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Dyeing of Cotton Fibres with Disperse Dyes in Supercritical Carbon Dioxide

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ABSTRACT

The dyeing of cotton, modified previously by reaction with benzoyl chloride, has been carried out using disperse dyes in supercritical carbon dioxide at 100°C and 300 bar and compared with the dyeing of polyester under the same conditions. The colour yields of fibres was assessed by K/S measurements before and after washing to investigate the quality of dyeing in this medium. Good colour intensity and wash fastness were obtained. © *1997 Elsevier Science Ltd*

Keywords: supercritical, CO_2, dyeing, cotton, disperse dyes.

INTRODUCTION

The use of water in dyeing processes causes environmental problems. For this reason, dyeing processes have been carried out from non-aqueous media for the dyeing of polyester fibres with disperse dyes. However, as 100% recycling of solvent residues could not be achieved and also toxicological problems occurred, this approach was not successful. A dyeing process for polyester fibres has been developed by Saus *et al.* [1] in which supercritical carbon dioxide (SCO_2) is used for a transfer medium. A dyeing method for cotton fibres from non-aqueous medium without causing environmental problems is also desirable. Gebert *et al.* [2] have shown that the dyeing of natural fibres in SCO_2 is possible. Their results suggest that further experiments are required to improve colour strength and wash fastness. In this paper we present results for dyeing modified cotton from SCO_2; the

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modification involved a pretreatment which covalently attaches aromatic residues to the fibre.

A supercritical fluid can be defined as a substance above its critical temperature and pressure. Under this condition the fluid has unique properties, in that it does not condense or evaporate to form a liquid or a gas [3]. Although a number of substances are useful as supercritical fluids, carbon dioxide has been the most widely used SCO_2 gives an option avoiding water discharge, it is low in cost, non-toxic and non-flammable. It has low critical parameters (31°C, 73.8 bar) and the carbon dioxide can also be recycled. When dyeing polyester fibres from an aqueous medium, reduction clearing of the dyed fibres is carried out to maximise wet fastness properties, thus producing further effluent problems. Reduction clearing is not necessary following disperse dyeing of polyester from SCO_2. Supercritical carbon dioxide also has other advantages. The application of the dye to the fabric can be controlled and a better quality of application achieved [4, 5]. Densities and viscosities in supercritical fluids are less and diffusion more rapid than liquids, thus shortening the process time. The solubility of non-polar substances, in this case disperse dyes, in SCO_2 is sufficient for dyeing. Furthermore, the solubilities of the dyes can be controlled by changing the pressure and the temperature. For these reasons, SCO_2 is attractive as a solvent and transport medium for disperse dyes.

Because of the success of dyeing polyester with disperse dyes in SCO_2, attempts to apply this technique to natural fibres have been made [2]. Although cellulosic fibres cannot be dyed with disperse dyes, modification of such fibres increases the substantivity of hydrophobic disperse dyes. Modification can be carried out to increase the hydrophobic character of these fibres by reactions which covalently bind bulky aryl residues to the fibres [6]. For example, the benzoylation of cellulosic fibres using benzoyl chloride was developed by Shikibo [7].

In this study, cotton was first impregnated with sodium hydroxide solution and the alkali activated cellulose then reacted with benzoyl chloride.

Nucleophilic cellulosate anion

The modified cotton was then dyed from SCO_2 with a specially synthesised dye, viz. 1-(4-aminophenylazo)-2-naphthol (APAN), and with C.I. Disperse Yellow 82 (DY82), at 100°C and 300 bar. Supercritical dyeing of polyester was carried out for comparison.

EXPERIMENTAL

Samples

Disperse dyes used in the dyeing experiments were APAN (which was synthesised at the University of Leeds Colour Chemistry Department) and DY82 (obtained from Holiday Chemical Holdings). Elemental analysis of the dyes are given in Table 1.

