Dyes and Pigments **16** (1991) 299–308

Further Studies of the Use of Commercial Syntans as Anionic Dye-Resist Agents for Wool

S. M. Burkinshaw & N. Nikolaides

Department of Colour Chemistry and Dyeing, The University,
Leeds LS2 9J1, West Yorkshire, UK

(Received 17 December 1990; accepted 28 January 1991)

ABSTRACT

The adsorption of two commercial syntans by wool serge was found to occur by virtue of ion–ion forces, hydrophobic interaction, together with both polar and non-polar forces; the marked contribution that the latter three forces made towards uptake was demonstrated by the finding that adsorption of each syntan followed a BET mechanism. Treatment with each syntan imparted to wool a high degree of resistance towards uptake of four hydrophilic anionic dyes, but a low resist effectiveness towards adsorption of two hydrophobic anionic dyes, when untreated wool, and wool which had been treated with each syntan, were dyed in competition. Syntan desorption that occurred during dyeing showed that the tanning agents are relatively weakly bound to the fibre; the desorbed syntan exerted a restraining effect on the uptake of all six dyes used.

INTRODUCTION

A previous paper[1] described the exhaustion application characteristics of the commercial synthetic tanning agent Cibatex RN (Ciba-Geigy, Basle, Switzerland) on wool and the anionic dye-resist effect imparted to the fibre by this compound. This paper concerns the adsorption and dye-resist characteristics of two further commercial syntans, namely Matexil FA-SN and Dyapol SB40, on wool fibre. The intention of this work and that described previously[1] is only to examine the nature of the interaction of such

Dyes and Pigments 0143-7208/91/$03·50

tanning agents with wool and the anionic dye-resist effects obtained; it is not intended, nor has any attempt been made, to promote the superiority of one commercial product over another.

EXPERIMENTAL

The two commercial synthetic tanning agents used, Matexil FA-SN and Dyapol SB40, were kindly supplied by ICI (Manchester, UK) and Yorkshire Chemicals plc (Leeds, UK), respectively; all other experimental materials and all procedures employed have been described earlier.[1]

RESULTS AND DISCUSSION

The previous work[1] demonstrated that the uptake of Cibatex RN by wool serge increased with decreasing application pH, indicating that ion–ion interaction greatly contributes to syntan–fibre substantivity. Figures 1 and 2 show that the extent of adsorption of both Matexil FA-SN and Dyapol SB40 also increased with decreasing application pH. This can, as discussed previously for Cibatex RN,[1] be attributed to an increase in the number of protonated amino groups available within the fibre. The high uptake of each tanning agent at pH 2·2 may be due to the syntans' greater diffusional power within the substrate, which will be more swollen at such low pH values.[2]

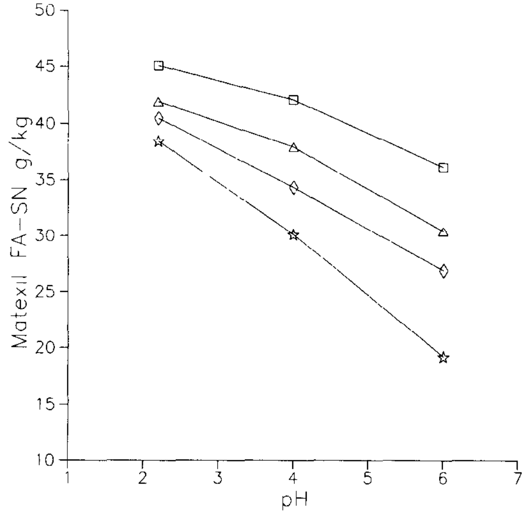

Fig. 1. Effect of pH and liquor ratio on the uptake of Matexil FA-SN (5% owf) at 95°C. Liquor ratios—10:1 (□), 20:1 (△), 50:1 (◇), 100:1 (☆).

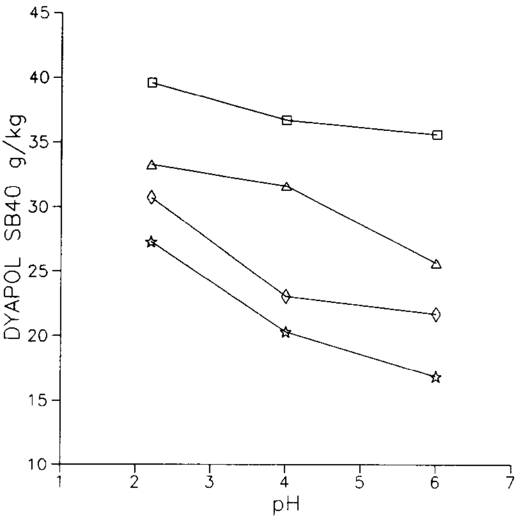

Fig. 2. Effects of pH and liquor ratio on the uptake of Dyapol SB40 (5% owf) at 95°C. Liquor ratios—10:1 (□), 20:1 (△), 50:1 (◇), 100:1 (☆).

