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Coloration Technology
Society of Dyers and Colourists

Photochromic ink formulation for digital inkjet printing and colour measurement of printed polyester fabrics

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The application of a series of commercial photochromic dyes to polyester fabric by a digital inkjet printing method was investigated. Solvent-based ink systems using the dyes were formulated. The inks were characterised in terms of their physical properties which are related to the jettability of the inks, and finally the prints were fixed onto polyester fabrics by thermal fixation. Colour measurement of the printed fabrics was used to measure their degree of photocoloration, fading rate, fatigue resistance, and storage stabilities. The measured properties of the inkjet-printed fabrics were compared with the same properties of the same dyes applied to polyester fabrics by dyeing methods. The printed fabrics demonstrated inferior performance in terms of the degree of photocoloration, superior performance in the case of background colours, a higher rate of fading, and a lower fatigue resistance compared with that shown by the same dyes applied to polyester fabric by dyeing methods.

Introduction

Inkjet printing may be defined as a process of building up coloured patterns by projecting tiny drops of inks of different colours onto a substrate surface such as textile fabrics [1]. After the successful application of photochromic dyes to polyester fabric by different dyeing methods, as discussed in our previous series of publications [2,3], the application of the same series of dyes to polyester fabric by digital inkjet printing is investigated in this study.

In spite of the challenges facing the development of inkjet printing technology for textiles that would have commercial implications for industry, this technology has attracted attention in recent years. This is due to associated advantages over the traditional flat and rotary screen printing and roller printing technologies [4–9]. Ink formulation is one of the most important factors affecting print quality and reliability owing to the dependence of the jettability of the ink by the printhead on the physical properties of the ink, which are optimised to comply with the printhead in use and to provide practically acceptable ink storage stability [10].

The ink system is determined mainly by the substrate onto which the ink will be applied. Thus, inkjet printing of polyester fabric, which is invariably dyed with disperse dyes, is normally carried out by using aqueous-dispersion-based ink systems. Special techniques are required to prepare the concentrated dye dispersions used for formulating aqueous-dispersion-based inks to achieve the required fine particle size of the dye. These techniques involve the use of special dispersing agents and high purification to give a mean particle size in the range 10–250 nm, which addresses storage and ejection stabilities and the elimination of the risk of nozzle blockage due to aggregation of dye particles by obtaining the targeted mean particle size. In fact, dispersing agents that are designed especially for this purpose are often used, which means that this process may be easier to achieve within the industry involved.

As an alternative choice, a solvent-based ink system was used to investigate the application of photochromic dyes to polyester fabric by an inkjet printing method.

The solvent-based dyeing method of polyester fabric with photochromic dyes was described in our previous series of publications [3]. On the basis of the results of the solvent-based dyeing method, dichloromethane was selected for a preliminary investigation as the solvent for formulations of solvent-based ink systems. Thus, dichloromethane was selected on the basis of the good solubility of the nonionic photochromic dyes in this non-polar solvent, the ease of diffusion of the dyes into the fabric from this solvent, and other criteria for selecting the appropriate solvent for solvent-based dyeing. However, this preliminary selection proved to be unsuccessful owing mainly to the inability to achieve the targeted viscosity of the formulated inks within the range of values that are compatible with the printhead. As an alternative solvent, isopropanol was selected for the reasons discussed below.

Experimental

Colour measurement methodology and conditions

Colour measurement was carried out using a Datacolor (UK) Spectraflash SF600 spectrophotometer, processed using Datamatch 3.1 software, using the small aperture, with specular reflectance included and the UV component excluded, under D65 illumination. For measurement of photocoloration, the fabric samples were irradiated with UV light for 4 min using a Philips (UK) TL20W/05 UVA bulb with an emission maximum of 365 nm. The UV light source was set up horizontally, and samples were mounted at a distance of 4.5 cm below it. Samples were measured at a fixed time of 3 s after removal from the UV light source, with an average of four measurements taken in each case. The UV light source and the spectrophotometer used were located in a laboratory with controlled temperature (20 ± 2 °C) and humidity (65 ± 2%). For thermal fixation of dyes on the fabrics, a Roaches (UK) TFO, 500 mm laboratory oven and steamer were used, set up to operate in dry heat mode.

Materials

The fabric used was woven twill, heat-set polyester (Toray Textiles, UK). Photochromic dyes **1** to **6**, the general chemical classes of which are given in Table 1, were used to formulate the inks used for application to polyester fabrics by an inkjet printing method.