Apparatus

Construction of a simple apparatus for dyeing in SCO_2 is shown in Fig. 1. It consists of a temperature controller; a vessel heater; a stainless-steel dyeing vessel of 50 cm^3 capacity, comprising two parts a quick release cap and the main body of the vessel in which the dye and material are placed; a manometer

TABLE 1
Elemental Analysis Results

Dyes		*Elemental Analysis Results*
APAN	Expected	73.0% C, 4.9% H, 6.2% O, 15.9% N
	Found	71.1% C, 4.2% H, 10.1% O, 14.6% N
DY82	Expected	72.1% C, 5.7% H, 9.7% O, 12.6% N
	Found	71.2% C, 5.1% H, 11.5% O, 12.2% N

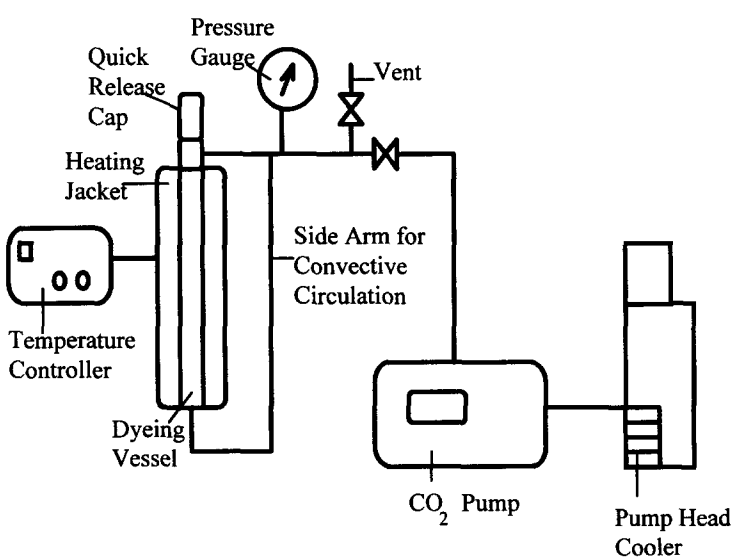

Fig. 1. The dyeing apparatus.

reading up to 600 atm; a Varex HPLC CO_2 pump and a cooler for cooling the head of the CO_2 pump. The apparatus was pressure tested for use up to 350 bar and 100°C. A side arm connects the top and bottom of the cell outside the heater to provide circulation of the SCO_2 by thermal convection.

Modification of Cotton

Firstly, the cotton fabric was padded with 20% (w/v) sodium hydroxide solution at room temperature and left for 30 min. After that, the sample was left for 2 min in benzoyl chloride (purity 99%, Alldrich), after which time the fabric was removed and washed with 5% (w/v) sodium hydroxide solution and then water. The sample was finally dried at 100°C.

Determination of Weight Gain

Weight gain for modified cotton was determined as the difference in dry weight measured before and after the application of the active compound. Fabrics were dried to a constant weight in an oven at 100°C for 1 h before weighing.

IR Analysis

Surface IR analysis was carried out using a Perkin Elmer 1740 Infrared Fourier Transform Spectrometer, with the 'Golden-Gate' diamond cell-horizontal ATR (Attenuated Total Internal Reflectance) spectroscopy attachment.

Dyeing

A mixture of disperse dye and sand was loaded on to a piece of stainless-steel mesh and placed on a pad of glass wool at the bottom of the cell. The sample of either the modified cotton or polyester to be dyed was wrapped around a stainless-steel mesh tube and loaded into the cell. The apparatus was then sealed and heated to the working temperature of 100°C, and during this time CO_2 was pumped in to a pressure of 300 bar. This was maintained for the dyeing period of 1 h, after which the CO_2 was released very slowly. When the system had reached to atmospheric pressure, the sample was removed. Throughout the dyeing process the liquor ratio was approximately 50:1.

Colour Yield Measurement and Fastness Testing

The following method for checking the fixation of the dye to the fabric and assessing the quality of the dyeing in SCO_2 was performed. The dyed material

was subjected to a simulated ISO2 wash fastness test using 5 g dm^{-3} soap solution at 50°C for 45 min. The ratio of colour on the fabric was determined by measuring K/S (λ_{max}) before and after washing using a Colorgen CS1100 spectrophotometer.

RESULTS AND DISCUSSION

After the modification of cotton with benzoyl chloride, a 22% weight gain was achieved. Modified cotton was analysed by IR spectroscopy and there was found to be very strong absorption at a frequency of 1718 cm^{-1}, which was due to the carbonyl group of the resulting benzoyl ester derivative.

