

Dyeing of modified cotton fibres with disperse dyes from supercritical carbon dioxide

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Cotton, previously modified by reaction with benzoyl chloride and sodium benzoylthioglycollate, was dyed with disperse dyes APAN and DY82 in supercritical carbon dioxide at 100 °C and 300 bar. This process is compared with the dyeing of polyester and unmodified cotton under the same conditions. The modification of the cotton fabric was confirmed using FTIR. The dyed fibre was also subjected to an ISO 2 wash fastness test. The colour yields were assessed by *K/S* measurements before and after washing. Microscopic cross-section analysis for both modified and dyed cotton and for polyester was also performed.

INTRODUCTION

A supercritical fluid can be defined as a substance above its critical temperature and pressure. Under these conditions the fluid has unique properties in that it does not condense or evaporate to form a liquid or a gas [1]. Although several substances are useful as supercritical fluids, carbon dioxide has been the most widely used. In dyeing, supercritical carbon dioxide gives the option of avoiding water discharge and is low in cost, non-toxic and non-flammable. It has low critical parameters (31 °C, 73.8 bar) and can be recycled.

Dyeing by traditional water-based methods and subsequent washing processes produce large amounts of waste water in which the pollutants are often highly visible. For example, when dyeing polyester fibres from an aqueous medium, reduction clearing of the dyed fibres is carried out, maximising wet fastness properties but producing effluent problems.

Reduction clearing is not necessary after disperse dyeing of polyester from supercritical carbon dioxide. In addition, the application of the dye to the fabric can be controlled and a better quality of application achieved [2,3]. Densities and viscosities in supercritical fluids are less and diffusion is more rapid than in liquids, shortening the process time. The solubility of disperse dyes in supercritical carbon dioxide is sufficient for dyeing and can be controlled by changing the pressure and the temperature. Supercritical carbon dioxide is therefore an attractive solvent and transport medium for dyeing with disperse dyes.

However, while synthetic fabrics such as polyester have been dyed successfully from supercritical carbon dioxide on a pilot scale for a number of years [4–8], a large proportion of the textile market consists of cellulosic fibres such as cotton. Dyeing from supercritical carbon dioxide is

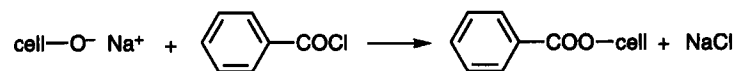
a straightforward process for polyester as disperse dyes dissolve in both carbon dioxide and polyester but these dyes are not attracted to polar cellulosic fibres, which contain many hydroxy groups.

One approach to this problem was undertaken by Gebert *et al.* who examined wool and cotton fibres after attempting to open the fibre surface with a swelling auxiliary so that dye molecules could be readily trapped in the fibre [9]. The results suggested that further experiments would be required before this method could be used to improve colour strength and wash fastness.

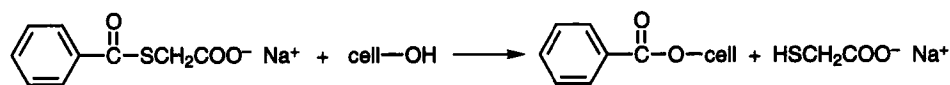
An alternative is modification of cellulosic fibres to increase the substantivity of hydrophobic disperse dyes. The hydrophobic character of these fibres can be increased by reactions that covalently bind bulky aryl residues to the fibres. Here we report attempts to facilitate the dyeing of cotton with disperse dyes in supercritical carbon dioxide by modifying the fibres by benzylation.

The benzylation of cellulosic fibres using benzoyl chloride was first developed by Shikibo [10]. For this process we first impregnated the cotton with sodium hydroxide solution and then reacted the alkali-activated cellulose with pure benzoyl chloride (Scheme 1). We also attempted a second method of benzylation: using sodium benzoylthioglycollate (BTG), a water-soluble benzylation agent that can be applied to cellulose fibres by padding and baking [11,12]. BTG is more pleasant to use than benzoyl chloride (Scheme 2).