Trade names are not disclosed for proprietary reasons. Solvents were of laboratory grade as supplied by Sigma-Aldrich (UK), and in the case of dichloromethane stabilised with amylene. Isopropanol and dichloromethane of laboratory grade were used as solvents for ink formulations. Ethylene glycol and polyethylene glycol used as humectants were also of laboratory grade. Dowanol DPM [2-(2-methoxypropoxy)propan-1-ol], and triethylene glycol monomethyl ether (TGME), both from Sigma Aldrich, (UK), were also used as humectants. Polyvinylpyrrolidone (PVP) from Sigma Aldrich, with an average molecular weight of 40 000, was used to increase the viscosity of the ink to the required level. 2-Pyrrolidone from Sigma Aldrich was used in ink formulations to improve the solubility of solid components in the ink. Some physical properties of these materials are given in Table 2 [11–14].

Ink formulation

The procedure for the optimised ink is given here. Similar procedures were used for other inks, as discussed below. The photochromic dyes (**1** to **6)** (0.1 g) were dissolved in isopropanol to give 40 g of dye solution, which was stirred for 1 h using a magnetic stirrer to dissolve the dye. While stirring the dye solution, ethylene glycol (30 g) and polyethylene glycol (5 g) were added, and then polyvinylpyrrolidone (5 g) was added over 10 min. The solution was stirred for a further 2 h to ensure complete dissolution of polyvinylpyrrolidone. After stirring, the ink was filtered through filter paper of 1 μm pore diameter, and then the filtered ink was left to stand in the dark at room temperature overnight. The ink was then filtered again using the same kind of filter paper to remove any traces of precipitated components. After the second filtration, the ink was degassed for 2 h using a Decon Minor ultrasound device to remove air from the ink. Air within the ink can cause reliability problems due to the generation of gas bubbles in the piezoelectric inkjet (PIJ) printhead used in this study. After degassing, the inks are ready to be applied to polyester fabric by inkjet printing. The viscosity and surface tension of the ink formulations were measured at room temperature using a Brookfield (UK) DV-II+ Pro viscometer and a Krüss (Germany) surface tension measuring device respectively.

Table 1 Commercial photochromic dyes

Dye	Colour	Chemical type
1	Green	Naphtho[1,2-*b*]oxazine
2	Blue	Naphtho[1,2-*b*]oxazine
3	Purple	Naphtho[2,1-*b*]oxazine
4	Red	Naphtho[2,1-*b*]oxazine
5	Ruby	Naphtho[2,1-*b*]pyran
6	Yellow	Naphtho[2,1-*b*]pyran

Digital inkjet printing of polyester fabric with photochromic dyes

All inkjet printing processes were carried out using a Xennia inkjet printer operating a Xaar 760 print unit fitted with a drop-on-demand piezoelectric inkjet (DOD-PIJ) printhead. The printer is operated by a computer with XUSB Windows application software. The print unit has two rows of nozzles, with each row containing 390 nozzles at a pitch of 141.1 μm. The ink is poured slowly into the ink tank, which is connected to the print unit, and then the ink tank is closed tightly with the airtight lid. Any air trapped in the print unit is removed using a syringe, which is connected manually to the printhead through a pipe supplied with a manual valve. The XUSB software enables the user to carry out the printing process, which starts with opening the image, adjusting the printing system parameters, and finally starting the printing process. The adjustment of the printing system parameters allows the user to set up the waveform for each row of the printhead. The fabric is laid on the printing board, and then the printhead is passed manually over the fabric. During the passage of the printhead over the fabric, nozzles jet the ink onto the fabric according to the image selected, which was a square shape in all cases investigated in this study. After printing, fabrics were transferred to a preheated oven for thermal fixation of the prints on the fabric at a temperature of 190 °C for 45 s. This was followed by a cold water rinse, and then reduction clearing at 70 °C for 20 min using an aqueous solution of sodium hydroxide (2 g l^{-1}), sodium dithionite (2 g l^{-1}), and Synperonic BD100, a nonionic surfactant (1 g l^{-1}). The printed samples were then rinsed with water, washed with an aqueous solution of Synperonic BD100 (1 g l^{-1}) for a few minutes, rinsed with water, and then air dried.

Table 2 Physical properties of materials used for ink formulation

Material	Phase	Viscosity at 25 °C, cP	Surface tension, mN m^{-1}	Vapour pressure at 25 °C, mmHg
Glycerol	Liquid	934	64.8	0.001316
Ethylene glycol	Liquid	16.1	48.4	0.0001052
Polyethylene glycol	Liquid	58.3	44	< 0.01
Polyvinylpyrrolidone	Solid	n/a	n/a	n/a
2-Pyrrolidone	Liquid	13.1	45.81	7.501
Dowanol DPM	Liquid	3.7	28.8	0.4
TGME	Liquid	6.25	37.8	0.009998

Fading characteristics, fatigue resistance, and shelf life

Fading time

The optimally printed samples were irradiated with UV light for 4 min, and then the degree of photocoloration ΔE_1 for all samples was measured and recorded against a fading time of up to 60 min. Fading charts were produced and compared. These charts consist of plots of ΔE_1 *vs* a fading time of up to 60 min in the dark after irradiation with UV light.

