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A Commercial Syntan as an Anionic Dye-Resist Agent for Wool

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ABSTRACT

The uptake of a commercial syntan by wool serge was found to increase with decreasing application pH, indicating that ion–ion interaction contributes to syntan–fibre substantivity; adsorption of the syntan also increased with decreasing liquor ratio, possibly as a result of syntan aggregation. Uptake of the tanning agent followed a BET mechanism, suggesting that adsorption involves the formation of multi-layers and that forces of interaction other than ion–ion contribute to syntan adsorption. Treatment with the syntan imparted to wool a low degree of resistance towards uptake of two hydrophobic anionic dyes, but a high resist effectiveness towards adsorption of four hydrophilic anionic dyes when untreated wool, and wool which had been treated with the syntan, were dyed in competition. Syntan desorption occurred during dyeing, indicating that the tanning agent is relatively weakly bound to the fibre; the desorbed syntan exerted a restraining effect on the uptake of all six dyes used.

INTRODUCTION

A resist process may be defined[1] as one which modifies a textile fibre in such a way that when the resist-treated fibre is subsequently dyed, it absorbs dye to a lesser extent or at a slower rate than does untreated fibre. Various treatments have been proposed for imparting dye-resist effects to wool, for example, sulphonation,[2–5] acetylation,[2,6] glyoxylation,[6,7] deposition of polymers,[8–10] alkaline chlorination[11,12] and treatment with formaldehyde,[10] sulphamic acid,[13,14] colourless reactive compounds,[15,16] tannic

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acid/metal salts[17] and also synthetic tanning agents (syntans).[6,12,18] However, with the exception of sulphamic acid, none of these treatments enjoys widespread commercial use; furthermore, treatment of wool with sulphamic acid entails the use of an impregnation/fixation application method. Although the use of syntans as an anionic dye-resist treatment for wool has been reported,[6,12,18] no information concerning the nature of the wool-syntan interaction is available. This paper describes the exhaustion application characteristics of a commercial synthetic tanning agent on wool and the anionic dye-resist effect imparted by this compound.

EXPERIMENTAL

Materials

Fabric

The lightweight (187 $\mathrm{g\,m^{-2}}$) wool serge, kindly supplied by the IWS, was scoured prior to use by treatment at 50°C for 15 min in a stirred, aqueous (distilled water) solution (50:1 liquor ratio) of Sandozin NIE (Sandoz) (2 $\mathrm{g\,l^{-1}}$) followed by thorough rinsing in distilled water.

Dyes

The structures of the six dyes, with the exception of CI Reactive Red 154 whose constitution is undisclosed,[19] are shown in Table 1; all dyes were commercial samples and were not purified prior to use.

Syntan

A commercial sample of Cibatex RN was kindly supplied by Ciba-Geigy.

Other reagents

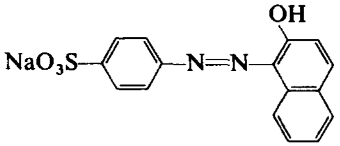
All other reagents were of general purpose grade.

Procedures

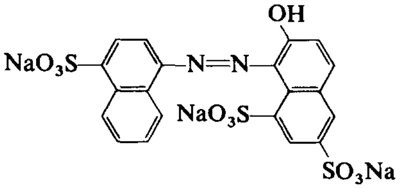
A. Adsorption of the syntans

McIlvaine buffers,[20] prepared using distilled water, were used to achieve the appropriate treatment pH value. The quantity of syntan adsorbed by the wool fibre was determined by spectrophotometric analysis (at 264 nm) of the syntan bath at the end of treatment using a 1 cm path-length quartz cell housed in a Pye-Unicam PU 8600 UV/Visible spectrophotometer (Cambridge, UK).