The cotton fibres modified with benzoyl chloride or BTG were dyed from supercritical carbon dioxide with the synthesised dye APAN [1-(4-aminophenylazo)-2-naphthol] and DY82 (CI Disperse Yellow 82) at 100 °C, 300 bar. Supercritical dyeing of polyester and unmodified cotton were carried out for comparison. A brief report was made at an earlier stage of the study [13].



Scheme 1



Scheme 2

EXPERIMENTAL

Materials

The 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 show the dyes to be reasonably pure. These and the dye structures are shown in Table 1. Benzoyl chloride was supplied from Aldrich (purity 99%). The fluorescent dye Uvitex EBF (CI Fluorescent Brightener 189) was from Ciba.

Dyeing apparatus

A simple apparatus for dyeing in supercritical carbon dioxide is shown in Figure 1. It consists of a temperature controller, a vessel heater which surrounds the vessel, a stainless-steel dyeing vessel of 50 ml capacity (with a quick-release cap), a manometer, a Varex HPLC carbon dioxide pump and a cooler for cooling the head of the carbon dioxide 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 allow the supercritical carbon dioxide to circulate by thermal convection.

Benzoyl chloride modification

The cotton fabric was padded with 200 g/l sodium hydroxide solution at room temperature and left for 30 min. The sample was then left for 2 min in benzoyl chloride, removed and washed first with 50 g/l sodium hydroxide solution then with pure water. The sample was then dried at 100 °C.

BTG modification

The cotton fabric was padded with a solution containing 200 g/l BTG (prepared as described previously [12]) and 20 g/l anhydrous sodium carbonate to give an 80% wet pick-up. The fabric was allowed to dry overnight at room temperature and was then thermofixed at 200 °C for 60 s.

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 FTIR spectrophotometer, with the Golden-Gate diamond cell-horizontal ATR (attenuated total internal reflectance) spectroscopy attachment.

Dyeing and wash fastness testing

A mixture of disperse dye and sand was loaded onto a piece of stainless steel mesh and placed on a pad of glass wool at the bottom of the cell. The sample 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, while carbon dioxide was pumped in to a pressure of 300 bar. This was maintained for the dyeing period of 1 h, after which the carbon dioxide was released very slowly. When the system had reached atmospheric pressure, the sample was removed. Throughout the dyeing process the liquor ratio was approximately 50:1. The amount of dye applied was varied between 0.1 and 1.5% owf to observe the effect of dye concentration on the dyeing properties of the cotton and polyester.

Table 1 Elemental analysis of dyes

Dyes	Elemental analyses results (mass %)				
		C	H	O	N
APAN	Calc.	73.0	4.9	6.2	15.9
	Obs.	71.1	4.2	10.1	14.6
DY82	Calc.	72.1	5.7	9.7	12.6
	Obs.	71.2	5.1	11.5	12.2

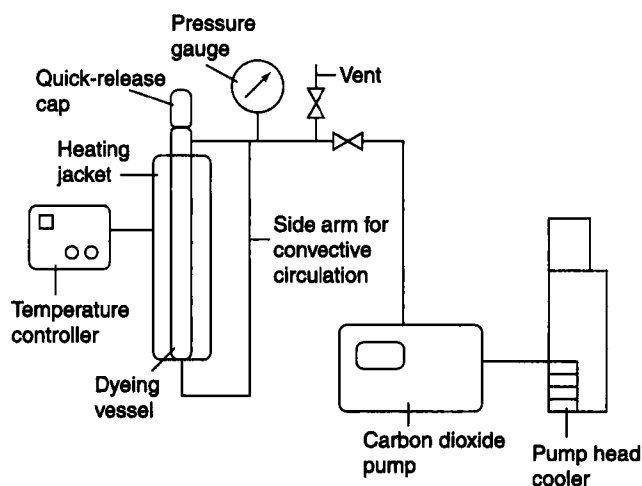


Figure 1 Dyeing apparatus

The resulting dyeings were subjected to ISO 2 wash fastness test using 5 g/l soap solution at a liquor ratio of 50:1 at 50 °C for 45 min. The sample was then washed with water and allowed to dry. The colour yields of the fabric were determined by measuring K/S (λ_{max}) before and after washing using a Colorgen CS1100 spectrophotometer.