Fatigue resistance

The optimally printed samples were irradiated with UV light for 4 min and then left in the dark for 2 h to fade back to their original unexposed states. This irradiation and fading cycle was repeated 20 times for each sample. ΔE_1 values were measured after 20 irradiation cycles, and then compared with the values recorded after the original UV exposure.

Storage stability/shelf life

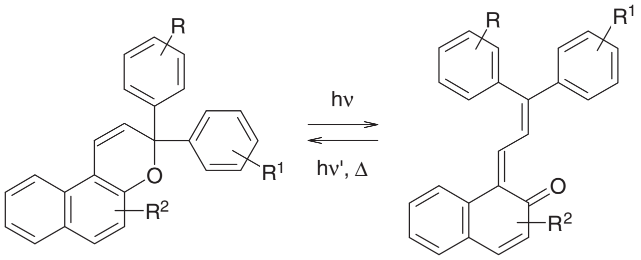
The optimally printed samples were irradiated with UV light for 4 min, measured, kept in the dark at room temperature for 170 days, and reactivated, and then their degree of photocoloration was remeasured.

Results and Discussion

The application of photochromic dyes to polyester fabric by an inkjet printing method

Generalised structures of spironaphthoxazine (**I**) and naphthopyran (**II**) dye classes are shown respectively in Schemes 1 and 2, which also illustrate the mechanism of photoinitiated conversion to coloured forms. The jettability of an ink by a printhead is determined mainly by the values of the viscosity and surface tension of the ink. These values should be within the ranges compatible with the printhead, which are given by the manufacturer of the printing unit. In the case of the printer used in this study, the viscosity of the ink used for printing is required to be in the range between 4 and 7 cP, as measured at room temperature, and the surface tension in the range between 28 and 35 mN m^{-1}. In addition, ink purification and degassing must be carried out to achieve the other necessary properties of the ink in terms of the targeted particle size of ≤ 1 μm and removing the trapped air to avoid nozzle blockage and print reliability problems.

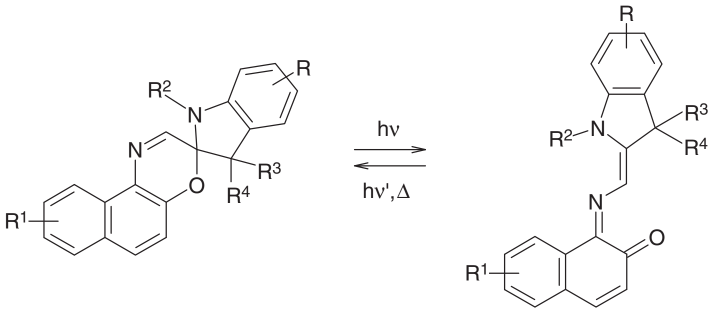
The optimisation process of the inkjet printing method was carried out by applying dye **2** and investigating the properties of the printed fabric in terms of achieving the maximum degree of photocoloration ΔE_1 and minimum background colour ΔE_2. Parameter ΔE_1 is defined as the colour difference between the background colour of the dyed fabric before irradiation with UV light and the colour developed after UV irradiation of the fabric for 4 min [2,3]. Parameter ΔE_2 is defined as the colour difference between the undyed fabric and the fabric after dyeing, without UV irradiation.



Scheme 2 General photochromic conversion of naphthopyran dyes

For preliminary investigation of ink formulation, dichloromethane was used as the solvent owing to the success achieved in using this solvent for dyeing polyester fabric [3]. The first formulation investigated consisted of dichloromethane, ethylene glycol, TGME, glycerol, Dowanol DPM, polyvinylpyrrolidone, and 2-pyrrolidone according to the amounts given in Table 3. Measurement of physical properties of the ink prepared according to formulation **1** gave a viscosity of 2.24 cP and a surface tension of 32 mN m^{-1}. This ink was applied to polyester fabric by inkjet printing. The printed fabric showed a presence of unprinted strips distributed randomly on the printed area owing to the presence of a significant number of missing nozzles in the printhead. This observation may be a result of the incompatibility between the ink and the printhead on account of an ink viscosity lower than the 4–7 cP range recommended by the manufacturer of the printhead used in this study.