Figures 1–4 show that uptake of both syntans increased with decreasing liquor ratio as previously observed,[1] which can be attributed to the increased tendency for adsorption and diffusion to occur, resulting from an increase in the effective concentration of each syntan in the treatment bath. Although no information is provided concerning the precise chemical composition and molecular weight of either Dyapol SB40 or Matexil FA-SN, it can be

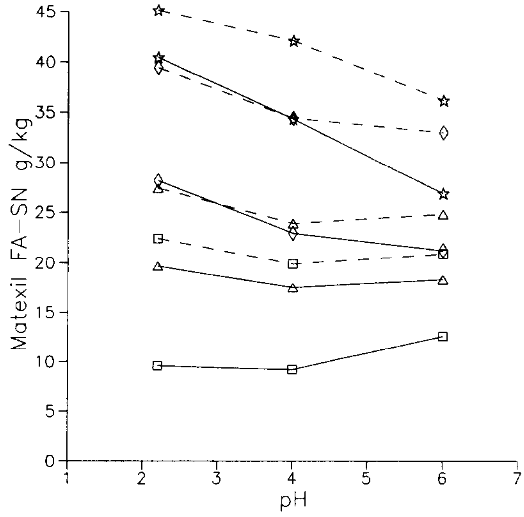

Fig. 3. Effects of liquor ratio, pH and temperature on the uptake of Matexil FA-SN (5% owf). Liquor ratios—10:1 (– – –), 50:1 (——); temperatures—30°C (□), 50°C (△), 70°C (◇), 95°C (☆).

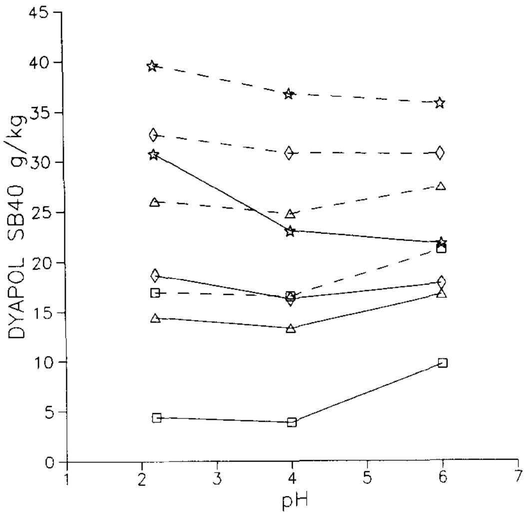

Fig. 4. Effects of liquor ratio, pH and temperature on the uptake of Dyapol SB40 (5% owf). Liquor ratios—10:1 (- - -), 50:1 (——); temperatures—30°C (□), 50°C (△), 70°C (◇), 95°C (☆).

proposed that aggregation of each syntan will arise in solution by virtue of both polar and non-polar forces together with hydrophobic interaction operating between the large-molecular-size syntan molecules. A decrease in liquor ratio (i.e. an increase in effective concentration of syntan in the treatment bath) can be expected to increase the degree of syntan aggregation in solution, which in turn will result in greater uptake of the tanning agent. It is reasonable to suggest that these aggregates will be bound to the fibre by those forces (e.g. polar, non-polar, hydrophobic interaction) responsible for the formation of the aggregates, and that adsorption of such aggregates, by virtue of their large molecular size, would be confined mostly to the periphery of the wool fibre.

Figures 3 and 4 show that uptake of each tanning agent increased with increasing application temperature for each pH value used and for both liquor ratios employed; this finding concurs with that obtained for Cibatex RN[1] and can be attributed to an increase in the diffusional power of the syntans within the substrate, resulting from the increase in fibre swelling and kinetic energy of the syntan molecules that attends an increase in application temperature. Figure 3 shows that at 30°C, using a liquor ratio of 50:1, uptake of Matexil FA-SN increased with increasing pH of application, whereas Fig. 4 demonstrates that uptake of Dyapol SB40 increased with increasing application pH at both 30 and 50°C using liquor ratios of both 10:1 and 50:1. These results differ to those obtained at 70 and also 95°C, where it was found that uptake of each syntan increased with decreasing application pH.