RESULTS AND DISCUSSION

Analysis of benzoylated cotton

After the modification of cotton with benzoyl chloride, 22% weight gain was achieved. The IR spectra showed very strong absorption at a frequency of 1718 cm^{-1} , which was due to the carbonyl group of the resulting benzoyl ester derivative. There was also absorption at 1601 and 1451 cm^{-1} which corresponds to IR absorption values for C=C double bonds of the benzene ring of the benzoyl ester derivative of cellulose, formed after modification.

The BTG modification process resulted in 8.8% weight gain: less than that produced by benzoyl chloride treatment. In addition, the IR spectrum of BTG modified cotton showed weaker peaks. This is because there was less benzoyl ester derivative on the BTG modified cotton.

Dyeing

Colour yield (K/S) results for cotton modified with benzoyl chloride and with BTG, unmodified cotton and polyester fibres dyed with DY82 and APAN are given in Tables 2 and 3. The variation of K/S in modified cotton and polyester

with amount of dye is shown in Figures 2 and 3.

Higher colour yields and good wash fastness for both APAN and DY82 were obtained with the cotton fabric that had been benzoylated with benzoyl chloride. The dye fixation values (difference in K/S before and after washing) were between 85 and 100%.

The colour yield for BTG modified cotton was low and wash fastness was poor. After the BTG modification process, an 8.8% weight gain was achieved, which is clearly insufficient to obtain good dyeing from supercritical carbon dioxide. Research into dyeing acylated wool fibres with disperse dyes from an aqueous medium also indicated that a 12–13% weight gain (benzoyl group incorporation) was required for the modification process [14]. However, the results were still better for BTG modified cotton than unmodified cotton. The dye fixation values on BTG modified cotton varied from 35 to 60%.

For polyester, good colour yield and wash fastness results were obtained, but the colour yield values for benzoyl chloride modified cotton were higher for both APAN and DY82. This is because the dyeing of polyester normally requires a higher temperature (130 °C) than the 100 °C used in our experiments. The dye fixation values for polyester were between 80 and 98%.

As expected, dyeing of unmodified cotton was unsuccessful and wash fastness poor. This was because its hydrophilic nature meant it had low substantivity for disperse dyes.

Table 2 Colour yield (K/S) values for dyeing with APAN before and after washing

Dye applied (% owf)	Cotton modified with benzoyl chloride		Cotton modified with BTG		Polyester		Unmodified cotton	
	Dyed	Washed	Dyed	Washed	Dyed	Washed	Dyed	Washed
0.1	6.00	5.43	1.40	0.92	1.69	1.57	0.92	0.38
0.3	10.87	8.55	7.12	2.50	3.62	3.78	1.54	0.63
0.5	15.46	15.41	7.30	3.09	4.74	4.21	2.00	0.75
0.7	19.17	18.78	8.37	4.25	6.88	6.77	2.11	0.88
0.9	21.04	18.02	9.80	6.09	8.48	8.22	2.15	0.90
1.1	20.56	20.56	12.42	5.83	8.98	8.75	1.94	0.77
1.3	21.84	21.64	12.14	6.59	10.87	10.31	2.08	0.98
1.5	23.52	24.14	13.30	6.61	11.40	12.39	2.44	1.15

