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# The dyeing of natural fibres with reactive disperse dyes in supercritical carbon dioxide

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**Abstract**

This paper describes the dyeing of natural and man-made fibres, in supercritical carbon dioxide, with C.I. Disperse Yellow 23 modified with 2-bromoacrylic acid and 1,3,5-trichloro-2,4,6-triazine as reactive groups. Cotton was dyed using these reactive disperse dyes without any pre-treatment of the fibre; on wool and silk, the colour depth was higher than on cotton. The wash, rub and light fastness of all dyeings was rated at between 4 and 5. A polyester/cotton-fibre blend was also dyed in a one step process.

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## 1. Introduction

In 1988, a new process for dyeing textile fibres using supercritical carbon dioxide ($CO_2$) instead of water was patented by Schollmeyer [1] and further developed by Knittel [2]. This dyeing system has since been developed from laboratory scale using a 400 ml autoclave to a semi-technical scale that utilises a 30 l autoclave [3,4]. Although the dyeing of polyester is satisfactory by this method, up to now it has not been possible to dye polar fibres, such as cotton, in this medium with good fastness properties and to acceptable colour depth. Due to the fact that cotton enjoys a global market share of 37% [5] and polyester 35% [6], it is important for this dyeing process that polar fibres can be dyed successfully. This would also enable a ‘‘one step’’ dyeing process to be developed for the important polyester/cotton blend fibres.

Different methods have been described to overcome the limitations of the $CO_2$-dyeing process of natural fibres. One possibility is to use polar co-solvents such as water or ethanol to increase the solubility of the dye and to altering the $CO_2$-dye–fibre-distribution. In this way, traditional reactive and direct dyes can be applied to cotton [1,7].

Giehl [8] dyed wool in the presence of water and methanol using non-polar natural, disperse or vat dyes and obtained a higher colour depth than in the absence of co-solvent. Akgerman [9] impregnated wool with metal cations [Cr(III) or Fe(II)] from water and used $CO_2$ soluble mordant dyes which formed complexes with the metal ions, producing dyeings of excellent wash fastness.

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The extent of disperse dye uptake in supercritical $CO_2$ can be increased by impregnating cotton with polyethylene glycol (e.g. PEG 5000); after removal of the PEG in $CO_2$ or water, the disperse dye is entrapped in the pores of the fibre [10–13].

Knittel [11] modified cotton permanently using cyclohexyl carbodiimide, making the fibre more hydrophobic so as to increase the interaction between cotton and disperse dyes, while Özcan [14] used benzoyl chloride for the same purpose. Cyclohexyl carbodiimide modified cotton was also used by Rossbach [15] who employed dyes containing sulfonyl-azido-groups which reacted with the cyclohexyl carbodiimide.

The combination of fibre modification and reactive disperse dyes in supercritical $CO_2$ has been used in which cotton was modified using alkyl amino-groups, where the alkyl chain increases the hydrophobicity of the fibre, while the amino group increases the nucleophilicity of the substrate. The modified cotton was then dyed with reactive disperse dyes based on monochloro-2,4,6-triazine which reacted with the fibre via a substitution reaction [16].

However, all of these methods suffer the disadvantage which are that pre-treatments of the fibre are necessary. Furthermore, a plant with the option to handle a high pressure system with an organic co-solvent is very expensive because it has to be explosion-proof and places high demands on the recycling of both $CO_2$ and solvent.

To overcome these disadvantages, it would be preferable to dye natural fibres with reactive dyes which are soluble in supercritical $CO_2$. In this context, disperse dyes which have been modified with epichlorohydrin are described which are able to react with wool by an addition reaction [17]. Disadvantageously, this particular fibre reactive group is not commercially available due to the toxicity of the intermediates used [18].

Another fibre reactive group for dyeing polyamide and cotton fibres in supercritical $CO_2$ is vinylsulphone [12,19,20]. For polyamide 6.6, optimum dyeing results are obtained at 120 °C at 315 bar [20]. Results have also been presented for dyeing wool with vinylsulphone dyes but in the case of cotton no results are available [19].

In this paper, C.I. Disperse Yellow 23 was modified by the introduction of fibre reactive groups via 1,3,5-trichloro-2,4,6-triazine and 2-bromoacrylic acid groups. These dyes were then used to dye natural and, for comparison, man-made fibres in supercritical $CO_2$.