TABLE 1
Structures of Dyes Used[19]



C.I. ACID RED 88



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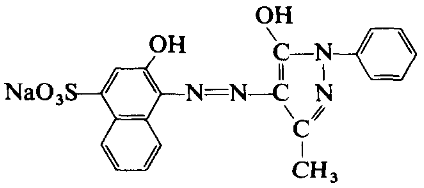
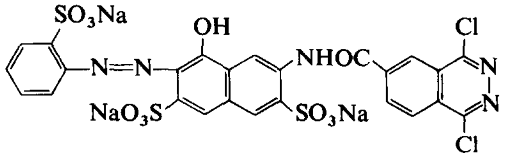
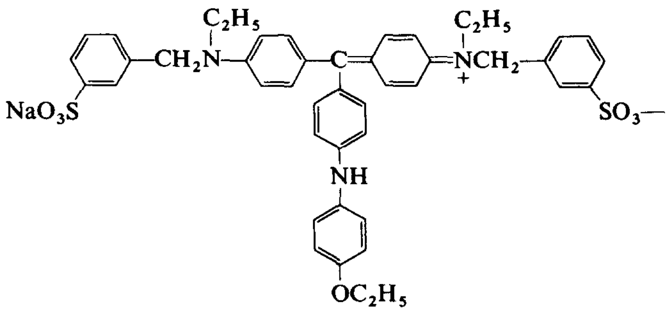


C.I. ACID VIOLET 90



C.I. REACTIVE RED 41



C.I. ACID BLUE 83

(i) Effect of pH and liquor ratio on adsorption. Wool samples were treated with the syntan (5% on weight of fibre (owf)) at pH values of 2·2, 5 and 7 at 95°C for 60 min using liquor ratios of 10:1, 20:1, 50:1 and 100:1 in partially sealed glass pots of 300 cm^3 capacity housed in a Zeltex Low Boy dyeing machine (Zeltex AG, Switzerland). The wool samples were conditioned prior to treatment, at the pH at which treatment was carried out, for 60 min at

ambient temperature using a liquor ratio of 20:1 in a stirred, open beaker; the conditioned samples were rinsed (distilled water) thoroughly and dried in the open air.

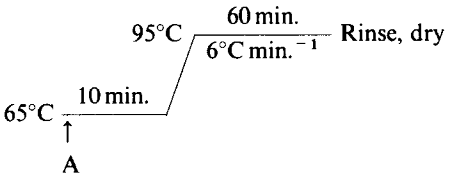
(ii) Effect of temperature on adsorption. Wool samples which had been conditioned at pH values of 2·2, 5 and 7, as described in (i) above, were treated with the syntan (5% owf) at 30, 50 and 70°C for 60 min at each of these three pH values for 1 h using liquor ratios of 10:1 and 50:1.

(iii) Equilibrium adsorption isotherm. Wool samples were treated, using a 100:1 liquor ratio, in a series of aqueous, acidic (pH 2·2) solutions of Cibatex RN of various concentrations (0·5–14 $g\,l^{-1}$) at 90°C for 7 h in sealed, stainless steel pots of 300 cm^3 capacity housed in a Zeltex PolyColor dyeing machine.

B. Resist effectiveness-desorption of syntans during dyeing

Wool samples (2 g) which had been pretreated with Cibatex RN at various temperatures, liquor ratios and pH values using the procedures described in A(i) and (ii) above, were dyed in competition with samples (2 g) of untreated (i.e. rinsed, scoured) wool using each of the six anionic dyes. The application methods used for the dyes are summarised in Fig. 1. The quantity of dye adsorbed by the two wool samples and the amount of syntan which had been desorbed from the pretreated sample during dyeing were determined by spectrophotometric analysis of the exhausted dyebath at 264 nm and at the appropriate λ_{max} of each dye (i.e. 507 nm for CI Acid Reds 18 and 88, 550 nm for CI Acid Blue 83, 523 nm for CI Acid Violet 90, 513 nm for CI Reactive Red 41 and 505 nm for CI Reactive Red 154) using a 1 cm quartz cell housed in a Pye-Unicam PU 8600 spectrophotometer. In order to carry out the combined spectrophotometric analysis of both syntan and dye, it was necessary to ensure that there was no interaction between the dye and syntan. A solution of each of the dyes (100 cm^3; *c.* 0·02 $g\,l^{-1}$) was prepared with either aqueous (distilled water) sulphuric acid (3% owf), acetic acid (2% owf) or ammonium acetate (3% owf) solution according to the dye used (Fig. 1) and the absorbance measured at its λ_{max} and at 264 nm. A 50 cm^3 aliquot of this solution was diluted to 100 cm^3 using an aqueous (distilled water) solution of the syntan (*c.* 0·03 $g\,l^{-1}$). The absorbance of the diluted solution was found to be exactly half that of the original dye solution at its λ_{max} and half that of the sum of both the original dye and syntan solutions at 264 nm. It was concluded that no interaction had occurred.