Table 3 Colour yield (K/S) values for dyeing with DY82 before and after washing

Dye applied (% owf)	Cotton modified with benzoyl chloride		Cotton modified with BTG		Polyester		Unmodified cotton	
	Dyed	Washed	Dyed	Washed	Dyed	Washed	Dyed	Washed
0.1	10.73	10.57	3.28	2.27	2.14	1.83	0.67	0.26
0.3	10.08	9.71	5.53	3.17	2.25	2.10	0.82	0.34
0.5	10.13	8.77	5.84	2.18	2.30	2.00	0.92	0.43
0.7	13.22	12.68	5.57	3.18	1.78	1.86	0.83	0.42
0.9	15.91	12.39	6.01	3.26	2.35	1.87	0.82	0.38
1.1	14.64	13.02	5.82	1.92	2.13	1.79	0.96	0.42
1.3	17.88	16.94	6.64	3.27	2.38	1.75	0.78	0.34
1.5	17.74	16.50	8.29	2.69	2.14	1.82	0.77	0.35

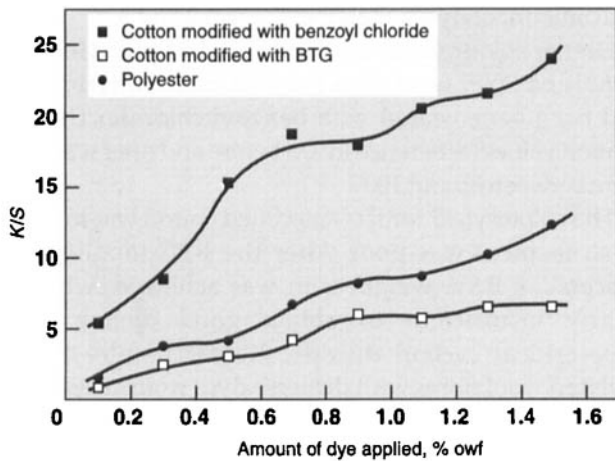


Figure 2 Colour yield values (*K/S*) for dyeing modified cotton and polyester with APAN versus amount of dye applied

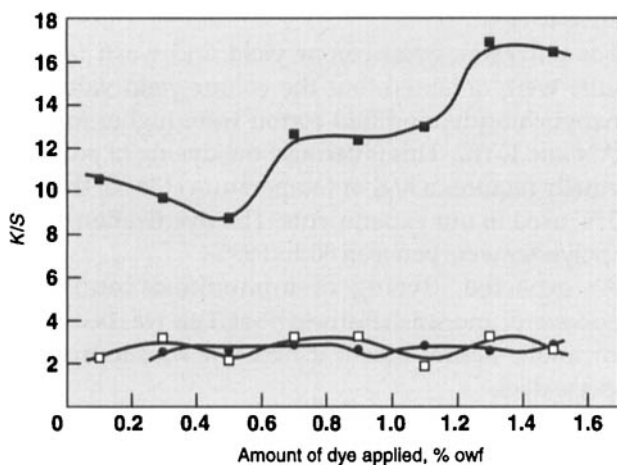


Figure 3 Colour yield values (*K/S*) for dyeing modified cotton and polyester with DY82 versus amount of dye applied; for key see Figure 2

The colour yields can be increased by increasing the amount of dye applied. Also, the colour yields for DY82 were less than those for APAN for both the polyester and the modified cotton. This may be because the solubility of DY82 in supercritical carbon dioxide (4.14×10^{-6} in terms of mole fraction) is less than that for APAN (7.03×10^{-5} in terms of mole fraction) at 100 °C and 300 bar [15].

Figures 2 and 3 show considerable scatter, with colour intensity showing a rising trend according to the percentage of dye applied. There is some evidence of saturation for benzoyl chloride modified cotton. Curves of this type should be obtained for different weight gains following modification with benzoyl chloride to investigate whether saturation is related to the amount of benzoyl ester incorporated in the fibre. Although the same conclusions can be drawn for BTG modified cotton, there are not enough benzoyl ester groups in the BTG modified cotton for it to have good dyeing properties.

