THE EFFECT OF NAPHTHOL SYNTANS ON THE ADSORPTION OF ACID DYES BY NYLON

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ABSTRACT

The effect of naphthol syntans on the uptake of acid dyes by nylon has been studied as has the desorption of the agents during the uptake of dye. Although the components have only a minor effect on the rate at which dye is adsorbed by the fibre, they reduce the extent to which dye is taken up at equilibrium. The restraining effect observed is governed by the affinity of both dye and agent.

INTRODUCTION

All polyamide fibres can be dyed with a wide range of dyes. but, commercially, acid dyes (including metal complex acid dyes) still represent the most useful class. Although the two most important nylon fibres, nylon 6,6, and nylon 6, exhibit many similarities, there are significant differences in their chemical and physical characteristics which become relevant when selecting suitable dyes and processing techniques. For example, the more crystalline structure of nylon 6,6, leads to a lower rate of dye uptake and for a given dye, wet fastness properties are usually superior to those found in an equivalent depth of the same dye on nylon 6[1]. As a consequence, dyes of larger molecular size are selected for coloration of nylon 6 so as to achieve comparable wet fastness properties. Nevertheless, there is a need for a simple and efficient aftertreatment for improving the fastness to washing of many acid dyes on both nylons 6 and 6,6. The traditional full backtan aftertreatment, which involves the formation of an insoluble complex, antimonyl tannate, in the outer region of the fibre has many disadvantages associated with its use. More recently, a range of synthetic tanning agents (syntans) has been developed for use in the coloration of nylon and the effect of these auxiliaries has many similarities to that of the full backtan process[2]. A number of the syntans used in the coloration of nylon have been described by their manufacturers as being phenol-based polycondensates, sulphonated or sulphurised phenols or naphthol sulphonic acids or sulphones condensation products with formaldehyde.[3]. This work describes dye uptake by nylon fibre pretreated with naphthol sulphonic acid/formaldehyde condensates.

EXPERIMENTAL

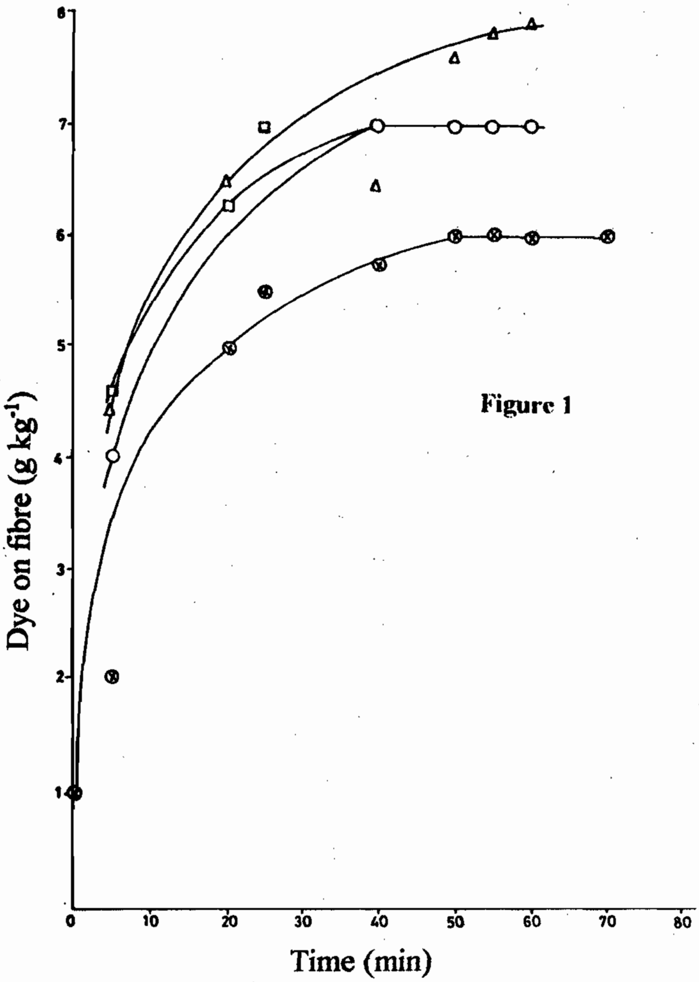
Acid dyes 13, 18, 41, 88, nylon filament and 2-naphthol-6-sulphonic acid (I), 2,2'-dihydroxy-1,1'-dinaphthyl-6,6'-disulphonic acid(II) and disodium-dinaphthyl-2,3,1",2",5,6-pyran-6',6"-disulphonate(III) condensed with formaldehyde were obtained from ICI.