Important fibre reactive groups used in traditional water dyeing processes for cotton are based on 1,3,5-trichloro-2,4,6-triazine. In contrast to monochloro-2,4,6-triazine dyes [16], the 1,3-dichloro-2,4,6-triazine group has the advantage that low dyeing temperatures of about 40 °C can be used for chemical reaction with the fibre [21]. For the fixation of these dyes in water, the relationship between the pH and the temperature of the dye bath is very important. By decreasing the pH by 1 unit, an increase in temperature of about 20 °C is needed to achieve the same degree of dye fixation [21]. In supercritical $CO_2$ the pH of natural fibres should be $<4$ due to the formation of carbonic acid by reaction with $CO_2$ and moisture in the fibre. If the pH-temperature relationship is also valid for $CO_2$ a dyeing temperature of 160 °C should be needed to obtain a high degree of dye fixation, because it is not possible to achieve a substitution reaction under alkaline conditions because of the alkali's low solubility in supercritical $CO_2$.

The other fibre reactive group examined in this paper is 2-bromoacrylic acid, which is well known in the dyeing of wool and other protein fibres. In water, it is formed in an alkaline dyeing bath from 2,3-dibromopropionic acid. Church et al. [22] postulate that reaction occurs via two addition and one substitution mechanisms. For dyeing in water, an alkaline dye bath supports only the substitution reaction but not the addition reactions [23].

## 2. Experimental

### 2.1. Chemicals

C.I. Disperse Yellow 23 (adulterant free, presscake) was purchased from Ciba Specialty Chemicals. 1,3,5-trichloro-2,4,6-triazine ($>98\%$), chlorobenzene ($>98\%$) and triethyl amine ($>98\%$) were from Fluka, while 2-bromoacrylic acid (>95%) and thionylchloride (>97%) were obtained from Aldrich. Ethanol (spectro grade) was from Acros. Dichloromethane (glass distilled grade) was received from Rathburn and silica gel (60 Å) 200–500 was obtained from Grace GmbH; the molecular sieve (4 Å) was purchased from Merck Eurolab GmbH. The $CO_2$ used (purity >99.5 vol.%) was obtained from Messer-Griesheim GmbH.

### 2.2. Fabrics

2.5-Acetate (92 g/cm$^2$), cotton (242 g/m$^2$; number of threads: warp 38/cm, weft 14/cm; warp 20/"cotton count", weft 12/"cotton count"), silk (60 g/m$^2$; number of threads: warp 50/cm, weft 37/cm; warp 2.3 tex×3, weft 2.3 tex×4) and wool (128 g/m$^2$; number of threads: warp 21/cm, weft 18/cm; 15.6 tex×2; weave 1/1 plain) were obtained from Testex Prüftextilien. Polyester (183 g/m$^2$; warp: 385 dtex, multifilament yarn, weft: 370 dtex, multifilament yarn) and polyamide 6.6 (67 g/m$^2$; warp: 44 dtex, multifilament yarn, weft: 78 dtex; multifilament yarn) were purchased from TAG.

### 2.3. Modification of C.I. Disperse Yellow 23 with 1,3,5-trichloro-2,4,6-triazine **1** (Fig. 1)

Three grammes (0.01 mol) C.I. Disperse Yellow 23, 1.85 g (0.01 mol) 1,3,5-trichloro-2,4,6-triazine and 1.01 g (0.01 mol) triethyl amine were dissolved in 300 ml dichloromethane. The solution was stirred at room temperature for 5 h. The product was purified by column chromatography on silica gel 60 Å 200–500 with dichloromethane as eluent; after removal of the solvent the purified product **1** was dried in vacuum. Yellow-orange needles were obtained [yield 0.33 g (0.7 mmol) (7%)].

### 2.4. Modification of C.I. Disperse Yellow 23 with 2-bromoacrylic acid **2** (Fig. 1)

For the synthesis of 2-bromoacrylic acid chloride, 3.0 g (0.02 mol) 2-bromoacrylic acid and 3.5 g (0.03 mol) thionylchloride were stirred under reflux with a dry pipe filled with silica gel blue on the condenser until gas formation finished. Excess thionylchloride was removed by distillation under vacuum. A light yellow oil was obtained [yield 2.1 g (0.014 mol) (70%)].