Cross-section analysis results

Cotton modified with benzoyl chloride and with BTG and polyester fibres were analysed under UV light in a fluorescence microscope.

Cross-section photographs of the two modified cottons after dyeing with the fluorescent dye Uvitex EBF (Figures 4 and 5) show that benzoyl chloride modifies the cotton outside the fibre bundles (yarns) while BTG modification penetrates into the bundles and individual fibres, making it difficult to see the yarns. Thus, modification with benzoyl chloride gives a better disperse dye uptake while benzoylation with BTG is unlevel. Also, while modification of cotton with benzoyl chloride is even, the fact that some parts of the BTG modified cotton did not dye with the fluorescent dye indicates that benzoylation had occurred randomly. For polyester (Figure 6), the individual fibres can be seen clearly and are well penetrated. This is because polyester has a hydrophobic character and can be readily dyed with this dye.

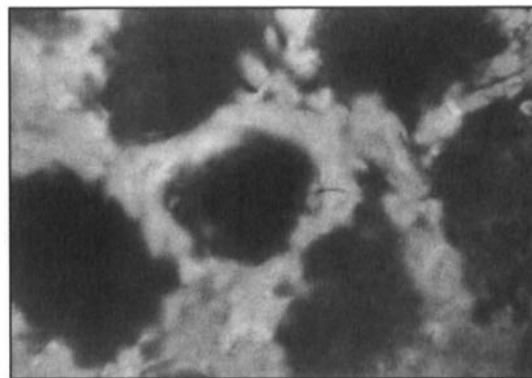


Figure 4 Cross-section of benzoyl chloride modified cotton dyed with the fluorescent dye Uvitex EBF (×100)

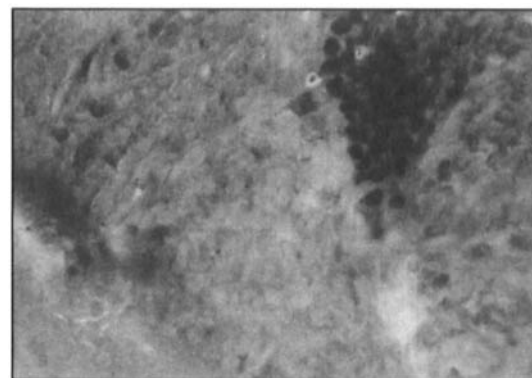


Figure 5 Cross-section of BTG modified cotton dyed with the fluorescent dye Uvitex EBF (×100)

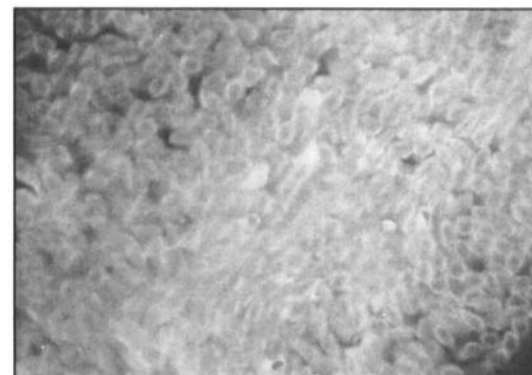


Figure 6 Cross-section of polyester dyed with the fluorescent dye Uvitex EBF (×100)

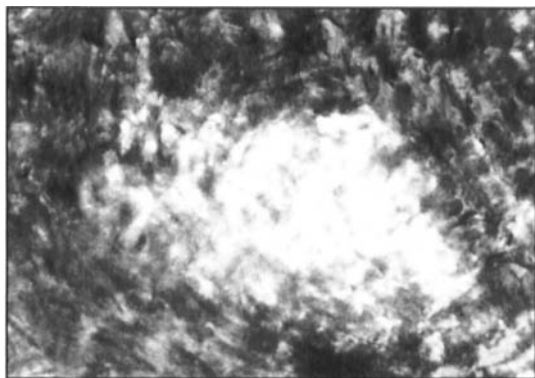


Figure 7 Cross-section of benzoyl chloride modified cotton dyed with APAN ($\times 200$)

