

# The Accessibility of Sulphonic Acid Groups in Basic Dyeable Polyester Fibers. II. The Influence of Plasticization on the Ion Exchange Process

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## Synopsis

The exchange of the sodium ions of the sodium sulphonate group in anionically modified polyester fibers has been measured. The accessibility of the sulphonate groups in the polymer is greatly improved by plasticization and is independent of the size of the exchanging ion.

## INTRODUCTION

Heat-setting Dacron T65 at temperatures of up to 100°C has little if any effect on the basic dyeing properties, but over a range of higher heat-setting temperatures both the diffusion coefficient (Fig. 1) and saturation value (Fig. 2) of C.I. Basic Red 14 pass through a minimum value. This situation is very similar to the corresponding response of disperse dyeing properties to the heat-setting of poly(ethylene terephthalate) fibers,<sup>1</sup> the results for which have been discussed in terms of changes in crystalline structure,<sup>2</sup> and similar explanations may also be applicable to the response to heat-setting of Dacron T65. The surprising result for both types of fiber is the occurrence of the minima because the im-

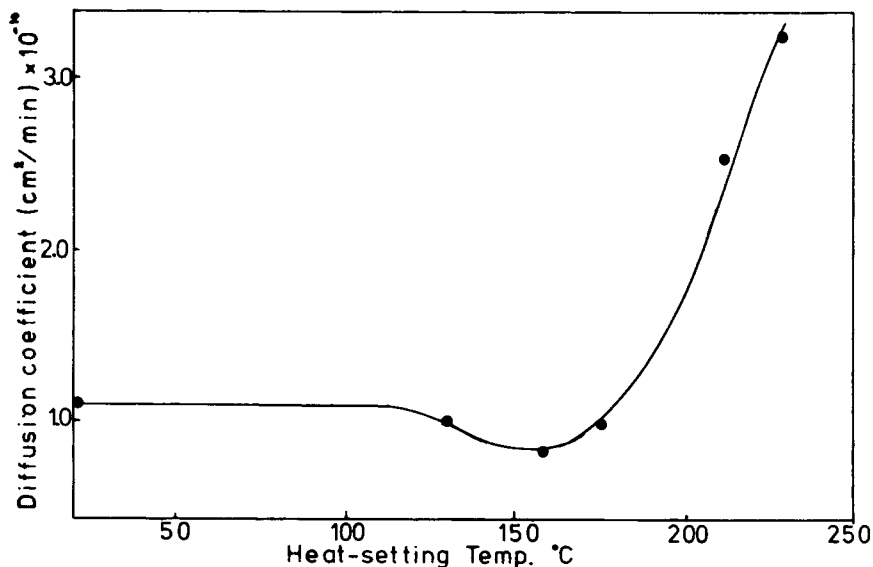


Fig. 1. The effect of heat-setting Dacron T65 on the diffusion of C.I. Basic Red 14.

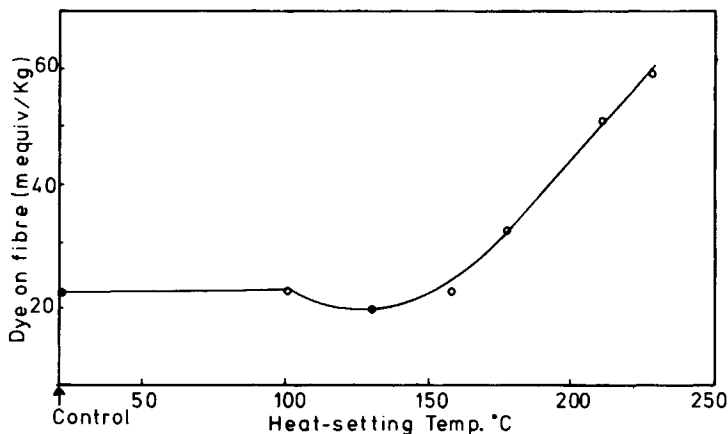


Fig. 2. The effect of heat-setting on the saturation value of C.I. Basic Red 14 dyed on Dacron T65.

proved accessibility at the higher end of the heat-setting temperature range is accompanied by an increase in fiber density. By inference, the accessibility should therefore show a decrease but it does not, and for this reason the formation of voids in the crystalline structure is an attractive theory.

However, addition to the results of previous investigations along these lines is outside the scope of the investigation reported here. The purpose of this experimental investigation was to determine the accessibility of the acidic dye sites in Dacron T65 during dyeing and to determine the influence of heat-setting on the hydrolysis of the polymer.