Purification of acid dyes

Aqueous solutions (5g dm^{-3}) of the acid dyes were repeatedly passed down a cation-exchange column (Zeo Kerb) and anion-exchange column (De Acidite), until no Na$^+$ could be detected by flame test. The solutions, free of Na$^+$ and inorganic anions, were evaporated to dryness under vacuum at 40°C. The materials were stored over phosphorus pentoxide.

Rate of sorption curves

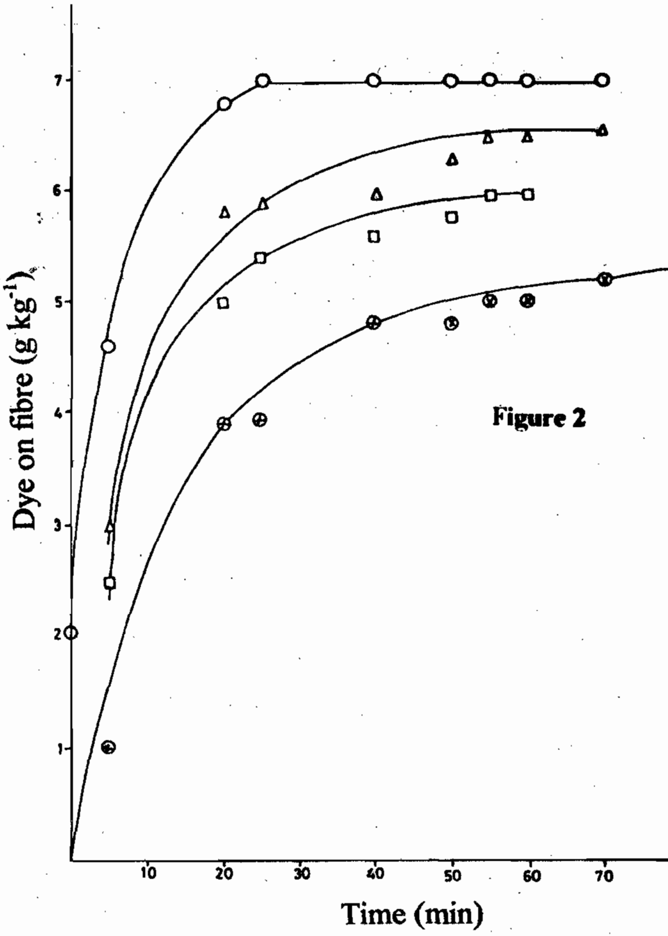
These were obtained in a round bottom flask joined to a calorimeter with flow through cuvette and recorder to uv-visible spectrometer. A solution of the naphthol sulphonic acid (200cm^3, 0.05g dm^{-3}) at pH 4.0 (formic acid) was introduced into the flask and the pump and agitator were set in action. The whole system was allowed to reach thermal equilibrium at 80°C after 1 hour. A weighed sample of nylon fibre (0.5g) previously wetted in distilled water was introduced into the flask and the rate of uptake of the component was monitored at its λ_{max} with a spectrometer. After 20 min, the pump and agitator were stopped and the sample was quickly removed and sponged dry with tissues. The remaining solution in the flask was removed and the whole apparatus flushed clean with distilled water. A solution of the dye being investigated (200cm^3, 0.02g dm^{-3}) at pH 4.0 (formic acid) was introduced into the reaction vessel and the system allowed to equilibrate. The treated sample of nylon was placed in the flask and the rate of dye uptake monitored with a coning calorimeter. Any possible desorption of agent was monitored with a u.v.-visible spectrometer.



Rate of Adsorption of Acid Dyes by Untreated Nylon, pH 4.0, 80°C. CI Acid Red: Δ, 13; □, 18; ⊗, 41; ○, 88.