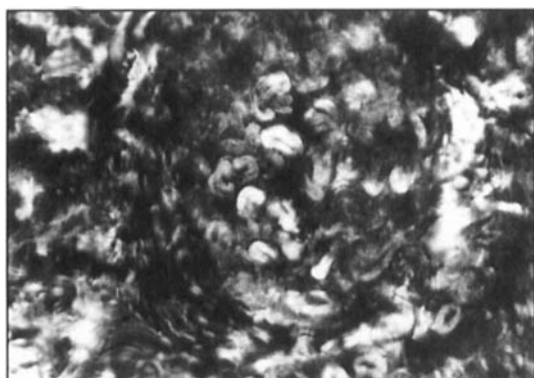


Figure 8 Cross-section of BTG modified cotton dyed with APAN ($\times 200$)

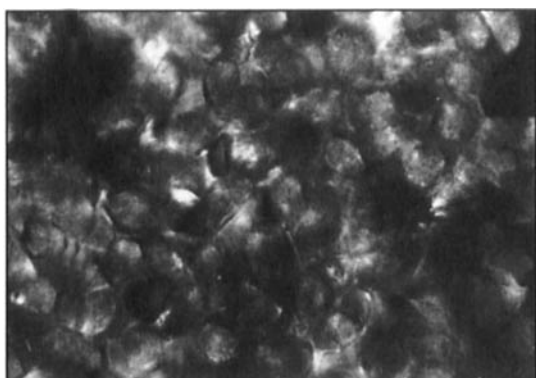


Figure 9 Cross-section of polyester dyed with APAN ($\times 200$)

Dyeing of three samples with the disperse dye APAN (Figures 7–9) gave similar results. In benzoyl chloride modified cotton the dyeing was accomplished outside of the yarn bundles, while in BTG modified cotton the dye penetrated inside the bundles and individual fibres. However, the wash fastness of the dyed BTG treated fabric was lower than that of the dyed benzoyl chloride treated samples. The dyeings of polyester fibres had a high degree of wash fastness but were weaker than normal, due to the impossibility of working at 130 °C in our equipment. Again, the dye penetrated into the polyester fibres due to their hydrophobic nature.

CONCLUSIONS

Dyeing of modified cotton with benzoyl chloride has been carried out successfully with two disperse dyes. A very high degree of modification (22% weight gain) was required. The benzylation of cotton was confirmed by IR spectroscopy of the fabric, which gave a high-intensity ester peak at 1718 cm^{-1} . The modification was also determined using cross-section analysis. Benzylation of cotton with benzoyl chloride was found to be effective but, because of the polarity differences during the modification process, ring dyeing resulted. The colour yields and ISO 2 wash fastness were good. Thus successful dyeing of cotton from supercritical carbon dioxide is possible. However, the process resulted in too great a weight gain and made use of an undesirable reagent.

In view of these problems, we then attempted to use BTG, which is water soluble and can be easily applied, for the modification process. This resulted in a weight gain of 8.8%. The IR spectra of this fabric showed a low-intensity ester peak. Cross-section analysis showed that fabric had a different structure to the benzoyl chloride modified cotton. This was because the modifications were carried out in water, making both fabric and the reagent hydrophilic. The dyeing results with this fabric were not as good, possibly due to the lower degree of arylation. To achieve successful dyeing from an aqueous medium, the weight gain percentage needs to be around 13% [14]. Further work needs to be carried out to find a modification agent that will result in successful dyeing with an acceptable weight gain.

Dyeing of polyester and unmodified cotton in supercritical carbon dioxide was carried out for comparison. The colour yield results were not optimal for polyester because dyeing was carried out at lower than optimal temperatures.

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