## EXPERIMENTAL

### Chemical Analysis

The figures given for chemical analysis of the fiber were determined as described in part I.

### Intrinsic Viscosity Measurements

The details of these experiments are also described in part I.

### Measurement of Fiber Density

The density of the fibre samples at  $23^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$  were measured using a density gradient column with a gradient formed from a mixture of carbon tetrachloride and dry ethanol. Fibers were placed carefully on the column and allowed to sink. Four hours was long enough for the equilibrium position to be reached. The density of at least three specimens of each sample was measured, and the average value taken.

### Ion Exchange of $\text{Na}^+$ for $\text{K}^+$ in the Fiber

Approximately 10 g of scoured Dacron T65 was refluxed in 1 L of a solution of 0.3M potassium chloride with and without 0.25M phenol, for times ranging

between 1 and 24 h. The fibres were then rinsed quickly in cold, distilled water and dried in a vacuum oven overnight. Analysis of the sodium and potassium content in the fiber was carried out as described in part I.

## Dyeing Experiments

### *Dyeing Conditions*

Dyeing was carried out in an experimental apparatus described in detail elsewhere.<sup>3</sup> An infinite dyebath was used (l.r. approximately 6000:1). Accurately weighed, purified C.I. Basic Red 14 was dissolved in 1800-mL distilled water at 60°C. The pH value of the dyebath was adjusted to fall between 4.5 and 4.8, using a small amount of 25% acetic acid. The dyebath also contained 0.1M sodium chloride to prevent hydrolytic degradation of the fiber (see part I). The pH of the dyebath was monitored throughout the experiment and adjusted when necessary by the addition of 25% acetic acid.

For long dyeing times, the dyebath was changed completely with a freshly prepared thermostatted solution every few hours to avoid difficulties arising from decomposition of the dye over the long dyeing times required to reach equilibrium.

### *Dye Saturation Values*

The saturation values of C.I. Basic Red 14 were determined for fibres heat-set at different temperatures with and without 0.25M phenol in the dyebath. Isotherms were measured at 90°C using a range of dye concentrations of 5–100 ( $\times 10^{-5}$ ) mol/L of dye in solution. 0.1 mol/L sodium chloride was also incorporated in the dyebaths.

### *Determination of the Diffusion Coefficient of C.I. Basic Red 14 in Dacron T64*

The rate of dyeing of Dacron T64 by C.I. Basic Red 14 was measured in the presence and absence of phenol at pH 4.5 and in the presence of 0.1M sodium chloride.

The diffusion coefficient for each dyebath was determined in the usual manner from the rate of dyeing curve by applying

$$D = \frac{\pi r^2}{16} \left( \frac{C_t}{C_\infty} / \sqrt{t} \right)^2 \quad (1)$$

where  $r$  is the radius of the fiber,  $C_t$  = amount of dye taken up after time  $t$ , and  $C_\infty$  = equilibrium dye uptake.

### *Determination of the Amount of Dye Absorbed by the Fiber*

10–50 mg of accurately weighed dry fibers were dissolved in a known volume of freshly distilled *m*-cresol. This took 5 min at 90°C. The solution was diluted with more *m*-cresol until the optical density of the solution was suitable for measurement on a Pye Unicam S.P. 600 spectrophotometer at 656 nm.

TABLE I  
The Effect of Heat-Setting Temperature on the Intrinsic Viscosity and Acidic Group Content of Dacron T65

Heat setting temperature (°C)	Carboxyl end groups	Sulphonate groups	Total acidic group content	Intrinsic viscosity using phenol/T.C.E (10:90 by weight), dL/g
		meq/kg fiber		
control	39	96.0	135.0	0.40
130	35.5	95.4	131.9	0.40
158	38.4	95.6	134.0	0.40
176	32.6	98.6	131.2	0.40
212	40.0	94.7	134.7	0.40
230	41.0	95.5	136.5	0.40

## DISCUSSION

If free carboxylic acid groups are produced by hydrolysis during heat-setting, they will add to the changes in basic dyeing properties caused by rearrangement of the molecular structure. Fortunately, the production of carboxylic acid groups during heat-setting is readily eliminated since within experimental error the intrinsic viscosity, the sulphonate group content and the carboxylic acid group content of the fiber remain unaltered after heat-setting (Table I).

The results given in Table I prove that the observed changes in the saturation value of the basic dye are due entirely to changes in the accessibility of the acidic groups within the fiber.

