

# Effect of a Synthetic Tanning Agent on the Diffusion Properties of an Acid Dye in Nylon 6

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## Synopsis

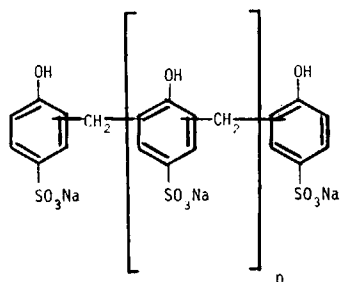
The diffusion coefficients of an acid dye in nylon 6 polymer have been measured using two different techniques, one based on the rate at which the fiber absorbs the dyestuff and the other employing the rate of transport of dye through a nylon film. Both of these methods yield diffusion coefficients of similar magnitude. The effect of a synthetic tanning treatment on the diffusion coefficients has been studied and it has been shown that a significant reduction in the diffusion coefficient is only obtained from data based on adsorption measurements. It is concluded that the decrease of rate of dye uptake caused by the presence of the syntan is due mainly to the prevention of initial dye adsorption rather than electrical repulsion or steric effects proposed in earlier studies. These results also highlight the dangers in using adsorption studies as a method for determining diffusion parameters.

## INTRODUCTION

It is well known that the wet-fastness properties of acid dyes on nylon 6 are inferior to those obtained for nylon 66. This is presumed to be due to the more open structure of the latter.<sup>1</sup> The traditional method of improving the wash fastness of these dyes has been the application of tannic acid followed by a treatment with potassium antimonyl tartarate. This system has been studied by Shore<sup>2</sup> and the efficacy of such treatments has been attributed to the formation of an insoluble complex in the outer regions of the fiber. In more recent years the use of tannic acid/antimonyl tartarate treatment has been superseded by the introduction of so-called synthetic tanning agents (syntans), which when applied to dyed nylon result in marked improvements in wash fastness.

These materials are described by their manufacturers as "high-molecular-weight condensation products of aromatic sulfonic acids and formaldehyde." Details of chemical structure are not generally known. A possible structure could be represented by Scheme I. Examples of such materials are Cibatex PA, FB (Ciba Geigy), and Matexil FA-SN (I.C.I.).

Earlier work<sup>3,4</sup> has shown that sulfonated phenol formaldehyde resins and synthetic tanning agents retard the uptake of acid dyes by nylon 6. Adsorption studies have received the most attention because of their greater amenability to quantitative analysis than desorption processes designed to correspond to a washing or wet treatment. On the basis of this earlier work it has been proposed that adsorption or desorption is suppressed because of the formation of a "ring" of high-molecular-weight material in the outer regions of the fiber. This ring may act as a barrier to dye transport in two ways. Firstly by some form of steric hindrance and blocking of the pores through which dye movement takes place or secondly by preventing dye adsorption at the fiber surface due to the neu-



Scheme I.

tralizing effect of the syntan anion on the overall positive potential of the fiber. The purpose of this work is to investigate which of these two possibilities is the most important by the measurement of the diffusion coefficient of the dye in untreated and syntanned nylon 6 using a technique based on the rate of dye adsorption and an alternative method based on the rate of transport through nylon 6 film.

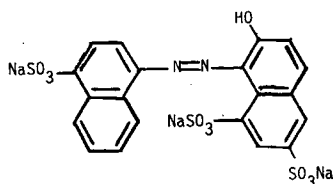
## EXPERIMENTAL

### Materials

Two samples of nylon 6 were investigated. Maranyl F400 nylon 6 film was supplied by I.C.I. and Full bright (titanium dioxide free) nylon 6 yarn (Celon) by Courtaulds Ltd. A commercial sample of the dyestuff C.I. Acid Red 18 was supplied by I.C.I. and a commercial sample of the syntan Cibatex PA by Ciba Geigy Ltd.

### Purification of C.I. Acid 18 (Scheme II)

The commercial dye (10 g) was dissolved in boiling dimethylformamide (400 mL), filtered, and the resultant solution free of inorganic material was precipitated by the addition of acetone (100 mL). The precipitate was removed by filtration, washed repeatedly with acetone, and dried at 100°C.



Scheme II.

### Pretreatment of Nylon Samples

Samples of fiber or film were treated at 85°C for 20 min in a solution containing 0.25 g/L Calgon T (A. & W.) and 0.5 g/L Synperonic NX (I.C.I.). The nylon was removed, rinsed thoroughly in distilled water, and air dried.