The extent of dye adsorption was also determined for each dry (open-air) dyed sample using a Macbeth reflectance spectrophotometer (10° Standard Observer; illuminant D65; UV included; specular excluded;



CI Acid Red 18 and CI Acid Red 88
A Na_2SO_4 (calcined) 20% owf; H_2SO_4 (98%) 3% owf.

CI Acid Violet 90 and CI Acid Blue 83
A CH_3COONH_4 3% owf.

CI Reactive Red 41 and CI Reactive Red 154
A CH_3COOH (60%) 2% owf.

Fig. 1. Dyeing methods.

normal aperture) (Macbeth, USA). Each sample was folded twice, giving a thickness of four layers of fabric, and measurement carried out on the face side of each sample. The resist effectiveness (R.E.) was calculated using eqn (1).

$$\text{R.E.} = ([K/S_{\text{untr}}] - [K/S_{\text{pret}}])/[K/S_{\text{untr}}] \cdot 100 \qquad (1)$$

where K = coefficient of absorption; S = coefficient of scatter; $K/S_{\text{untr}} = K/S$ value of the dyed untreated sample at the λ_{max} of the dyeing; $K/S_{\text{pret}} = K/S$ value of the dyed pretreated sample at the λ_{max} of the dyeing.

RESULTS AND DISCUSSION

The major textile use of syntans is as an aftertreatment of polyamide fibre that has been dyed with various (predominantly non-metallised acid) classes of dye to affect improved wet fastness properties; an excellent review of this area is given by Cook.[21] Syntans are also employed to reserve nylon fibre against the uptake of anionic dye during the dyeing of wool/polyamide and cellulosic/polyamide fibre blends[21,22] and to impart stain-resistance to nylon fibres.[23] The majority of syntans marketed for such applications are, typically, water-soluble anonic formaldehyde polycondensates of sulphonated dihydroxydiarylsulphones;[23,24] Cibatex RN is described[25] as a 'condensation product of aryl-sulphonate and formaldehyde'.

It is currently viewed[21,22] that such syntans, which are usually applied to nylon under weakly acidic (e.g. pH 4–5) conditions, are adsorbed onto such fibres by virtue of ion–ion interaction operating between the anionic syntan and the protonated amino end groups in the substrate, hydrogen bonding between phenolic hydroxyl groups in the tanning agent and amide groups in

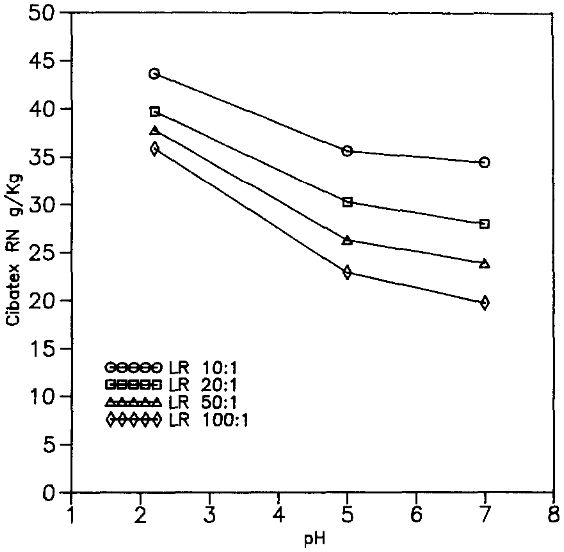


Fig. 2. Effect of liquor ratio and pH on the uptake of Cibatex RN.

the nylon, together with non-polar forces of interaction occurring between the syntan and the fibre. Owing to the large molecular size of syntans and their consequent low diffusional character, it is proposed that their adsorption is mostly confined to the periphery of the polyamide fibre. The ability of syntans to resist the uptake of acid dyes by nylon fibre under acidic dyeing conditions has been discussed by several workers;[21,22,26] this ability can be attributed to ion–ion repulsion effects operating between the anionic syntan and the incoming anionic dye molecules, occupation of protonated amino end-group dye sites in the substrate by the syntan and a reduction of the diffusional behaviour of the dye molecules within the fibre resulting from the presence of the large molecular size syntan.