The first point in need of clarification is the extent to which the sulphonate groups are accessible in the fibre as supplied by the manufacturer, because a discrepancy exists between the saturation value of the basic dye and the acid group content (Fig. 3, bottom and top curves, respectively). It is clear that a

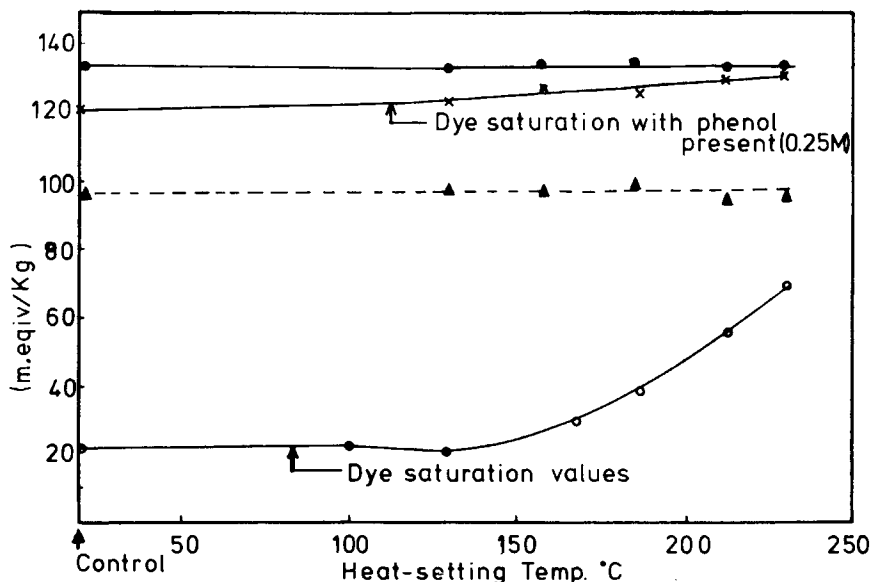


Fig. 3. The influence of heat-setting temperature on the saturation values of C.I. Basic Red 14 on Dacron T65 showing the acidic group content of the fiber. ( $\blacktriangle$ ) ( $-\text{SO}_3\text{Na}$ ); ( $\bullet$ ) [ $-\text{SO}_3\text{Na}$  + ( $-\text{COONa}$ )].

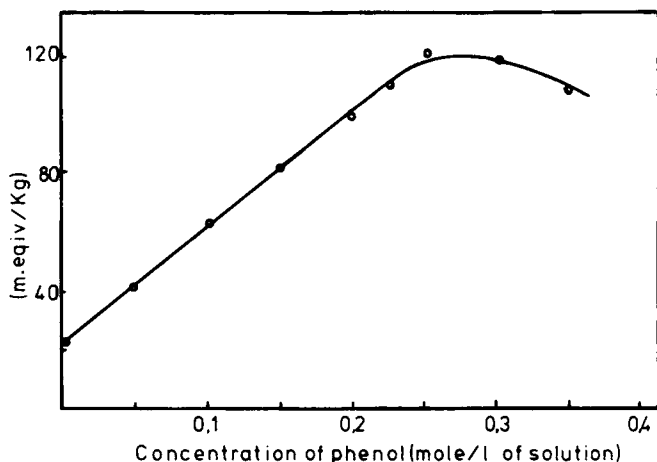


Fig. 4. C.I. Basic Red 14—dye saturation values: pH = 4.5, temp = 100°C; NaCl = 0.1 mol/L, phenol—as shown.

considerable proportion of the acid groups remain unoccupied when the practical dye saturation value is reached.

This need not be a permanent state of affairs because the use of a carrier in the dyebath releases the inaccessible sites, their accessibility being subject to control up to saturation by the adjustment of the carrier concentration (Fig. 4). Furthermore, the dye saturation values almost reach the value expected from the chemically determined acidic group content of the fiber irrespective of the changes in fiber morphology introduced by heat-setting (Fig. 3).

The effect of plasticization on the accessibility of ionic sites has been noted before in an investigation of the basic dyeing of acrylic fibres.<sup>3</sup> In that case the accessibility was related to  $T-T_g$  and the variation with temperature of the saturation value of basic dye for reprecipitated basic dyeable polyester fibres,<sup>4</sup> and the removal of the effects of heat-setting on the diffusion of disperse dyes into polyester fibres by carrier treatment<sup>5,6</sup> also appear to be part of the same phenomenon.