### Amino End-Group Estimation

This was carried out using the method described by Knott et al.<sup>5</sup>

### Rates of Sorption Curves

Rates of dyeing curves for the untreated and syntanned nylon 6 fiber were obtained using the apparatus illustrated in Figure 1.

A solution of Cibatex PA (ca. 0.05 g/L, 200 mL) at pH 4.0 (formic acid) was introduced into the reaction vessel and the pump and agitator set in motion. The system was then allowed to reach thermal equilibrium. This was judged to have been reached after 1 h. An accurately weighed sample of nylon fiber (0.5 g) previously wetted out in distilled water, was introduced into the flask. After 20 min the pump and agitator were stopped and the sample quickly removed, rinsed in ice cold water, and sponged dry with paper tissues. This treatment corresponds to an industrial syntanning process. The whole apparatus was flushed clean with distilled water. A solution of the dye (ca. 0.02 g/L, 200 mL) at pH 4.0 (adjusted with formic acid) was introduced into the reaction vessel and the system allowed to equilibrate. The treated sample of nylon fiber was in-

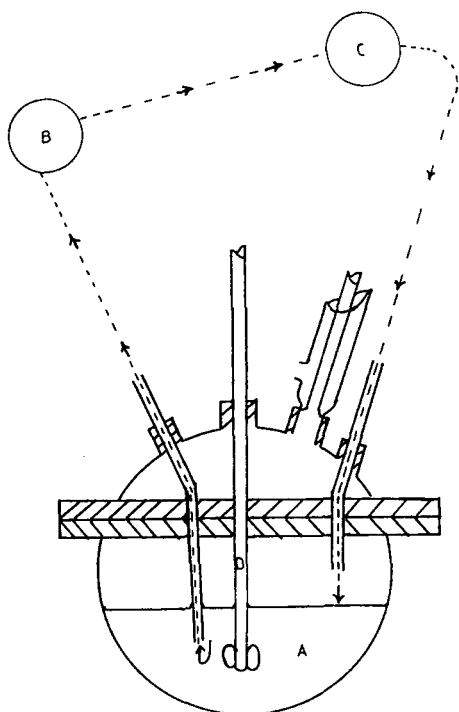


Fig. 1. Apparatus for measurement of rate of dye uptake, pH 4.0, 80°C. A, dyeing vessel; B, peristaltic pump; C, colorimeter with flow-through cuvet and recorder; D, agitator.

roduced and the rate of dye uptake monitored in the visible region of the spectrum using the colorimeter (Vitatron) fitted with a flow-through cuvet.

### Measurement of Diffusion Coefficient of Acid Red 18 in Untreated and Syntanned Nylon 6 Film

The transport of Acid Red 18 through nylon 6 film was measured in the apparatus illustrated in Figure 2. The apparatus was assembled as in the diagram with distilled water (120 mL) adjusted to pH 4.0 with formic acid in compartments A and B. The system was allowed to equilibrate at 80°C for 24 h in a thermostatically controlled water bath. Water (50 mL) was removed from compartment A and replaced with 50 mL dye solution (50 g/L) at pH 4.0 heated to 80°C to give a total concentration in compartment A of approximately 20 g/L. Three-mL samples were removed from compartment B at various time intervals and the dyestuff concentration determined spectrophotometrically. The weight of dye transported across the membrane was plotted against time and the diffusion coefficient calculated using the Daynes time-lag method.<sup>6</sup>

The diffusion coefficient of the dye through syntanned nylon film was measured in the same way using film which had been treated for 20 min in a solution of Cibatex PA corresponding to a loading of 2% on weight of nylon at 80°C, pH 4.0 (adjusted with formic acid).

## RESULTS AND DISCUSSION

### Measurement of Diffusion Coefficient from Rate of Dyeing Curves

The rates of dye uptake for untreated and syntanned nylon 6 can be seen in Figure 3. Many complex equations have been developed for the calculation of the apparent diffusion coefficient for a diffusion-controlled process. The most appropriate solution applicable to diffusion into an infinite or endless cylinder from a finite dye bath is that derived by Wilson.<sup>7,8</sup> The total amount of dye  $M_t$

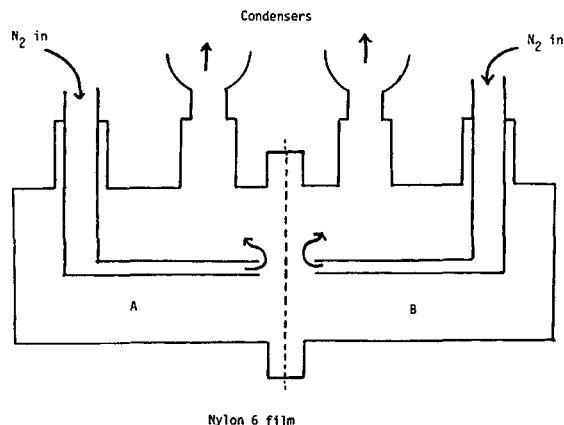


Fig. 2. Apparatus for measurement of the diffusion coefficient of C.I. Acid Red 18 through nylon 6 film, pH 4.0, 80°C.

