.

Figures 7 and 8 demonstrate that both the rate and extent of adsorption of the stainblocker on to both types of nylon 6.6 fabric increased with increasing application temperature. These results also concur with those obtained for the adsorption of a syntan on nylon 6.6,<sup>9</sup> and as previously suggested in the case of syntan adsorption,<sup>9</sup> can be attributed to the higher kinetic energy of the stainblocker molecules and their consequent greater diffusional power within the substrate, together with the higher extent of fiber swelling that accompanied an increase in application temperature.

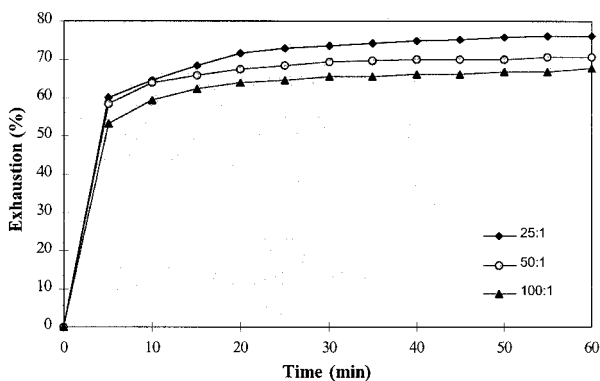


**Figure 7** Effect of temperature on stainblocker uptake on to 45 AEG nylon 6.6 (2% omf; 50:1 liquor ratio; pH 5).

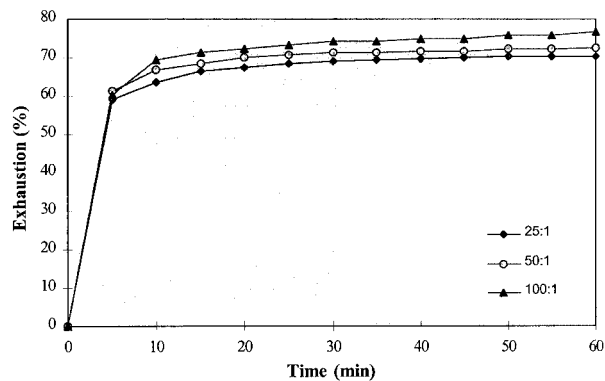


**Figure 8** Effect of temperature on stainblocker uptake on to 70 AEG nylon 6.6 (2% omf; 50:1 liquor ratio; pH 5).

Figure 9 shows that both the rate and extent of uptake of the stainblocker on 45 AEG nylon 6.6 increased with decreasing liquor ratio; these findings agree with those obtained for the adsorption of a syntan on nylon,<sup>9</sup> and as previously suggested in the case of syntan adsorption,<sup>8,9</sup> can be attributed to a corresponding increase in the effective concentration of stainblocker in the treatment bath that accompanied a reduction in liquor ratio. Although no information is provided concerning the chemical composition and relative molecular mass ( $M_r$ ) of the stainblocker, it can be suggested that aggregation of the stainblocker will occur in solution by virtue of both polar and nonpolar forces operating between the large molecular size stainblocker molecules. Thus, as proposed earlier for the adsorption of syntans,<sup>8,9</sup> the increased effective concentration of stainblocker that accompanied a decrease in liquor ratio can be expected to increase the degree of stainblocker