Figure 2 clearly shows that the extent of adsorption of Cibatex RN increased with decreasing application pH. This implies that ion–ion interaction, operating between the protonated amino groups in the wool fibre and the anionic syntan, contributes greatly to syntan–fibre substantivity. The observed marked increase in uptake of the tanning agent that occurred below pH 5 can be attributed to a correspondingly greater number of protonated amino groups available within the fibre; also the fibre will be more swollen at such low pH values[27] and consequently the syntan may diffuse more readily within the more swollen substrate. Figure 2 also shows that uptake of the syntan increased with decreasing liquor ratio. A reduction in liquor ratio will increase the effective concentration of the syntan in the treatment bath and thereby increase the tendency for adsorption and diffusion to occur (by the establishment of a higher concentration gradient

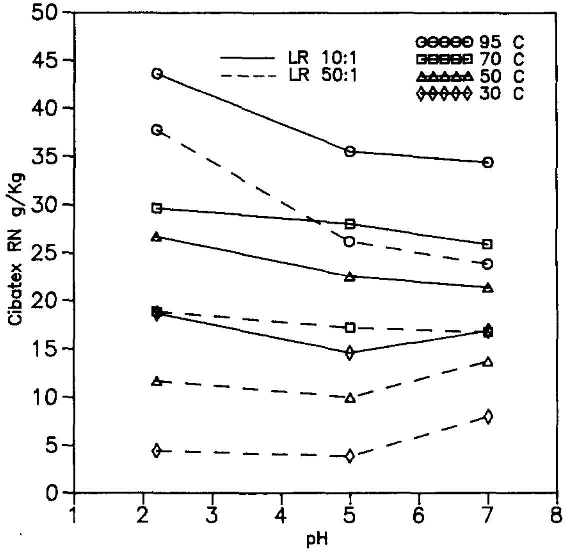


Fig. 3. Effect of temperature and pH on the uptake of Cibatex RN at liquor ratios 10:1 and 50:1.

across the fibre). Although no information is provided concerning the precise chemical composition and molecular weight of Cibatex RN, it can be proposed that aggregation of the syntan will arise in solution by virtue of polar and non-polar forces and hydrophobic interaction operating between the large molecular size syntan molecules. The increased effective concentration of syntan in the application bath that accompanied a reduction in liquor ratio can be expected to increase the degree of syntan aggregation in solution, which in turn results in greater uptake of the tanning agent. Such syntan aggregates can be considered to be bound to the fibre by those forces (e.g. 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.

Figure 3 shows that uptake of the tanning agent increased with increasing application temperature for each pH value used and for both liquor ratios employed. This can be attributed to the higher kinetic energy of the syntan molecules and their consequent greater diffusional power within the substrate, together with the greater extent of fibre swelling that accompanies an increase in application temperature. Figure 3 also shows that uptake of the syntan using a 10:1 liquor ratio was higher than that obtained using a 50:1 liquor ratio. This result, as with those presented in Fig. 2 as discussed above, can be explained in terms of the increased effective syntan concentration and the greater degree of syntan aggregation present at the lower liquor ratio. Figure 3 also shows that at both 30 and 50°C and using a liquor ratio of 50:1, uptake increased with increasing pH of application. These results differ to those obtained using a 10:1 liquor ratio at these two temperatures and for both liquor ratios used at 70°C and also 95°C, where it was found that uptake of the syntan increased with decreasing application pH. This can be explained in terms of the low diffusional power of the tanning agent in the fibre and the low effective concentration of syntan at the 50:1 liquor ratio employed. At pH 2·2, the fibre will possess a large number of protonated amino groups and, consequently, syntan–fibre substantivity will be much greater than at pH 5 or 7. The high syntan–fibre substantivity at pH 2·2 will result in rapid initial adsorption of the agent at the fibre surface. At low temperature (i.e. 30 and 50°C), owing to the low degree of fibre swelling, the low kinetic energy of the syntan molecules and the extensive ion–ion, syntan–fibre interaction, diffusion of the large molecular size tanning agent within the fibre will be low, with the result that the initially adsorbed syntan molecules provide a 'barrier' to further syntan uptake. At pH 5, however, a lower initial uptake of syntan will occur and fibre–syntan interaction will be less extensive, with the result that there is a greater probability that initially adsorbed syntan can diffuse within the fibre and so present less of a 'barrier' to further adsorption. Consequently, syntan uptake was higher at pH 5 than at pH 2·2; in a similar manner, uptake of the syntan was greater at pH 7. The observation that this increase in syntan uptake, which accompanied an increase in application pH at 30 and 50°C, occurred only in the case of a 50:1 liquor ratio can be attributed to the low effective concentration of the tanning agent in the treatment bath at this particular liquor ratio. This would result in a lower tendency for adsorption and diffusion to occur than at a 10:1 liquor ratio, with the effect that the initially adsorbed syntan molecules at the fibre surface provide a greater barrier to adsorption at the higher liquor ratio.