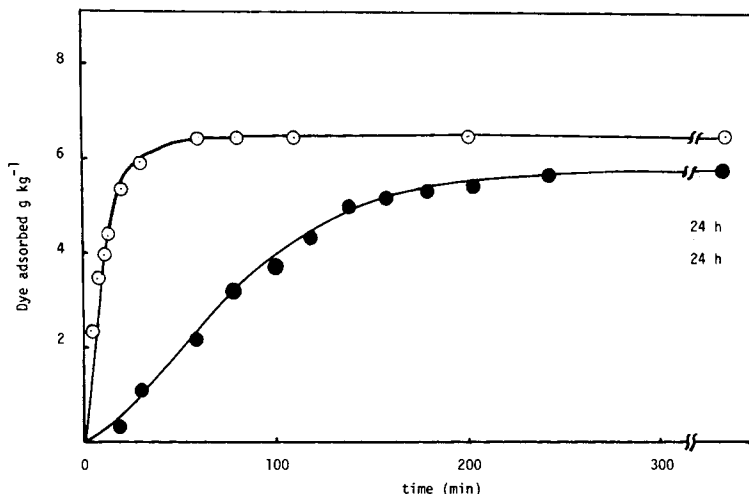


Fig. 3. Rate of uptake of C.I. Acid Red 18 by nylon 6. pH 4.0, 80°C. (○) Untreated, (●) syn-tanned.

in a cylinder of radius  $a$  after time  $t$  is expressed as a fraction of the corresponding amount  $M_\infty$  after infinite time by the relationship:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4\alpha(1 + \alpha)}{4 + 4\alpha + \alpha^2 q_n^2} \exp\left(-q_n^2 \frac{Dt}{a^2}\right) \quad (1)$$

where  $\alpha = (1-E)/E$ ,  $E$  is the fractional equilibrium exhaustion,  $D$  is the concentration independent diffusion coefficient, and  $q_n$  are the positive (nonzero) roots of the transcendental equation

$$\alpha q_n J_0(q_n) + 2J_1(q_n) = 0 \quad (2)$$

where  $J_0$  and  $J_1$  are zero- and first-order Bessel functions of the first kind.

The convergence of the series in eq. (1) becomes inconveniently slow for numerical evaluation when  $Dt/a^2$  is small. A more convenient expression which is suitable for small values of  $Dt/a^2$  has been derived by Crank.<sup>7,9</sup>

$$\frac{M_t}{M_\infty} = \frac{1 + \alpha}{1 + \alpha/4} \cdot [1 - \exp(4x^2) \operatorname{erfc}(2x)] \quad (3)$$

where

$$x = (1/\alpha + 0.25)(Dt/a^2)^{1/2}$$

Barrett and Cook<sup>10</sup> have published detailed tables relating fractional equilibrium uptake to the dimensionless parameter  $(Dt/a^2)^{1/2}$  for a wide range of equilibrium exhaustions (i.e.,  $E = 30 - 99.5$ ). Values of  $(Dt/a^2)^{1/2} > 0.01$  were obtained from eq. (1) and for values of  $(Dt/a^2)^{1/2} < 0.01$ , eq. (3) was used. The use of these tables enables a series of diffusion coefficients to be calculated from one rate of dyeing curve. The effect of dye concentration in the fiber on the diffusion coefficient can thus be examined. The variation of  $D$  with relative dye concentration ( $M_t/M_\infty$ ) is shown in Figure 4. In calculating these values of the diffusion coefficient the radius of the fiber in the dry state  $1 \times 10^{-3}$  cm was used. Obviously this does not necessarily represent the fiber radius under dyeing conditions, but can be used safely for comparative studies. It can be seen that