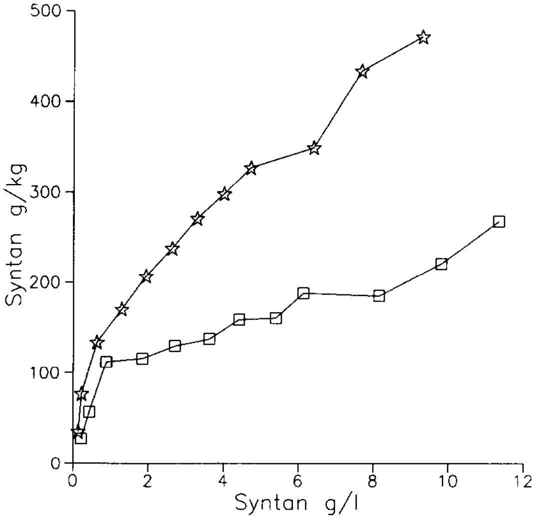

Fig. 5. Adsorption isotherms for Dyapol SB40 (□) and Matexil FA-SN (☆) (95°C; pH 2·2; 100:1 liquor ratio).

The findings for Dyapol SB40 and Matexil FA-SN differ only slightly to those previously obtained[1] for Cibatex RN; consequently, the results displayed in Figs 3 and 4 can be explained, as before,[1] in terms of the differences in diffusional power, substantivity and effective concentration of the syntans prevailing at the different liquor ratios, pH values and temperatures employed.

The sigmoidal nature of the equilibrium isotherms obtained for each syntan (Fig. 5) shows that adsorption of both Dyapol SB40 and Matexil FA-SN follows a BET mechanism, which implies that uptake involves the formation of multilayers of adsorbed syntan molecules. In the case of Dyapol SB40 the presence of two distinct plateau regions is observed, which correspond to syntan concentrations of between, approximately, 1 and 2 g/litre and also 6 to 8 g/litre. This result is virtually identical to that obtained for Cibatex RN[1] and demonstrates that at low concentrations (up to about 2 g/litre) adsorption of Dyapol SB40 occurs primarily on the protonated amino groups in the substrate. At higher concentrations (up to about 6 g/litre) 'stacking' of the large-molecular-size syntan molecules occurs within the fibre, which can be considered to arise by virtue of, for example, hydrophobic interaction together with both polar and non-polar forces operating between the syntan molecules. In the concentration range 6–8 g/litre this multilayer attachment results in the establishment of a 'surface' within the substrate comprising adsorbed syntan molecules; subsequent uptake (in excess of 8 g/litre) occurs by virtue of adsorption onto the adsorbed syntan molecules present within this 'surface'. The adsorption of Matexil FA-SN differs to that of both Dyapol SB40 (Fig. 5) and Cibatex RN[1] in that, at concentrations of up to about 5 g/litre, uptake progressively increases with increasing concentration of tanning agent applied, suggesting that adsorption does not primarily occur by means of electrostatic interaction operating between the anionic syntan and the protonated amino groups in the substrate. The presence of a plateau region within the concentration range 5–7 g/litre implies, however, the establishment of a 'surface' of adsorbed syntan molecules onto which subsequent uptake (in excess of 7 g/litre) occurs.

From the foregoing it can be suggested that adsorption of Dyapol SB40 (and that of Cibatex RN) on wool fibre occurs by virtue of ion–ion interaction operating between the anionic syntan and the protonated amino groups in the substrate, together with both polar and non-polar forces of interaction. Hydrophobic interaction occurring between hydrophobic regions in both fibre and syntan, together with hydrogen bonding between the phenolic groups of the tanning agent and appropriate groups in the substrate, can also be expected to contribute to adsorption. Although Figs 1 and 3 demonstrate that electrostatic forces contribute towards the substantivity of Matexil FA-SN for wool, the results shown in Fig. 5 imply that other forces of interaction may perhaps predominate. The finding that forces of interaction other than ion–ion greatly contribute to adsorption of the commercial syntans on wool agrees with similar observations made on the adsorption of a commercial tanning agent on nylon 6.6 fibre.[3]

When a sample of wool which had been pretreated with each syntan (at 5, 10 and 15% owf) was dyed in competition with a sample of untreated wool at 95°C for 60 min with CI Acid Red 18 using the method described earlier,[1] a resist effect (as given by the low K/S_{pret} values) was obtained (Table 1). The

TABLE 1

Effect of Pretreatment with Matexil FA-SN and Dyapol SB40 on Competition Dyeing of CI Acid Red 18