300 ml dichloromethane, dried over a molecular sieve (4 Å), 3.0 g (0.01 mol) C.I. Disperse Yellow 23 and 1.7 g (0.01 mol) 2-bromoacrylic acid chloride were stirred at room temperature for 5 h. The product was purified by column chromatography on silica gel 60 Å 200–500 using dichloromethane as eluent. After removal of the solvent, the purified product **2** was dried under vacuum. Orange needles were obtained [yield of 0.44 g (1 mmol) (10%)].

### 2.5. Dyeing in supercritical carbon dioxide

The dyeing experiments (2%omf dye) in supercritical $CO_2$ were carried out in a 400 ml autoclave fitted with a temperature controller, pressure indicator and a stirring basket, as described previously [24]. The amount of disperse reactive dye used (2%omf dye) ensured that maximum dye uptake of the fibre occurred during the static dyeing process. The modified dye was ground, put into a crucible and placed at the bottom of the autoclave. The fabric (stored for 24 h under standard conditions of 20.5 °C±0.5, rel. atmospheric humidity 65% prior to dyeing) were placed inside the basket. The autoclave was closed and filled with gaseous $CO_2$ up to 55 bar. The temperature was increased to 120 or 160 °C under stirring of the basket at 600 rpm. After reaching a constant temperature, the $CO_2$ pressure was increased up to 280 bar. The dyeing experiments at 120 °C were carried out for between 30 and 240 min; at 160 °C the dyeing time was 240 min. After dyeing the $CO_2$ in the autoclave was depressurized and the dyed samples removed.

### 2.6. Characterisation of the dyed textiles

#### 2.6.1. Fastness properties

The rub, light and wash fastness of the fibre was examined according to DIN 54021, DIN 54004 and to ISO 105-C06, C1S, respectively.

#### 2.6.2. Colour strength

The reflectance spectra of the dyeings were measured using a Cary 5E (Varian) using an

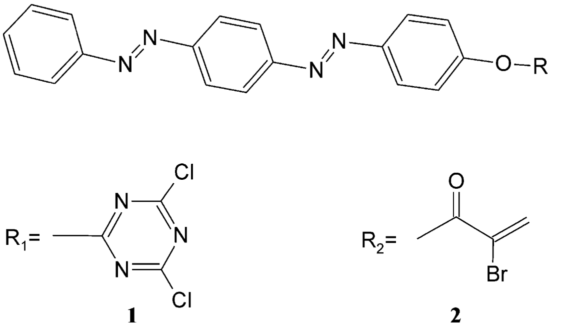

Fig. 1. C.I. Disperse Yellow 23 esterified with 1,3,5-trichloro-2,4,6-triazine ($R_1$; **1**) or 2-bromoacrylic acid ($R_2$; **2**).

Ulbricht globe and the *K*/*S* values of the dyed samples were calculated.

### 2.7. Characterisation of the dyes

The melting points of the dyes were measured using a DSC 2910 (TA Instruments) and a Thermal Analyst 2000 (TA Instruments).

UV–Vis-spectra were measured using a Cary 5E (Varian) spectrophotometer using ethanol as solvent.

The $^1$H-NMR spectra were recorded using a Bruker WM using acetone-$d_6$ (Fluka) as solvent.

Mass spectra data were obtained using an AMD 604 (AMD Intectra).

## 3. Results and discussion

### 3.1. Characterisation of the reactive disperse dyes

The melting point of dye **1** was 126.6 °C and of dye **2** 143.1 °C, while the unmodified C.I. Disperse Yellow 23 melted at 186.3 °C.

The modifications were confirmed by $^1$H-NMR and mass spectroscopy. In this context the $^1$H-NMR spectrum of C.I. Disperse Yellow 23 was also measured, because in dye **1** the peak of the hydroxy-group proton should be absent and no additional proton should appear. For dye **2** the absence of the hydroxy-proton is also valid, but here additional vinylic protons were expected.

C.I. Disperse Yellow 23: $\delta=7.1$ (2 H, m, aromat.); $\delta=7.5$–$7.6$ (3 H, m, aromat.); $\delta=7.9$–$8.2$ (8 H, m, aromat.); $\delta=9.3$ (1 H, s, OH).

Dye **1**: $\delta=7.2$ (2 H, m, aromat.); $\delta=7.5$–$7.6$ (3 H, m, aromat.); $\delta=7.9$–$8.2$ (8 H, m, aromat.).