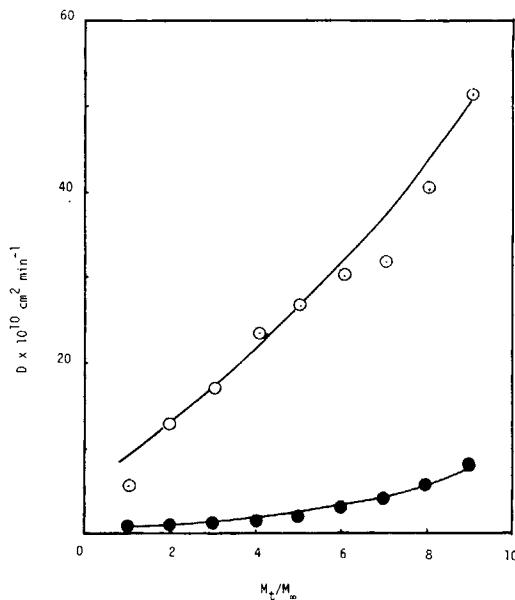


Fig. 4. Concentration dependence of diffusion coefficients of C.I. Acid Red 18 in nylon 6 filament. (○) Untreated, (●) syntanned.

the diffusion coefficient of the dye is not constant in both the untreated and syntanned nylon samples. The deviations, however, are not as marked as those obtained by McGregor et al.<sup>11</sup> This illustrates the possible shortcomings of adsorption studies as a method of calculating diffusion parameters. The reason for this lies in the fact that measurements are made concerning the rate at which the polymer becomes colored or adsorbs a species in contrast to Peters' work where the transport of dye through a membrane is actually measured in the form of concentration profiles. The results, however, do give a useful parameter for comparing the rate at which dyeing takes place. An average apparent diffusion coefficient  $D_A$  can be used to compare the rate of uptake of dye by untreated nylon with syntanned nylon. This can be defined as the value of the calculated diffusion coefficient when  $M_t/M_\infty = 0.5$ . From Figure 4 the values are  $2.63 \times 10^{-9} \text{ cm}^2/\text{min}$  for untreated nylon and  $2.06 \times 10^{-10} \text{ cm}^2/\text{min}$  for syntanned nylon. It can be seen therefore that the diffusion coefficient of the dye in nylon 6 treated with Cibatex PA as measured by this technique results in a tenfold decrease in the size of the diffusion coefficient.

#### Measurement of Diffusion Coefficients by a Study of Dye Transport through Nylon 6 Membranes

This technique was originally developed by Daynes<sup>6</sup> and has been used by other workers<sup>12,13</sup> in the study of the diffusion properties of dyes in polymers. The method involves the use of eq. (4) which has been derived for the flow of a substance through a membrane of thickness  $l$ .

$$\frac{Q_t}{lC_1} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(\frac{-Dn^2\pi^2t}{l^2}\right) \quad (4)$$

$Q_t$  is the amount of diffusant passing through the film in time  $t$  and  $C_1$  is the concentration of diffusant on the entry side of the membrane. Initially diffusant begins to build up in the film and the rate of transport within the film varies with time until steady state conditions are reached, i.e., a linear concentration gradient. As  $t$  becomes very large the exponential term becomes negligibly small and the plot of  $Q_t$  vs.  $t$  approaches a straight line

$$Q_t = (DC_1/l)(t - l^2/6D) \quad (5)$$

Rearrangement of this equation gives

$$t = lQ_t/DC_1 + l^2/6D \quad (6)$$

which shows that a plot of  $Q_t$  vs.  $t$  has an intercept on the time axis  $L = l^2/6D$ . Knowledge of the film thickness and  $L$  enables the diffusion coefficient to be calculated. The use of these equations assumes that the concentration of diffusant on the exit side of the membrane is effectively zero. From Figure 5 it can be seen that the amount of diffusant passing through the membrane is so small that this assumption is valid during the course of the experiment. As in the case of the fibers the value ascribed to  $l$  is the dry thickness of the film. Again this will not represent the true wet thickness or take into account tortuosity factors but it was felt that for purely comparative measurements these shortcomings could be ignored. It can be seen that for both the syntanned and untreated nylon 6 the time lag  $L$  is extremely large. This is due to the relatively large thickness of the film,  $4.6 \times 10^{-3}$  cm. The values of the diffusion coefficients obtained are shown in Table I. Unlike the results obtained from adsorption studies the values of  $D$  for untreated and syntanned nylon differ by a factor of less than 2.