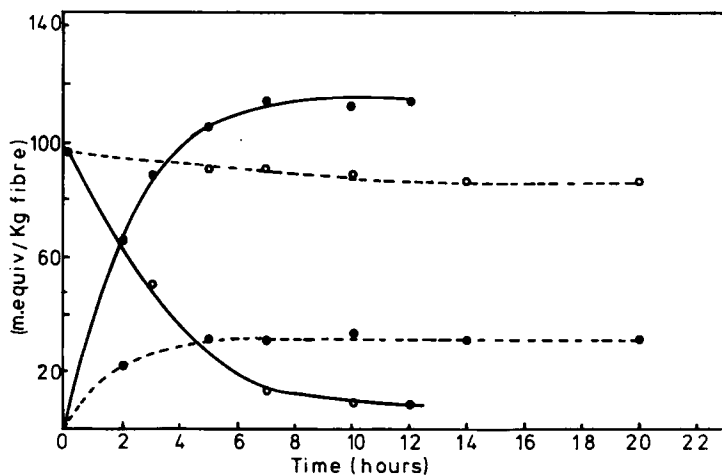


Fig. 5. The influence of phenol on the exchange of Na<sup>+</sup> for K<sup>+</sup> in Dacron T65. (●) K<sup>+</sup>; (○) Na<sup>+</sup>; (---) KCl solution; (—) KCl + phenol.

TABLE II  
Concentration of Different Cations Present in Dacron T65 at Equilibrium after Ion Exchange

Experimental conditions	Concentration of ions (meq/kg)			Experimental saturation values of C.I. Basic Red 14
	K <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup> + Na <sup>+</sup>	
Refluxed in 0.3 <i>M</i> KCl for 7 h	28.20	95.65	123.85	—
Dyed with C.I. Basic Red 14 for 48 h	—	—	—	20.65
Refluxed in 0.3 <i>M</i> KCl + 0.25 <i>M</i> phenol for 6 h	112.5	8.69	121.1	—
Dyed with C.I. Basic Red 14 and 0.25 <i>M</i> phenol for 6 h	—	—	—	121.3

Total acidic group content of Dacron T65 determined by chemical analysis = 125 meq/kg.

An incidental advantage of the use of carrier with basic dyeable polyester in experiments of this nature is that the time required to reach equilibrium is reduced to fall within dyeing times for which no fibre degradation whatever could be detected (see Fig. 2, part I).

### The Effect of Accessibility of the Acidic Groups on the Ion-Exchange Process in the Fibers

Since dyeing with basic dyes is an ion exchange process in which the cationic dye displaces the sodium ion of the acidic group, the size of the dye molecule is likely to influence the ease with which the chemical combination between dye and fiber takes place. It is reasonable to assume that sulphonate groups which happen to be embedded in a closely packed region of the fibre structure are less likely to be accessible to the large dye cations than they are to small cations like sodium or potassium. Consequently, the ability of the sodium or hydrogen ions of the acidic groups to exchange with potassium can be compared with that of the dye, to give an indication of the extent to which the size of the dye molecules hinder the exchange process. The time required to reach equilibrium in the exchange process was the same (6–7 h) whether or not the experiment was carried out in the presence of phenol (Fig. 5). Nevertheless, there is a marked difference in the extent to which exchange takes place and it is apparent that the use of carrier improves the accessibility of the acidic groups for the small inorganic ions as well as the large dye cations.

Comparison of the equilibrium figures from the different experiments clarifies the situation further (Table II). In the absence of carrier only 28.20 meq/kg of acidic groups are accessible to the potassium ions, a value close to that for dye saturation value obtained under the same conditions. Clearly only a small fraction of the total number of dye sites are involved in the ion exchange process. The quantitative effect of the carrier on the exchange process is the same for both dye and potassium ions. The exchange is near to completion, and the dye content matches the total content of the ions involved in the exchange process when the carrier concentration reaches 0.25*M*.

Even though the maximum saturation value for the dye and the concentration of exchangeable sodium ions are in agreement, chemical analysis of the content of acidic groups in the fibre indicates that a small proportion of the total dye sites remain inactive during the exchange process. The latter result may be due to self-consistent errors in the different analytical methods used, but the main conclusion drawn from the results is still tenable.

### CONCLUSION

The results presented lead to the conclusion that the accessibility of the dye sites in the fiber is independent of the size of the attacking ion, but dependent upon the molecular arrangement of the fiber molecules.

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