Modified cotton, unmodified cotton and polyester fibres were dyed with DY82 and APAN at 100°C and 300 bar for 1 h. The amount of dyes applied was between 0.1 and 1.5% omf (i.e. % weight of dye per weight of fabric) to observe how this affected the dyeing properties for both modified cotton and polyester fibres. These results are given in Tables 2 and 3, and comparisons of modified cotton and polyester are shown in Figs 2 and 3. As expected, dyeing of unmodified cotton was unsuccessful and the wash fastness was poor. For modified cotton and polyester, Tables 2 and 3 show the colour yields (K/S) increasing with increasing the amount of dye applied. Higher colour yields were obtained for modified cotton than for polyester for both APAN and DY82. This was because the dyeing of polyester normally requires a higher temperature. The yields for DY82 were less than these for APAN for both the polyester and the modified cotton. This may be because the solubility of DY82 in SCO_2 (4.14×10^{-6} in terms of mole fraction) is less

TABLE 2
K/S Values for Dyeing with APAN Before and After Washing

	Polyester		*Cotton modified with benzoyl chloride*		*Unmodified cotton*	
Dye applied % omf	*Colour yield (K/S) Before washing*	*After washing*	*Colour yield (K/S) Before washing*	*After washing*	*Colour yield (K/S) Before washing*	*After washing*
0.1	1.69	1.57	6.00	5.43	0.92	0.38
0.3	3.62	3.78	10.87	8.55	1.54	0.63
0.5	4.74	4.21	15.46	15.41	2.00	0.75
0.7	6.88	6.77	19.17	18.78	2.11	0.88
0.9	8.48	8.22	21.04	18.02	2.15	0.90
1.1	8.98	8.75	20.56	20.56	1.94	0.77
1.3	10.87	10.31	21.84	21.64	2.08	0.98
1.5	11.40	12.39	23.52	24.14	2.44	1.15

TABLE 3
K/S Values for Dyeing with DY82 Before and After Washing

	Polyester		*Cotton modified with benzoyl chloride*		*Unmodified cotton*	
Dye applied % omf	*Colour yield (K/S) Before washing*	*After washing*	*Colour yield (K/S) Before washing*	*After washing*	*Colour yield (K/S) Before washing*	*After washing*
0.1	2.14	1.83	10.73	10.57	0.67	0.26
0.3	2.25	2.10	10.08	9.71	0.82	0.34
0.5	2.30	2.00	10.13	8.77	0.92	0.43
0.7	1.78	1.86	13.22	12.68	0.83	0.42
0.9	2.35	1.87	15.91	12.39	0.82	0.38
1.1	2.13	1.79	14.64	13.02	0.96	0.42
1.3	2.38	1.75	17.88	16.94	0.78	0.34
1.5	2.14	1.82	17.74	16.50	0.77	0.35

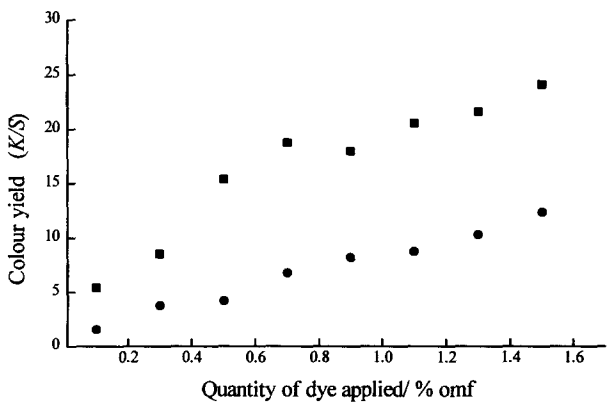

Fig. 2. Colour yield values, *K/S*, for dyeing with APAN versus amount of dye applied. Graph shows experimental points: (■) cotton modified with benzoyl chloride; (●) polyester.

than that for APAN ($7{\cdot}03\times10^{-5}$ in terms of mole fraction) at 100°C and 300 bar. The solubilities of DY82 and APAN at various temperatures and pressures are shown in Figs 4 and 5 [8]. With benzoyl chloride modification, good wash fastness results were obtained, with fixation values between 85% and 100%.

Figures 2 and 3 show considerable scatter, with colour intensity showing a rising trend with the percentage of dye. There is some evidence of saturation. It is desirable that curves of this type should be obtained for different weight gains following modification with benzoyl chloride to observe if saturation is related to the amount of benzoyl ester incorporated in the fibre.