Although the two samples of polymer investigated were from different sources and probably differ in physical properties such as crystallinity and degree of orientation, etc., the amino end-group analysis showed that both contained  $40 \times 10^{-3}$  mol/kg of amino groups. This corresponds to a molecular weight of approximately 25,000. Despite these possible physical differences, the diffusion coefficients of the dye in both samples as measured by the two techniques were in good agreement. If we now compare the effect of the Cibatex PA on the diffusion coefficient of the acid dye in the nylon 6, it can be seen from Table I that measurements made using a method based on the rate of transport of dye through the polymer show that the diffusion coefficient is only decreased by a factor of 2. However, measurements based on adsorption studies show a decrease of tenfold. These discrepancies obviously arise from the way in which the values have been obtained. The Daynes time lag method is based on a model derived to describe the actual transport of the species through the polymer. From the very small effect of the syntan on the apparent diffusion coefficient it would seem reasonable to assume that the syntan does not act as a physical barrier to dye

TABLE I  
Apparent Diffusion Coefficients of C.I. Acid Red 18 in Nylon 6

	Method of measurement	
	Daynes time lag (cm <sup>2</sup> /min)	Rate of adsorption (cm <sup>2</sup> /min)
Untreated nylon	$1.61 \times 10^{-9}$	$2.63 \times 10^{-9}$
Syntanned nylon	$0.98 \times 10^{-9}$	$2.06 \times 10^{-10}$

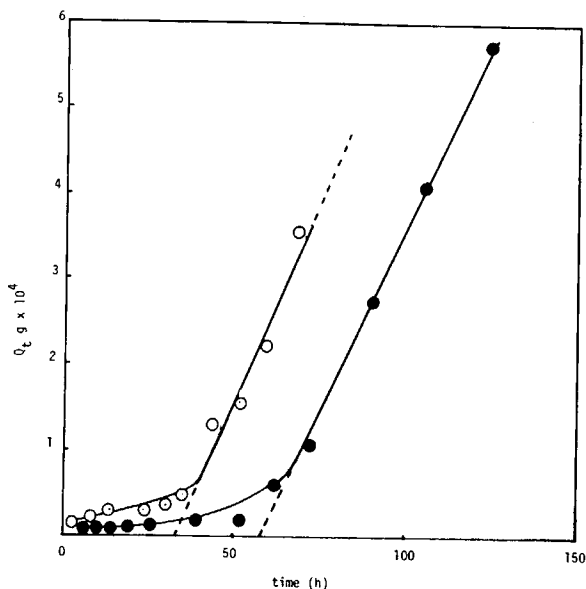


Fig. 5. Transport of C.I. Acid Red 18 through nylon 6 film. (○) Untreated, (●) syntanned.

diffusion to an extent required to give the much retarded dye uptake as seen in Figure 3.

Diffusion coefficients measured from rates of dye adsorption are based not on the transport of a substance through the polymer but rather on how quickly the polymer adsorbs the diffusant. Consequently any substance which suppresses the initial adsorption of dye presumably by electrostatically neutralizing the protonated amino groups within the nylon would result in very small values for the apparent diffusion coefficient. This illustrates the danger in using adsorption studies as a method of determining diffusion coefficient. It would seem reasonable to conclude that more reliable data concerning diffusion can only be obtained from experiments which monitor the passage of a diffusant through a material, particularly if one can construct concentration-distance profiles as has been carried out by other workers.<sup>11,14,15</sup>

## CONCLUSIONS

From measurements made on the transport of Acid Red 18 through nylon 6 film it is concluded that treatment with a synthetic tanning agent does not suppress dye diffusion significantly. There is obviously some retarding effect but this alone cannot be used to explain the reduction in the rate at which dye is adsorbed by the polymer. Studies carried out using adsorption experiments show that the rate of dye uptake is greatly reduced and gives rise to erroneous values for the diffusion coefficient. It is postulated that the effects result not from steric factors such as blocking of pores within the polymer matrix but by suppression of dye adsorption. If the synthetic tanning agent is as stated by its manufacturer to have a relatively high molecular weight, then the result of a pretreatment with Cibatex PA as described herein would be a ring of syntan in



the outer regions of the fiber or film. This would effectively neutralize the net positive charge on the polymer present under dyeing conditions and prevent dye adsorption. As the dyeing process proceeded, one would expect this ring of syntan to become dissipated through the fiber and to slowly allow dye adsorption to occur. This retarding effect gives rise to very low values of diffusion coefficients because the model for dye uptake assumes that the diffusion coefficient of the dye is the rate-determining factor. It would, however, appear that the diffusion of the syntan within the fiber is a more important parameter. The measurement of the diffusion properties of the syntan in nylon 6 is currently being investigated.

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Received August 12, 1981

Accepted January 12, 1982