Dye **2**: $\delta=4.1$ (2 H, m, vinylic); $\delta=7.4$ (2 H, m, aromat.); $\delta=7.5$–$7.6$ (3 H, m, aromat.); $\delta=7.9$-$8.2$ (8 H, m, aromat.).

The mass spectra for dye **1** show a single $M^+$ of 450 u and for dye **2** a doublet $M^+$ of 434 and 436, due to the bromine atom in the reactive group, which has an atomic mass of 79 and 81 u by a ratio of nearly 1:1. For C.I. Disperse Yellow 23 a $M^+$ of 302 u was found.

The $\lambda_{max}$ measured in ethanol shifted from 383 to 362 nm for both modifications, due to the lower -I-effect of the ester group compared to that of the hydroxy group.

### 3.2. Dyeing in supercritical carbon dioxide

#### 3.2.1. C.I. Disperse Yellow 23 modified with 1,3,5-trichloro-2,4,6-triazine 1

As expected, after dyeing natural fibres such as cotton with C.I. Disperse Yellow 23 in supercritical $CO_2$ all of the dye could be removed by rinsing the fibre with acetone due to the low substantivity of the dye for the fibre. Therefore, a method was developed to dye natural fibres in supercritical $CO_2$ using reactive disperse dyes dye **1** or **2**.

Due to the fact that alkaline compounds are visually insoluble in supercritical $CO_2$, it is not possible to support the substitution reaction of 1,3-dichloro-2,4,6-triazine of dye **1** with cotton. Consequently, a higher reaction temperature in $CO_2$ needs to be used to affect dye–fibre reaction. The dyeing experiments with dye **1** were carried

Table 1

*K*/*S* values at 378 nm before and after a treatment with acetone of cotton dyed with dye **1** under different conditions at 280 bar

| Dyeing temperature | 120 °C | | 160 °C | |
|---|---|---|---|---|
| Dyeing time | 60 min | 240 min | 60 min | 240 min |
| *K*/*S* value before treatment with acetone | 1.14 | 1.30 | 1.75 | 1.67 |
| *K*/*S* value after treatment with acetone | 0.95 | 1.16 | 1.70 | 1.62 |

Table 2
Fastness data of cotton and silk dyed with dye **1** in supercritical carbon dioxide under different conditions at 280 bar

| | | | Wash fastness | Rub fastness | | Light fastness |
|---|---|---|---|---|---|---|
| | | | | Dry | Wet | Stage 5 |
| Cotton | 120 °C | 60 min | 4–5 | 5 | 5 | 4 |
| | | 240 min | 3 | 5 | 5 | 4 |
| | 160 °C | 60 min | 3 | 5 | 5 | 4 |
| | | 240 min | 1–2 | 5 | 5 | 4 |
| Silk | 120 °C | 60 min | 4–5 | 5 | 5 | 2 |
| | | 240 min | 4–5 | 5 | 5 | 2 |

out at 120 and 160 °C for 60 and 240 min with cotton; under all conditions used level dyeings are obtained.

The *K*/*S* values of cotton which had been dyed with dye **1** are presented in Table 1 before and after treatment with acetone for the removal of unfixed dye. Increasing the dyeing temperature or the dyeing time increased the *K*/*S* values. For both dyeing times at 160 °C, full penetration of the fibre was observed. The highest *K*/*S* value was achieved at a dyeing time of 60 min at 160 °C.

Under all conditions used the rub- and light-fastness were acceptable (Table 2). The poor wash-fastness obtained after dyeing at 160 °C for 240 min can be attributed to decomposition of the dye–fibre bond [25] by HCl which is released during the substitution reaction of the hydroxy-groups of cellulose with the dye. To examine the influence of the moisture content of the fibre on this decomposition, cotton was dried by microwave radiation before dyeing. This pre-treatment of the textile had no influence on the fastness data, fixation or colour yield achieved but resulted in a significant decrease in the quality of the fibre due to excess drying of the fabric.

Silk was only dyed at 120 °C in supercritical $CO_2$ for 60 and 240 min using dye **1** due to decomposition of the fibre at 160 °C [26]. After dyeing the dye could be completely removed from the fibre with acetone. When the dyed fibre was treated in an alkaline wash bath the wash fastness was 4–5 (Table 2). This can be explained by the fact that the $CO_2$-dyeing process is a "transport of the dye to the fibre" step, in which the dye is not fixed to the silk. In this case the fixation takes place only under alkaline conditions leading to the rub fastness of 5 (Table 2). Besides the low colour depth, the light fastness also are unacceptably low [27].