Table 1: Desorption of syntan components during dyeing

Acid dye	Syntan remaining on fibre after 24 hours (%)		
	I	II	III
Acid Red 88	49	57	59
Acid Red 13	18	53	62
Acid Red 18	63	63	67
Acid Red 41	36	61	77



Rate of Adsorption of Acid Dyes by Nylon pre-treated for 20 min. with 2-Naphthol-6-sulphonic acid(I), pH 4.0, 80°C. CI Acid Red: Δ, 13; □, 18; ⊕, 41; ○, 88.

Investigation of interaction between dyes and naphthol sulphonic acid condensate

A solution of each of the dyes (100cm^3, 0.02gdm^{-3}) was made up in distilled water and the absorbance measured. A portion of this (25cm^3) solution was diluted to 50cm^3 with a solution of the agent (0.05gdm^{-3}) and the pH adjusted to 4.0 with formic acid and absorbance measured.

RESULTS AND DISCUSSION

When they were applied to untreated nylon (Figure 1) all four dyes gave similar degrees of exhaustion (60-75%) and very little difference exists between their rate of dyeing. However, Acid Red 41 was taken up most slowly and gave the lowest degree of exhaustion. This could be due to the fact that the equilibrium exhaustion is very close to the saturation value in 40mmol kg^{-1}. In general the percentage exhaustion decreased as the basicity of dye increased. Shimizu and Ohya,[4] have compared the diffusion coefficients of a number of dyes having different basicities and have shown that the diffusion coefficient decreases with increase in sulphonation. Similar results have been observed by other workers.[5,6] The observed decrease in diffusion coefficient is probably due to an increase in molecular size. It is possible, however, that the diffusion coefficients obtained from rates of dye uptake are misleading as they do not take into account the concentration dependent nature of the diffusion coefficient. In addition, such measurements are a reflection of how quickly the material becomes coloured which may be more dependant on the affinity of the dye rather than on its diffusion properties.[7]

Table 2: Rate index(R) for the effect of syntan on the adsorption of acid dyes by nylon.

		R for syntan		
Acid dye	Untreated (k_o)min^{-1})	I	II	III
Acid Red 88	1.40	0.77	0.16	0.18
Acid Red 13	0.78	0.46	0.24	0.22
Acid Red 18	0.65	0.31	0.74	0.26
Acid Red 41	0.42	0.40	0.83	0.55

The effect of syntan on dye uptake is shown in Figs. 2-4. When the desorption of syntan is expressed by percentage desorption of the original applied concentration after 24 hour dyeing (Table 1), the affinity of dye anion increases, and the effect of the compound on the equilibrium exhaustion is less. This is also reflected by the extent to which the syntan components are desorbed when the dye is