	Matexil FA-SN (owf)			*Dyapol SB40 (owf)*		
	5%	*10%*	*15%*	*5%*	*10%*	*15%*
S_F (g/kg)	45·1	68·3	87·5	39·6	59·1	66·9
S_D (%)	23·1	32·8	52·4	33·5	42·3	44·6
E_D (%)	98·1	95·5	87·2	97·9	89·1	88·1
K/S_{untr}	28·4	24·3	22·8	28·4	24·9	24·1
K/S_{pret}	6·8	2·1	2·2	8·2	4·5	2·7
RE (%)	76·2	91·4	90·4	71·1	81·9	88·9

Pretreatment 95°C, 10:1 liquor ratio, pH 2·2; dyebath exhaustion for untreated wool was 98·5% corresponding to a K/S of 30·1.

resistance towards dye uptake imparted by each syntan can be attributed to ion–ion repulsion operating between the adsorbing dye anions and the anionic syntan within the fibre, reduced availability/accessibility of protonated amino groups in the substrate, together with reduced diffusional behaviour of the dye molecules within the fibre caused by the presence of the large-molecular-size tanning agent. Table 1 also shows that, for both syntans, a high proportion of tanning agent desorbed from the pretreated fibre during dyeing (as shown by the S_D values), and that the extent of this desorption increased with increasing concentration of each syntan originally present (S_F) on the fibre. Furthermore, the desorbed syntan exerted a restraining effect on the dye within the dyebath (as shown by the low K/S_{untr} values); the degree of dye restraint increased with increasing concentration of syntan desorbed from the fibre. The uptake (S_F) of Matexil FA-SN, at all concentrations used, was greater than that of Dyapol SB40, a fact that is reflected in the isotherm shown in Fig. 5. However, despite this difference in extent of uptake of the two syntans, the exhaustion of CI Acid Red 18 (E_D) obtained for concentrations of 5, 10 and 15% owf of each tanning agent was very similar, as was also the resist effectiveness (*RE*) achieved for each syntan.

Although the results presented in Table 1 for Matexil FA-SN and Dyapol SB40 differ quantitatively to each other and to those obtained for Cibatex RN,[1] the behaviour of each of the three tanning agents is identical in so far as each syntan is readily desorbed from pretreated fibre during dyeing and the desorbed syntan exerts a restraining effect on uptake of CI Acid Red 18.

The extent of desorption of each syntan, together with the extent of dye uptake that occurred during competition dyeing with CI Acid Red 18, were determined (Table 2) when the syntan (5% owf) had been applied using a 10:1 liquor ratio at different pH values and temperatures (this particular concentration of tanning agent was used in all further work, since, as Table 1 shows, it gave the lowest restraining effect on dye uptake). As Table 2 shows, desorption of both Dyapol SB40 and Matexil FA-SN during dyeing (S_D) was greatest when application had been carried out at 30°C, which can be attributed to adsorption of the tanning agent at this lower temperature having occurred mainly at the periphery of the fibre; such a surface deposition of the tanning agent can be expected to be readily desorbed. The lower extent of syntan desorption that occurred when pretreatment had been carried out at 50 and 95°C suggests that, at these higher temperatures, syntan diffusion within the fibre was greater and adsorption may not be confined mostly to the periphery of the substrate. The amount of each tanning agent remaining on the fibre at the end of dyeing (S_R), at each pH used, decreased with decrease in application temperature and, with the exception of Dyapol SB40 when applied at 30°C, for each temperature used

TABLE 2

Extent of Syntan Desorption and Uptake of CI Acid Red 18 during Competition Dyeing

	Dyapol SB40			*Matexil FA-SN*		
	pH 2·2	*pH 4*	*pH 6*	*pH 2·2*	*pH 4*	*pH 6*
95°C						
S_D (%)	33·5	37·2	37·0	23·1	22·3	23·1
S_R (g/kg)	26·4	23·0	22·4	34·7	32·8	27·8
K/S_{untr}	28·4	29·9	28·6	28·4	28·4	28·4
K/S_{pret}	8·2	8·8	16·7	6·8	7·9	18·9
RE	71·1	70·6	41·5	76·2	72·0	33·4
50°C						
S_D (%)	50·2	47·9	50·8	41·5	44·7	40·8
S_R (g/kg)	12·9	12·9	12·4	16·0	13·2	14·7
K/S_{untr}	26·6	26·8	26·2	25·3	25·9	25·9
K/S_{pret}	22·6	23·2	23·8	20·9	21·5	21·2
RE	15·2	13·5	9·2	17·7	16·8	18·5
30°C						
S_D (%)	68·1	63·9	58·0	52·3	56·2	50·2
S_R (g/kg)	5·3	5·9	8·9	10·7	8·7	10·4
K/S_{untr}	24·1	24·5	23·8	24·8	24·3	24·8
K/S_{pret}	23·6	24·2	23·8	23·2	23·9	23·5
RE	2·2	1·2	2·9	6·6	1·2	5·3