In conclusion an increase in the dyeing time or temperature increased the degree of dye fixation on cotton but did not lead to a significant increase in colour depth on cotton and silk. Therefore, 2-bromoacrylic acid was examined as fibre reactive group.

### *3.2.2. Dyeing with C.I. Disperse Yellow 23 esterified with 2-bromoacrylic acid* **2**

*3.2.2.1. Protein fibres.* As described in the case of 1,3-dichloro-2,4,6-triazine, for the 2-bromoacrylic acid group of dye **2** an alkali-support of the substitution reaction with protein fibres in $CO_2$ is not possible. Furthermore, the 2-bromoacrylic reactive group has to be formed in an external step. Generally, if the supporting influence of alkali is neglected, the same dyeing reaction mechanism in $CO_2$ can be assumed as in water for all amino-group containing fibres, such as wool and silk.

In contrast to the 1,3-dichloro-2,4,6-triazine group, 2-bromoacrylic acid is able to fix to protein fibres in supercritical $CO_2$ as shown by the *K*/*S* of wool which had been dyed in supercritical $CO_2$ (Fig. 2). After all dyeing experiments with wool, the $\lambda_{max}$ were at 378 nm and the *K*/*S* values were always higher than 4.90. An increase in the dyeing time from 120 to 240 min increased the colour strength while at a dyeing time of 240 min and an increase in temperature from 120 to 160 °C, the *K*/*S* value was further increased [Fig. 2; curve (b) and (c)].

For all protein fibres dyed with dye **2**, level dyeings were obtained as well as full penetration of the fibres at a dyeing temperature of 160 °C. At 120 °C ring dyeing was obtained for a dyeing time of 120 min while after 240 min, full penetration was observed but with a gradient in the colour depth from outside to inside.

The fastness data of both protein fibres dyed in supercritical $CO_2$ with dye **2** are summarized in Table 3. For wool good fastness data were obtained while for silk, better light fastness is found at the higher dyeing temperature of 160 °C,