At 70°C (Fig. 3) the initially adsorbed syntan molecules provide much less of a barrier to further adsorption and so uptake of the agent increased with decreasing application pH for both liquor ratios employed. At 95°C there will be effectively no diffusional barrier and so a marked increase was observed in syntan uptake with decreasing application pH.

The equilibrium isotherm of the syntan (Fig. 4) shows that adsorption follows a BET (Brunauer, Emmett and Teller) mechanism, which implies that uptake involves the formation of multilayers of adsorbed syntan molecules. Figure 4 demonstrates that at low concentration (about 2–3 $\mathrm{g\,l^{-1}}$) adsorption of the syntan may occur on the protonated amino groups in the substrate, whereas at higher concentrations, 'stacking' of the syntan molecules occurs within the fibre. Such multilayer adsorption, which will be confined mostly to the surface of the substrate, may arise by virtue of, for

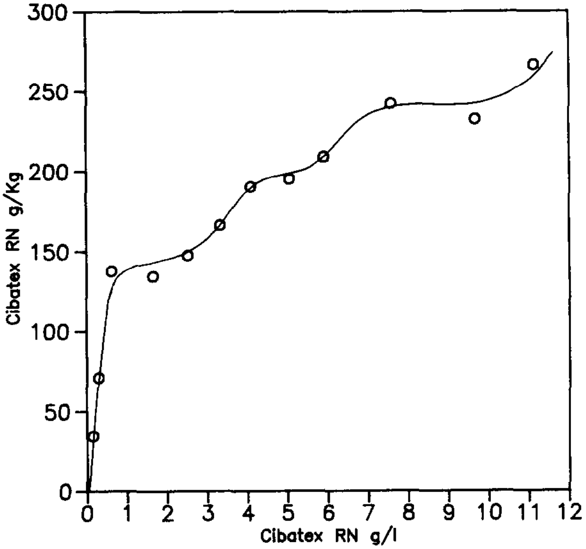


Fig. 4. Adsorption isotherm of Cibatex RN.

example, hydrophobic interaction, hydrogen bonding and non-polar forces operating between the syntan molecules.

From the foregoing it can be suggested that adsorption 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.

The dyebath exhaustion ($\%E_D$), obtained when two untreated wool samples had been dyed in competition using CI Acid Red 18, was 98·5%, corresponding to a K/S value of 30·1. Table 2 shows that these values were greater than those obtained when samples of untreated wool, and wool which had been pretreated with Cibatex RN (5, 10 and 15% owf), had been dyed in competition. Also, dyebath exhaustion decreased as the concentration of syntan originally present on the pretreated sample (S_F) increased. These results indicate that not only has syntan been desorbed from the pretreated fibre during dyeing and has exerted a restraining effect on the dye within the dyebath, but also that the extent of desorption increases with increasing concentration of syntan originally present in the fibre. The restraining effect is clearly reflected by the K/S values of the dyed, untreated wool samples (i.e. the K/S_{untr} values) which show that the degree of dye restraint increases with increasing concentration of syntan applied to

TABLE 2
Effect of Pretreatment with Cibatex RN on Competition Dyeing of CI Acid Red 18

	Cibatex RN (owf)		
	5%	*10%*	*15%*
S_F (g kg^{-1})	43·6	62·2	88·9
$\%E_D$	97·9	90·2	85·7
K/S_{untr}	29·9	27·6	21·5
K/S_{pret}	2·2	1·2	1·4
R.E. (%)	92·6	95·7	93·5

Pretreatment 95°C, 10:1 liquor ratio, pH 2·2.

the fibre. Table 2 also shows that Cibatex RN exerted a high degree of resist towards uptake of CI Acid Red 18 (as shown by the low K/S_{pret} values), which can be attributed to ion–ion repulsion operating between the anionic syntan and the adsorbing dye anions, reduced availability/accessibility of protonated amino groups in the wool and reduced diffusional behaviour of the dye molecules within the substrate resulting from the presence of the large molecular size syntan. The resist effectiveness (R.E.) of the syntan was greatest for a 10% owf application; the lower R.E. observed for a 15% owf application is attributable to the greater extent of syntan desorption (i.e. higher dye restraint) obtained whilst the lower R.E. furnished by the 5% owf syntan application is due to the lower dye resist (i.e. higher K/S_{pret} value) achieved.