Pretreatment 5% owf, 10:1 liquor ratio.

the maximum value for S_R occurred when application had been carried out at pH 2·2. The degree of restraint exerted towards uptake of CI Acid Red 18 (as shown by the K/S_{untr} values) increased with decrease in temperature of application of each tanning agent, which can be attributed to the observed increase in syntan desorption that accompanied a decrease in application temperature. The increase in resistance to dye uptake (as given by the K/S_{pret} values) that occurred with increasing application temperature can be attributed to a corresponding increase in the amount of syntan on the fibre; for identical reasons the resist effectiveness (*RE*) obtained was observed to markedly increase with increase in temperature of application of each syntan. Table 2, therefore, demonstrates that maximum resistance and minimum restraint to adsorption of CI Acid Red 18 were achieved when application of both Matexil FA-SN and Dyapol SB40 had been carried out at 95°C and pH 2·2; these particular conditions had earlier been found (Figs 1–4) to yield maximum uptake of each syntan.

The results shown in Table 2 again show close similarity to those previously obtained for Cibatex RN.[1]

TABLE 3
Extent of Syntan Desorption and Uptake of Five Anionic Dyes during Competition Dyeing

	Matexil FA-SN					*Dyapol SB40*				
	I	II	III	IV	V	I	II	III	IV	V
S_D (%)	22·5	36·9	24·4	19·0	56·3	29·6	41·9	35·1	30·0	54·6
S_R (g/kg)	34·9	28·6	34·1	36·5	19·7	27·9	2·3	25·7	27·7	17·9
K/S_{untr}	30·1	14·9	9·3	24·3	30·3	31·5	11·4	9·1	23·6	29·1
K/S_{pret}	30·1	3·4	3·1	3·3	27·4	31·3	3·3	3·2	3·6	28·1
RE	0	77·2	66·7	88·3	9·4	0·7	71·4	65·3	84·8	3·6

Pretreatment 5% owf, 95°C, 10:1 liquor ratio, pH 2·2. **I**, CI Acid Red 88; **II**, CI Acid Violet 90; **III**, CI Reactive Red 41; **IV**, CI Reactive Red 154; **V**, CI Acid Blue 83.

Table 3 shows that, as found for Cibatex RN,[1] both Dyapol SB40 and Matexil FA-SN exerted a high resist effectiveness towards uptake of the hydrophilic dyes CI Reactive Reds 41 and 154 and CI Acid Violet 90; adsorption of these three dyes (together with that of CI Acid Red 18 for which a high *RE* was also secured) can be considered to occur primarily by means of ion–ion interaction with the protonated amino groups in the wool. Thus the high degree of resist obtained for these four hydrophilic dyes can be attributed to a reduction of this interaction caused by the presence of each anionic syntan on these sites, together with ion–ion repulsion operating between the anionic dyes and the anionic syntans. The low degree of resist obtained for the two comparatively more hydrophobic dyes, CI Acid Blue 83 and CI Acid Red 88, whose adsorption will occur primarily by virtue of forces other than electrostatic, may, as previously proposed,[1] be due to a reduction of the diffusional behaviour of the dyes caused by the presence of the large-molecular-size syntan molecules within the fibre.

CONCLUSIONS

The adsorption of both Dyapol SB40 and Matexil FA-SN occurs by virtue of both ionic and non-ionic forces of interaction. Each tanning agent imparts anionic dye resistance to the fibre by means of a reduction in both the availability/accessibility of protonated amino groups and the diffusional power of the dye within the fibre. The extent of dye resistance furnished is greater for dyes that are adsorbed on wool mainly by interaction with amino groups in the substrate, which suggests that dye resistance occurs predominantly by means of reduced availability/accessibility of the amino groups in the fibre. The relatively high extent of syntan desorption that occurred during dyeing demonstrates the low strength of the syntan–fibre interaction. The results obtained for the two syntans used in this work closely resembled those previously secured for Cibatex RN,[1] which in turn implies that the mechanism of interaction of each syntan with wool and the manner by which anionic dye resistance is imparted to the fibre are similar for each tanning agent.

ACKNOWLEDGEMENT

The authors wish to thank the Wool Foundation for provision of a scholarship to Dr Nikolaides.

REFERENCES

1. Burkinshaw, S. M. & Nikolaides, N. F. *Dyes and Pigments* **15** (1991) 225–38.
2. Alexander, P. & Hudson, R. F. *Wool: Its Chemistry and Physics*. Chapman Hall, London, UK, 1954.
3. Burkinshaw, S. M. *Colorage* (in press).