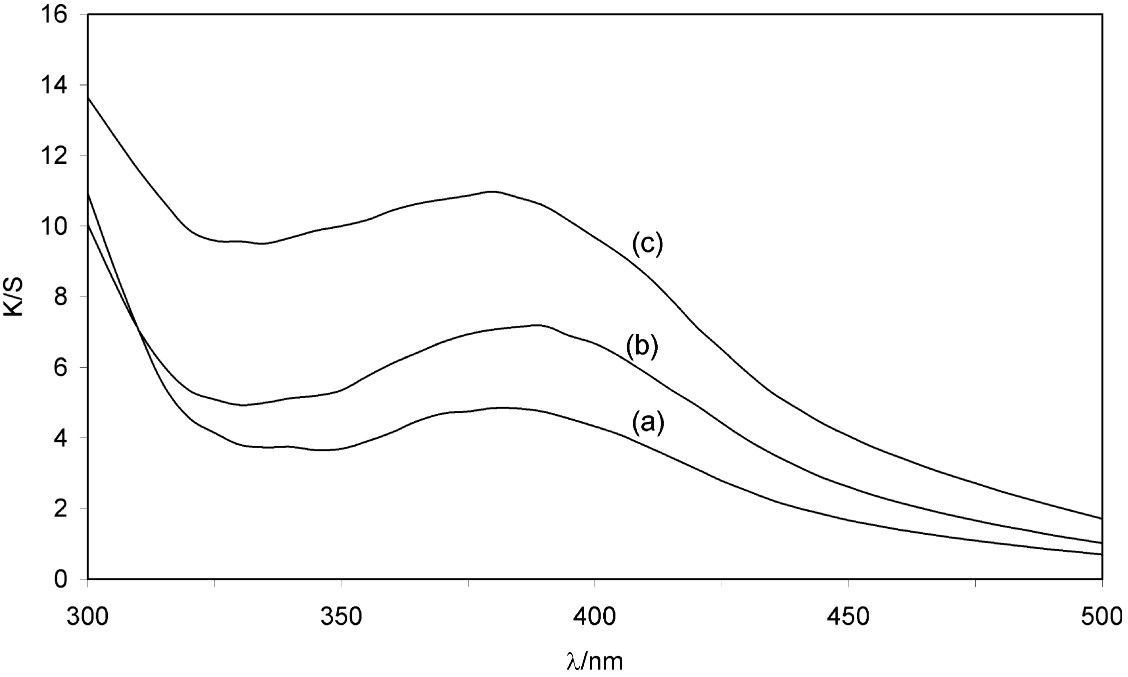

Fig. 2. UV–Vis spectra of wool dyed with dye **2** in supercritical carbon dioxide at 280 bar under different conditions: 120 °C/120 min (a); 120 °C/240 min (b); 160 °C/240 min (c).

but under these conditions, the decomposition of the fibre was unacceptably high [26]. As shown later, the colour depth of protein fibres was comparable with that of polyester dyed with dye **2** in supercritical $CO_2$.

*3.2.2.2. Cotton.* A possible reaction mechanism between cotton and dyes containing the 2-bromoacrylic acid ester or amide reactive group is presented in Fig. 3. In this case only one addition and one substitution reaction can be postulated and not two addition and one substitution reactions as for amino-groups presented by Church [22].

After dyeing with dye **2** for 60 min at 120 °C in supercritical $CO_2$, a $K/S$ value of 2.34 was obtained at 378 nm [Fig. 4; curve (a)]. This was higher than the $K/S$ value of 1.46 at 378 nm achieved for cotton under the same dyeing conditions with dye **1**. An increase in dyeing time from

Table 3
Fastness data of protein fibres dyed with dye **2** in supercritical carbon dioxide at 280 bar under different conditions

| | | | Wash fastness | Rub fastness | | Light fastness |
|---|---|---|---|---|---|---|
| | | | | Dry | Wet | Stage 5 |
| Wool | 120 °C | 120 min | 4–5 | 5 | 5 | 5 |
| | | 240 min | 5 | 5 | 5 | > 5 |
| | 160 °C | 240 min | 5 | 5 | 5 | > 5 |
| Silk | 120 °C | 120 min | 4–5 | 5 | 5 | 3 |
| | | 240 min | 5 | 5 | 4–5 | 3–4 |
| | 160 °C | 240 min | 4 | 5 | 5 | > 5 |

Table 4
Fastness data of cotton dyed with dye **2** in supercritical carbon dioxide at 280 bar under different conditions

| | | | Wash fastness | Rub fastness | | Light fastness |
|---|---|---|---|---|---|---|
| | | | | Dry | Wet | Stage 5 |
| Cotton | 120 °C | 30 min | 4–5 | 5 | 5 | 5 |
| | | 60 min | 4 | 5 | 5 | > 5 |
| | | 120 min | 4–5 | 5 | 5 | 5 |
| | | 240 min | 4 | 5 | 5 | 5 |
| | 160 °C | 240 min | 5 | 5 | 5 | 5 |

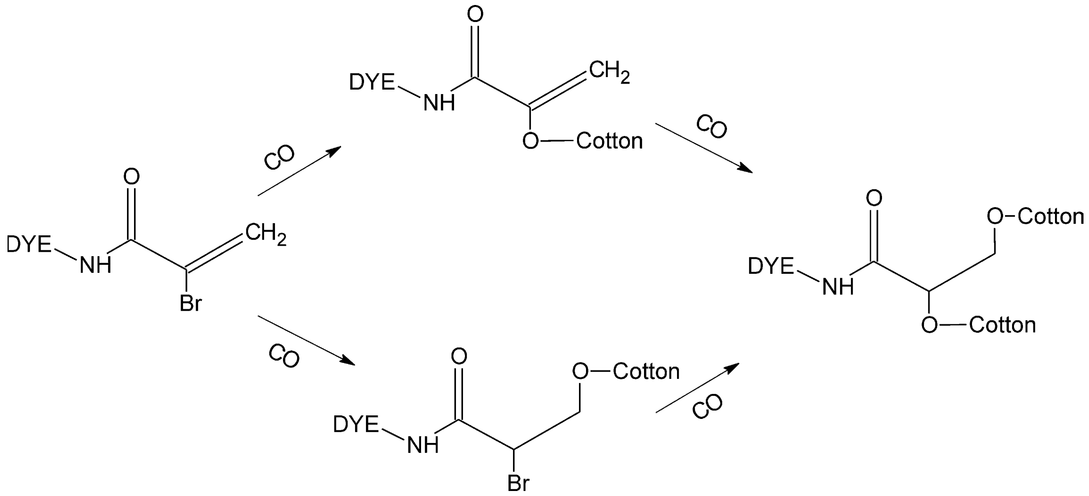

Fig. 3. Proposed mechanism for the reaction of cotton (CO) with 2-bromoacrylamide reactive group.