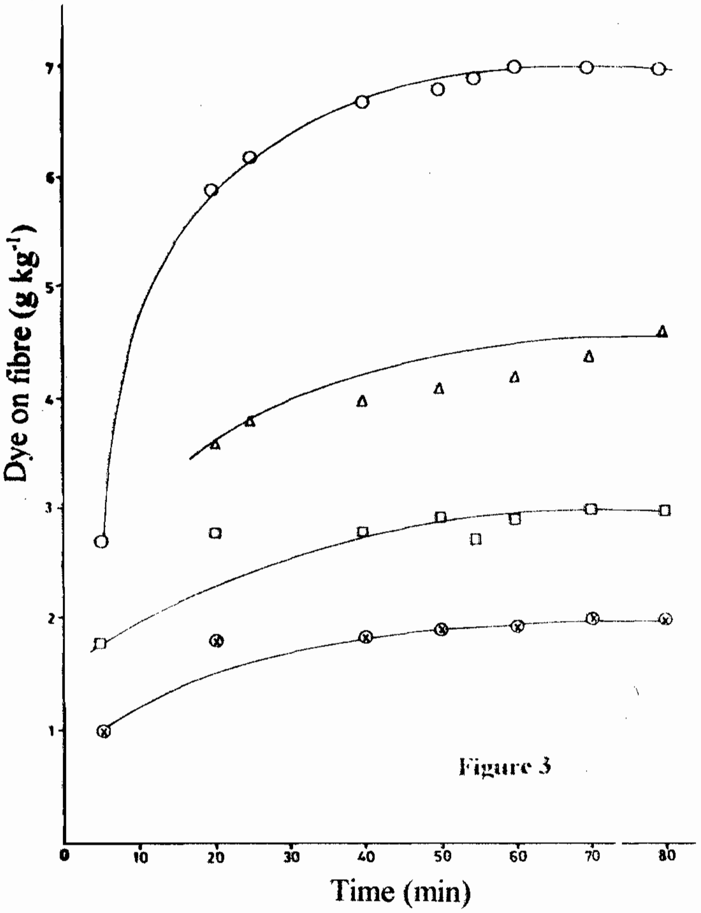


Figure 3

Rate of Adsorption of Acid Dyes by Nylon pre-treated for 20 min with 2,2'-Diydroxy-1-1'-dinaphthyl-6, 6'-disulphonic acid(II), pH 4.0, 80°C.

CI Acid Red: Δ , 13; □ , 18; ⊗ , 41; ○ , 88.

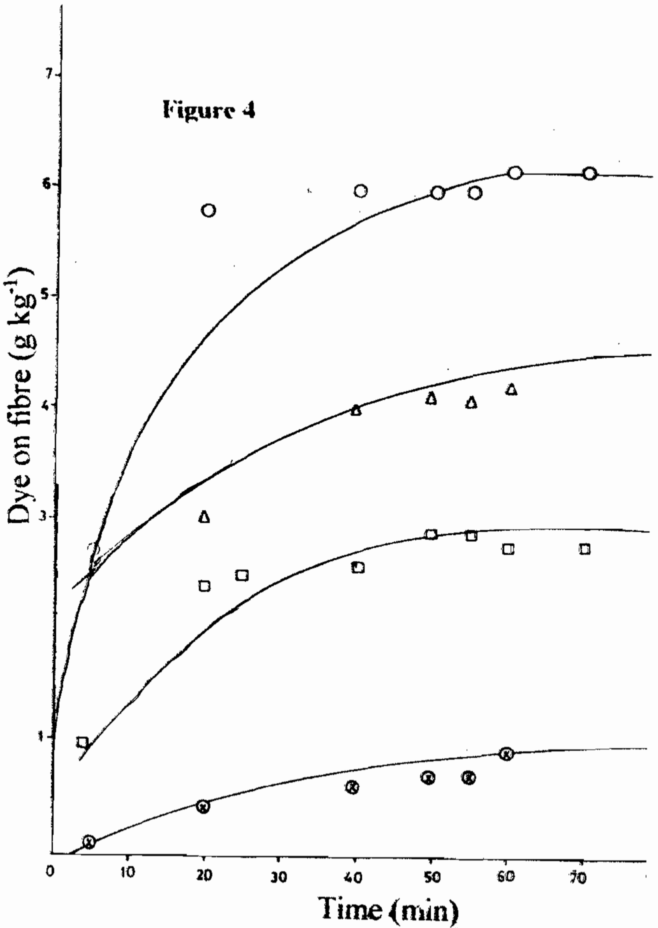


Figure 4

Rate of Adsorption of Dye by Nylon pre-treated for 20 min with Disodium-dinaphthyl-2,3,1",2",5,6-pyran-6', 6"-disulphonate(III), pH 4.0, 80°C.

CI Acid Red: Δ , 13; □ , 18; ⊗ , 41, ○ , 88.

taken up by the fibre. Similarly, the effect of the syntan component on the uptake of a given dye appears to increase as the syntan anion becomes more complex. This is because the more complex, high affinity syntans can protonate greater amino sites on the nylon thereby restricting adsorption of dye. Since analysis of results on kinetic basis which makes use of half-dyeing (t ½) values is a misleading exercise. one method is to use the values of rate index (R) or ratio of dyeing constants for pretreated and untreated nylons as in Table 2.

CONCLUSION

When a syntan is applied as a pretreatment, it exercises a restraining effect on acid dyes but the action depends on the complexity and affinity of sulphonic acid groups of the syntan. The more complex and greater the number of sulphonic acid groups, the more strongly held on the nylon the syntan is and the larger its restraining influence on acid dyes.

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