The extent of syntan desorption together with the extent of dye uptake that occurred during competition dyeing with CI Acid Red 18 were determined (Table 3) when the syntan (5% owf) had been applied using a 10:1 liquor ratio at different pH values and temperatures. This particular concentration of the tanning agent was used in all further work since, as Table 2 shows, it gave the lowest restraining effect on dye uptake. As Table 3 shows, desorption of Cibatex RN during dyeing (S_D) was greatest when application had been carried out at 30°C, which may, as previously discussed, be due to adsorption of the tanning agent at this low application 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 extent of syntan desorption that occurred when pretreatment had been carried out at 50 and 95°C was considerably lower than that obtained at 30°C, which implies that at the higher application temperatures, syntan diffusion within the fibre was greater and adsorption was not confined to the periphery of the substrate. Table 3 also shows that the

TABLE 3
Extent of Syntan Desorption and Uptake of CI Acid Red 18 During Competition Dyeing

	pH		
	2·2	*5*	*7*
95°C			
S_D (%)	21·8	28·5	27·6
S_R (g kg^{-1})	34·1	25·5	24·9
K/S_{untr}	29·9	29·1	28·4
K/S_{pret}	2·1	3·2	15·9
R.E.	92·7	88·9	43·8
50°C			
S_D (%)	22·8	27·7	28·5
S_R (g kg^{-1})	20·6	16·3	17·5
K/S_{untr}	27·6	25·6	25·8
K/S_{pret}	7·5	18·9	15·3
R.E.	70·1	26·4	40·6
30°C			
S_D (%)	63·6	79·8	65·5
S_R (g kg^{-1})	6·8	2·95	5·8
K/S_{untr}	20·9	24·7	23·6
K/S_{pret}	20·2	21·7	23·2
R.E.	3·5	11·8	2·0

Pretreatment 5% owf, 95°C, 10:1 liquor ratio.

amount of Cibatex RN remaining on the fibre at the end of dyeing (S_R), at each pH used, decreased with decrease in application temperature; furthermore, for each temperature used the quantity of syntan remaining on the fibre was greatest when application had been carried out at pH 2·2. These results can be explained in terms of those shown in Fig. 3, namely that syntan uptake increased with increasing temperature of application at the 10:1 liquor ratio employed and that maximum uptake occured at pH 2·2 at 95°C. 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 the tanning agent which can be attributed to the observed increase in syntan desorption that accompanied a decrease in application temperature (Fig. 3). The dramatic reduction in resistance to uptake of the dye (as given by the K/S_{pret} values) that occurred with decreasing application temperature can be attributed to a corresponding decrease in the amount of syntan on the fibre; for identical reasons, the R.E. obtained was observed to decrease markedly with decrease in temperature of the syntan. Thus, Table 3 clearly

TABLE 4
Extent of Syntan Desorption and Uptake of Five Anionic Dyes During Competition Dyeing

	I	*II*	*III*	*IV*	*V*
S_D (%)	22·3	25·4	21·5	19·8	47·6
S_R ($g\,kg^{-1}$)	33·9	32·6	34·3	35·0	22·9
K/S_{untr}	29·5	15·2	9·7	24·9	30·5
K/S_{pret}	28·8	2·9	1·6	1·1	24·4
R.E.	2·5	81·3	83·4	95·5	19·9

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.

demonstrates that maximum resistance and minimum restraint to adsorption of CI Acid Red were achieved when application of the tanning agent had been carried out at 95°C and pH 2·2; these particular conditions had earlier been found (Fig. 3) to yield maximum uptake of the syntan.

Table 4 shows the extent of syntan desorption and the extent of dye uptake that occurred during competition dyeing with the five other dyes used. The substantivity of CI Acid Violet 90 and both reactive dyes, together with that of CI Acid Red 18, can be considered to arise primarily from ion–ion interaction with the protonated amino groups in the wool. The high degree of resist and R.E. obtained for these four hydrophilic dyes may therefore mainly be attributed to a reduction of this interaction due to the presence of syntan on these sites together with ion–ion repulsion effects operating between the anionic dyes and the anionic syntan. Conversely, adsorption of the comparatively more hydrophobic CI Acid Blue 83 and CI Acid Red 88 will occur primarily by forces other than ion–ion and thus the low degree of resist and R.E. obtained for these two dyes may result mainly from a reduction of the diffusional behaviour of the dyes caused by the presence of the large molecular size syntan molecules.