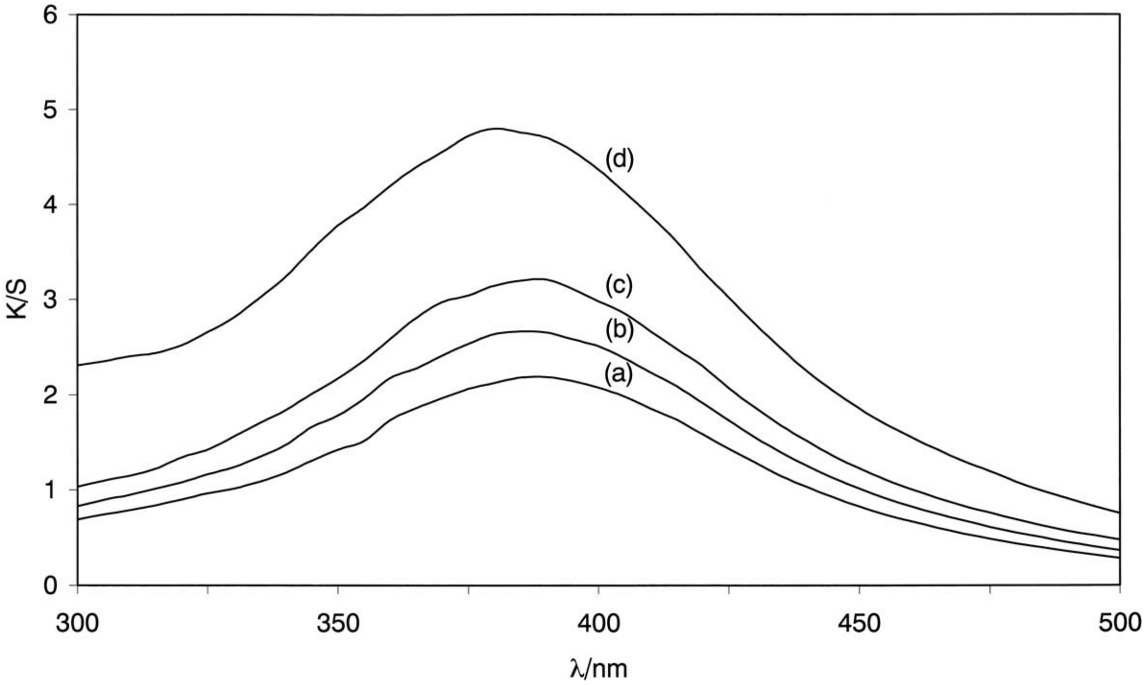

Fig. 4. UV–Vis spectra of cotton dyed with dye **2** in supercritical carbon dioxide at 280 bar under different conditions: 120 °C/60 min (a); 120 °C/120 min (b); 120 °C/240 min (c); 160 °C/240 min (d).

60 to 120 and 240 min increased colour strength by 0.33 and 0.52 units, respectively [Fig. 4; curves (a–c)]. An additional increase in temperature up to 160 °C increased the $K/S$ value by 1.64 to a value of 4.83 [Fig. 4; curve (d)].

The fastness data are comparable between both fibre reactive groups (Table 4).

All cotton samples were extracted with dimethylsulfoxide, by which unfixed dye is removed. Due to the fact that no change in the colour strength was observed, in all dyeing experiments carried out with dye **2** on cotton a chemical bond between the dye and the fibre was formed. As for protein fibres for cotton level dyeing results are obtained with dye **2**. Furthermore fibre cross-sections show that the dye distribution becomes more homogenous after increasing the dyeing time at 120 °C from 30 to 240 min, while at a dyeing temperature of 160 °C a full penetration of cellulose by dye is obtained.

The drying of cotton by microwave radiation before dyeing had no influence on the colour or fastness achieved.