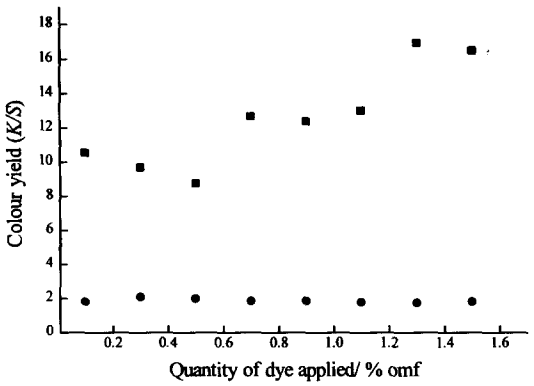

Fig. 3. Colour yield values, K/S, for dyeing with DY82 versus amount of dye applied. Graph shows experimental points: (■) cotton modified with benzoyl chloride; (●) polyester.

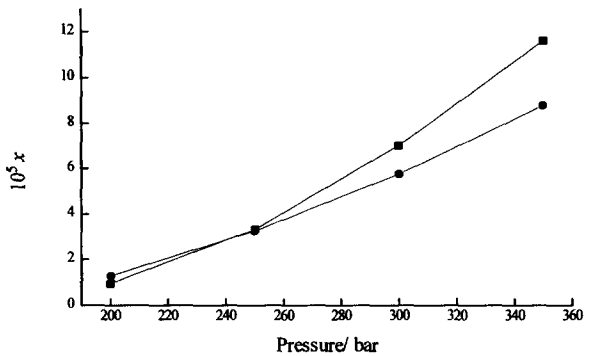

Fig. 4. The solubility in mole fraction, x, for APAN. Graph shows experimental points: (■) 100°C; (●) 80°C plotted versus pressure.

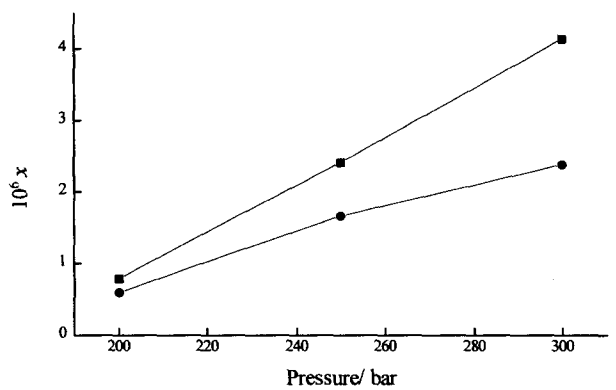

Fig. 5. The solubility in mole fraction, x, for DY82. Graph shows experimental points: (■) 100°C; (●) 80°C, plotted versus pressure.

CONCLUSIONS

Successful dyeing of cotton has been carried out with two dyes after esterification of the hydroxyl groups in cotton with benzoyl chloride. The colour yields and ISO2 wash fastness were good. Dyeing was achieved at lower temperatures than required for polyester dyeing. A very high degree of modification of the cotton (22% weight gain) was used to obtain these initial successful results. A lower degree of modification is desirable and whether good colour intensity can be achieved with less modification needs to be investigated. Also a search for a reagent which is less unpleasant to use than benzoyl chloride would be worthwhile.

REFERENCES

1. Saus, W., Knittel, D. and Schollmeyer, E., *Textile-Praxis*, **47** (1992) 1052–1054.
2. Gebert, B., Saus, W., Knittel, D., Buschman, H. J. and Schollmeyer, E., *Text. Res. Journal*, **64** (1994) 371–374.
3. McHugh, M. A. and Krukonis, V. J., *Supercritical Fluid Extraction: Principles and Practice*, (1994).
4. Saus, W. and GmbH, J., *Textile and Technology International*, (1995) 145–150.
5. Clifford, A. A. and Bartle, K. D., *Textile and Technology International*, (1996) 113–117.
6. Broadbent, P. A., Lei, X. P. and Lewis, D. M., *Cellulosics: Materials for Selective Separations and After Technologies*, Ellis Horwood Ltd., Chichester, (1993).
7. Shikibo, *Japan Textile News*, **255** (1976) 75.
8. Özcan, A. S., Clifford, A. A., Bartle, K. D. and Lewis, D. M., *Journal. Chem. Eng. Data*, submitted for publication, (1996).