**Figure 9** Effect of liquor ratio on stainblocker uptake on to 45 AEG nylon 6.6 (2% omf; pH 5; 95°C).

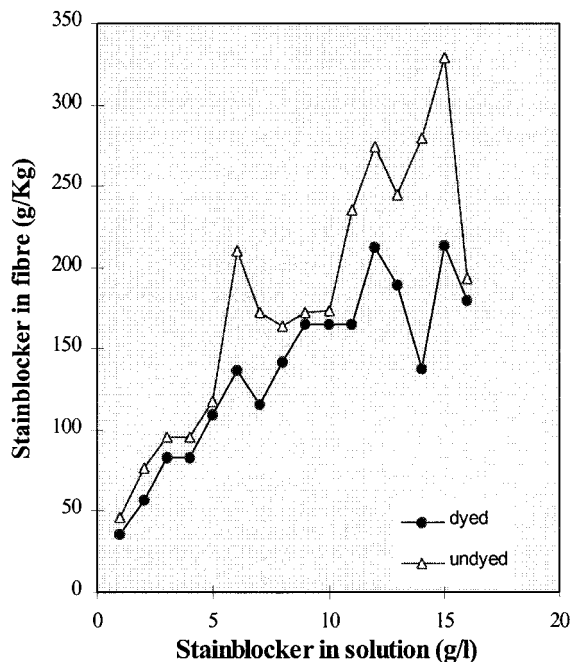


**Figure 10** Effect of liquor ratio on stainblocker uptake on to 70 AEG nylon 6.6 (2% omf; pH 5; 95°C).

aggregation in solution that, in turn, could result in greater uptake of the stainblocker.

However, as can be clearly seen in Figure 10, the rate of stainblocker uptake on 70 AEG nylon 6.6 was unaffected by a decrease in liquor ratio and the extent of uptake increased with increasing liquor ratio. An explanation of this finding that differs to that secured for the 45 AEG fiber (Figure 9) will be given later, after the adsorption isotherm results have been discussed.

The equilibrium adsorption isotherms of the stainblocker on undyed 45 AEG (Figure 11) and



**Figure 11** Equilibrium absorption isotherm of stainblocker uptake on to 45 AEG nylon 6.6 (pH 4; 100:1 liquor ratio; 80°C).

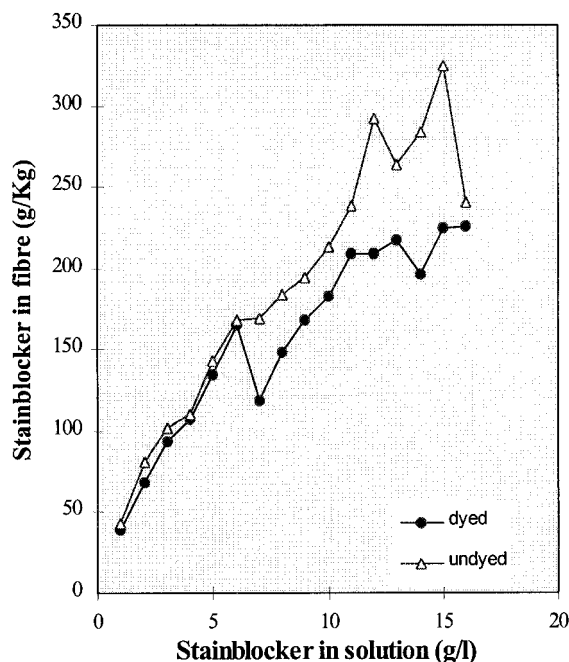
70 AEG (Figure 12) nylon 6.6 fibers show that uptake on to both types of fiber followed a Brunauer–Emmett–Teller (BET) mechanism, which implies that adsorption involves the formation of multilayers of adsorbed stainblocker molecules. These results agree with those obtained for the adsorption of a commercial syntan on nylon 6.6<sup>9</sup> and indicate that stainblocker adsorption on to undyed nylon does not occur simply by virtue of ion–ion interaction operating between the anionic stainblocker molecules and specific sites (namely, the protonated amino groups) in the fiber. Thus, other forces of interaction, for example, hydrogen bonding and ion–dipole forces, contribute toward stainblocker–fiber interaction. In view of the BET adsorption mechanism obtained in the present work (Figures 11 and 12), such forces can also be considered to contribute toward multilayer adsorption of the stainblocker, which would also contribute toward stainblocker–fiber substantivity.