*3.2.2.3. Man-made fibres.* Under all conditions used, level dyeings and full penetration of all man-made fibres used by dye was obtained.

After dyeing polyester for 60 min at 120 °C the $K/S$ value was approx. 4.33 at $\lambda_{\max}$ of 378 nm, while an increase in the dyeing time or the dyeing temperature increased colour strength to approx. 12.57. On polyester which had been dyed for 120 min at 120 °C the dye uptake seemed to reach a maximum $K/S$ value of 14.07. The fastness data of the dyed polyester fabrics were always 5 (Table 5). This is similar to that typified in dyeing of polyester with conventional disperse dyes in supercritical $CO_2$ [2].

For comparison polyester was also dyed with the unmodified dye C.I. Disperse Yellow 23. The dyeing temperatures in $CO_2$ were 120 and 160 °C each for 60 and 240 min at 280 bar. Under all conditions used, the $K/S$ values of the dyed polyester fabrics at 378 nm were about 13.30 and no dye could be removed from the fibre by an after-treatment with acetone. But the polyester could be completely discoloured by an extraction with hot chlorobenzene.

Table 5
Fastness data of synthetic fibres and polyester/cotton-blend dyed with dye **2** in supercritical carbon dioxide at 280 bar under different conditions

| | | | Wash fastness | Rub fastness | | Light fastness |
|---|---|---|---|---|---|---|
| | | | | Dry | Wet | Stage 5 |
| Polyester | 120 °C | 60 min | 5 | 5 | 5 | > 5 |
| | | 120 min | 5 | 5 | 5 | > 5 |
| | | 240 min | 5 | 5 | 5 | > 5 |
| | 160 °C | 240 min | 5 | 5 | 5 | > 5 |
| Polyamide 6.6 | 120 °C | 120 min | 5 | 5 | 5 | > 5 |
| | 160 °C | 240 min | 5 | 5 | 5 | > 5 |
| Polyester/ cotton 65/35 | 120 °C | 60 min | 5 | 5 | 5 | > 5 |
| 2.5-Acetate | 120 °C | 120 min | 5 | 5 | 5 | > 5 |

In this context it was also decided, to dye polyester/cotton 65/35 blends with dye **2** in one step at 120 °C for 60 min. Under these conditions the $K/S$ value at 378 nm was 3.09. The fastness of the dyed samples was always 5 or better (Table 5) and also no dye could be removed by treatment with cold acetone or dimethylsulfoxide. With hot chlorobenzene the dye fixed on polyester was completely extracted because as expected no reaction between the dye and the fibre has taken place.

The $K/S$ value of polyamide 6.6 fabric which had been dyed for 120 min at 120 °C is 9.66 at 378 nm and after 240 min at 160 °C 15.68 but under these conditions the decomposition of the fibre was unacceptably high [26]. Nevertheless, a chemical bond was formed between the dye and the fibre as proven by an extraction with hot chlorobenzene, by which no dye could be removed. After dyeing of 2.5-acetate with dye **2** in supercritical $CO_2$ at 120 °C for 120 min a similar $K/S$ value at 378 nm (10.93) as for polyamide 6.6 was obtained. As for polyester no reaction between the fibre and the reactive group of the dye took place as shown by extraction with hot chlorobenzene.

The fastness data of polyamide 6.6 and 2.5-acetate dyed with dye **2** were comparable to polyester, see Table 5.

## 4. Conclusions

The results show that it is possible to dye natural fibres in supercritical $CO_2$ without pre-treatment of the fibre. Generally, high colour yields and excellent fastness dyeings were obtained with 2-bromoacrylic acid while the results for 1,3-dichloro-2,4,6-triazine as fibre reactive group are significantly lower.

Furthermore for the 2-bromoacrylic acid modified dye it was found that protein fibres can be dyed in higher colour yields than cotton, because amino- and thiol-groups are generally easier to activate than hydroxy-groups. The highest colour depth on cotton and protein fibres was obtained at 160 °C for 240 min, but disadvantageously under these conditions the fibres were damaged.

Man-made fibres such as polyester or polyamide 6.6 and 65/35 polyester/cotton blend fabrics could also be dyed with 2-bromoacrylic acid modified dyes in supercritical $CO_2$.

Generally, these results open new ways to dye natural fibres in supercritical $CO_2$ and help to expand the field of application of supercritical dyeing technology.

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