CONCLUSIONS

When applied to wool by an exhaustion method, Cibatex RN is adsorbed by virtue of both ionic and non-ionic forces of interaction. Pretreatment of wool with the tanning agent imparts anionic dye-resistance to wool 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 findings that a high degree of resist was obtained for dyes which are adsorbed on wool mainly by interaction with amino groups in the substrate and that a low extent of resist was obtained for dyes whose adsorption on wool can be considered to occur primarily by forces other than ion–ion, implies that dye-resistance occurs predominantly by means of reduced availability/accessibility of the amino groups in the fibre. Despite the relatively high extent of syntan desorption that occurred during dyeing, which shows that syntan–fibre interaction is weak, the results obtained demonstrate that the tanning agent, when applied at a concentration of 5% owf by an exhaustion technique, can impart considerable dye-resistance to wool.

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REFERENCES

1. *Textile Terms and Definitions*, 8th edn, Textile Institute, Manchester, 1986.
2. Noble, E., *Text. J. Austr.*, **20** (1945) 433.
3. Stevens, C. B., *Wool Sci. Rev.*, **15** (1956) 14.
4. Maclaren, J. A. & Kilpatrick, D. J., *Text. Res. J.*, **40** (1970) 880.
5. Maclaren, J. A. & Kilpatrick, A., *Text. Res. J.*, **44** (1974) 753.
6. Elliot, G. H. & Speakman, J. B., *JSDC*, **59** (1943) 185.
7. Ekeley, F. & Fulmer, H., *J. Amer. Chem. Soc.*, **52** (1930) 2026.
8. Lipson, M. & Speakman, J. B., *JSDC*, **65** (1949) 390.
9. Howard, L., Sarsfield, L. & Dawhariuk, D., *Text. Res. J.*, **42** (1972) 558.
10. Elliot, G. H., *JSDC*, **60** (1944) 273.
11. Townend, F. & Simpson, W., *JSDC*, **62** (1946) 47.
12. Simpson, W. S., *WRONZ Comm.*, No. L17, December 1976.
13. Sandoz, US Pat. 2 726 133 (1955).
14. Lewis, D. M., Cameron, B.; Lewis, D. M. & Pailthorpe, M. T., *Proc. 7th Int. Wool Text. Res. Conf. Tokyo*, **5** (1985) 79, 89.
15. Bell, V. A. & Lewis, D. M., *Text. Res. J.*, **53** (1983) 125.
16. Bell, V. A., Lewis, D. M. & Pailthorpe, M. T., *JSDC*, **100** (1984) 223.
17. Simpson, W. S., *Text. Res. J.*, **45** (1975), 796, 868.
18. Asquith, R. S., Campbell, B. & Hobson, M. A., *Proc. 3rd Int. Wool Text. Res. Conf. Paris*, **3** (1965) 231.
19. Colour Index, 3rd edn, Society of Dyers and Colourists, Bradford, UK, 1987.
20. Vogel, A., *A Textbook of Quantitative Inorganic Analysis*, Longmans, London, 1944.
21. Cook, C. C., *Rev. Prog. Col.*, **12** (1982) 79.
22. Shore, J., *JSDC*, **87** (1971) 3.
23. Harris, P. W. & Hangey, D. A., *Text. Chem. Col.*, **21** (11) (1989) 25.

24. Tomita, M. & Tokitaka, M., *JSDC*, **96** (1980) 297.
25. Ciba-Geigy Safety Data Sheet T 1436/A, 1984.
26. Cook, C. C. & Hajisharifi, M., *Text. Res. J.*, **47** (1977) 244; Cook, C. C. & Herbert, C., *J. Appl. Chem. Biotech.*, **28** (1978) 105; Cook, C. C. & Guthrie, J., *Polymer*, **22** (1981) 1439; JSDC, **98** (1982) 6.
27. Alexander, P. & Hudson, R. F., *Wool it's Chemistry and Physics*. Chapman & Hall, London, 1954.