Figures 11 and 12 also reveal that the extent of uptake of the stainblocker on to 70 AEG nylon was slightly greater than that obtained on 45 AEG fiber. This finding was not surprising in view of the observation (Figures 4–6) that stainblocker uptake was pH dependent, and therefore, involved ion–ion forces operating between protonated terminal amine groups in the fiber. However, although the difference between the two types of fiber in terms of AEG content was 55%, a comparison of Figures 11 and 12 show that this significant difference in AEG content was not reflected in the difference in uptake of the stainblocker on to the two fiber types. Hence, this particular finding further implies that stainblocker adsorption on to the substrate does not occur primarily by virtue of ion–ion interaction operating between the anionic stainblocker molecules and the protonated amino groups in the fiber, and therefore that other forces of interaction contribute to stainblocker–fiber interaction.

An attempt was made to further examine the influence that ion–ion interaction has on stainblocker adsorption. Since it is widely held<sup>14,15</sup> that the adsorption of a small molecular size, anionic dye, such as CI Acid Blue 25, onto nylon 6.6 is confined to the amino end groups within the polymer, the presence of the dye should affect the adsorption of the stainblocker if uptake of the stainblocker occurred mainly by virtue of ion–ion forces of interaction at the terminal amino groups in the substrate. Figures 11 and 12 clearly show that the presence of 1% of the dye on the

substrate reduced the extent of ads, and therefore, that the presence of the dye did not affect the mechanism of adsorption of the stainblocker. These findings support the earlier proposal that adsorption of the stainblocker does not occur primarily by virtue of ion–ion forces of interaction, and therefore that other polar and nonpolar forces contribute toward stainblocker–fiber substantivity. In the context of the mechanism of adsorption of the stainblocker on nylon 6.6, the evidence presented suggests that uptake of the stainblocker onto both types of nylon 6.6 fiber occurs by virtue of ion–ion forces together with both polar and non–polar forces of interaction operating between the anionic stainblocker and the fiber.

Returning to the observation (Figure 10) that the extent of stainblocker uptake increased with increasing liquor ratio in the case of 70 AEG fiber, which was in contrast not only to the finding for the 45 AEG fiber but also for the adsorption of a syntan on nylon 6.6.<sup>9</sup> As mentioned earlier, stainblockers are, in essence, very similar or even identical to syntans that are used in the aftertreatment of dyed nylon; thus it can be proposed that like syntans, the  $M_r$  of the stainblocker used in this work will be high, and it can further be postulated that adsorption of the stainblocker would



**Figure 12** Equilibrium absorption isotherm of stainblocker uptake on to 70 AEG nylon 6.6 (pH 4; 100:1 liquor ratio; 80°C).

be confined mostly to the periphery of the fiber, as proposed for syntans.<sup>9</sup> As previously discussed, a decrease in liquor ratio can be expected to increase stainblocker aggregation in solution that, in turn, would increase substantivity, and thus increase the uptake of the stainblocker on the substrate. Figures 4–10 showed that the rate and extent of stainblocker uptake was higher on 70 AEG fiber. Thus, as discussed previously, as the effective concentration of stainblocker in solution increased because of a decrease in liquor ratio, stainblocker adsorption on the 70 AEG fiber increased. If it is assumed that stainblocker uptake would be confined mostly to the periphery of the fiber owing to the low diffusional power of the large  $M_r$  stainblocker, then the increased substantivity of the stainblocker caused by a decrease in liquor ratio could result in a “layer” of stainblocker at the fiber surface that effectively blocked further adsorption of the stainblocker. Thus, it can be envisaged that the stainblocker tended to “ring-dye” the 70 AEG fiber because of the very high substantivity of the large  $M_r$ , low diffusing stainblocker.

## CONCLUSIONS

The adsorption of the stainblocker on 70 AEG nylon 6.6 differs from that onto its 45 AEG counterpart insofar as uptake of the stainblocker occurred at a slightly faster rate and, in general, to a slightly higher extent. However, the mechanism of adsorption of the stainblocker is identical for both types of fiber—namely, that in addition to

ion–ion interaction, other forces contribute to stainblocker–fiber substantivity, giving rise to a BET adsorption mechanism.

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