In an attempt to overcome the problem of low ink viscosity, polyvinylpyrrolidone (PVP), 6 g per 100 g of ink, was added to the ink formulation with no change in the amounts of the other ingredients, as shown in Table 3. The result was an increase in the viscosity and a decrease in the surface tension of the ink to 4.23 cP and 31.5 mN m^{-1} respectively. The ink, referred to as formulation **2**, showed difficulties in the filtration process owing to the formation of a gel-like material of high viscosity precipitated on the filtration paper, which prevented the ink from passing through the paper. This gel-like material may be formed as a result of the interaction between the excessive amount of polyvinylpyrrolidone, which is not completely dissolved in dichloromethane, and the other ingredients of the ink. Thus, the next stage in improving the formulation was to decrease the amount of polyvinylpyrrolidone, from 6 to 2%,



Scheme 1 General photochromic conversion of spironaphthoxazine dyes

in an attempt to avoid the formation of the gel-like material, and to increase the amount of 2-pyrrolidone from 2 to 3% in order to improve the solubility of polyvinylpyrrolidone in formulation **3**, as shown in Table 3. At the same time, Dowanol DPM, which has a low viscosity, as shown in Table 2, was not used in formulation **3** in an attempt to avoid any reduction in viscosity to a low level that might result from reducing the amount of polyvinylpyrrolidone. Although these changes overcame the issue of the formation of a gel-like material, the viscosity of the formulated ink decreased to 2.04 cP, which is lower than the range recommended. Consequently, the prints produced by applying this ink to polyester fabric showed too many missing nozzles, as demonstrated by unprinted strips in the printed area on the fabric.

In the next stage, the amount of polyvinylpyrrolidone was increased to 5% in an attempt to increase the viscosity to within the recommended range, and at the same time the amount of 2-pyrrolidone was increased to 5% to improve the solubility of the additional polyvinylpyrrolidone. The resulting ink, referred to as formulation **4** in Table 3, showed, as expected, an increase in the viscosity to 3.06 cP owing to the increased level of polyvinylpyrrolidone, and a decrease in the surface tension owing to the increased level of 2-pyrrolidone. Inkjet printing of polyester fabric using this ink gave rise again to unprinted strips in the printing area as a result of inactivation of some of the nozzles in the printhead because of the incompatibility of the ink with the printhead.

Further attempts to increase the ink viscosity by increasing the amount of polyvinylpyrrolidone and increasing the amount of 2-pyrrolidone, as is necessary to improve the solubility of polyvinylpyrrolidone, led to an increase in the viscosity to 4.03 cP and a decrease in the surface tension to 26 mN m^{-1}, which is lower than the recommended range for compatibility with the printhead, as shown for formulation **5** in Table 3. Consequently, the ink formulated according to formulation **5** was not jetted successfully by the printhead, giving rise to the presence of missing nozzles.

On the basis of the results obtained using dichloromethane as the solvent, it was not possible to achieve the required values of viscosity and surface tension of the ink at the same time. Therefore, the next stage was an investigation into the use of isopropanol, instead of dichloromethane, as the solvent. Isopropanol was selected on the basis of its higher viscosity compared with dichloromethane, as shown in Table 4 [15–17], which is closer to the range

Table 3 Formulation of dichloromethane-based inks

Material	Weight, g per 100 g of ink Formulation **1**	Formulation **2**	Formulation **3**	Formulation **4**	Formulation **5**
Ethylene glycol	19	19	19	19	19
TGME	8	8	8	8	8
Glycerol	3	3	3	3	3
2-Pyrrolidone	2	2	3	5	7
Dowanol DWP	6	6	0	0	0
Polyvinylpyrrolidone PVP)	0	6	2	5	7
Dye	0.1	0.1	0.1	0.1	0.1
Dichloromethane	As required to make up to 100 g	As required to make up to 100 g	As required to make up to 100 g	As required to make up to 100 g	As required to make up to 100 g
Ink properties	Viscosity 2.24 cP, surface tension 32 mN m^{-1} before and after filtration)	Viscosity 4.23 cP, surface tension 31.5 mN m^{-1} (before and after filtration)	Viscosity 2.04 cP, surface tension 30.5 mN m^{-1} (before and after filtration)	Viscosity 3.06 cP, surface tension 29 mN m^{-1} (before and after filtration)	Viscosity 4.03 cP, surface tension 26 mN m^{-1} (before and after filtration)
Observations	Unprinted strips in the printed area	Filtration not successful	Unprinted strips in the printed area	Unprinted strips in the printed area	Unprinted strips in the printed area

Table 4 Some physical properties of isopropanol and dichloromethane

Property	Solvent Isopropanol	Dichloromethane
Molecular formula	$CH_3CHOHCH_3$	CH_2Cl_2
Boiling point at atmospheric pressure (760 mmHg), °C	82	39.8–40.0
Viscosity at 25 °C, cP	2.040	0.413
Surface tension at 20 °C, mN m^{-1}	21.74	28.12

Table 5 Ink formulation of isopropanol-based inks

Material	Weight, g per 100 g of ink				
	Ink **1**	Ink **2**	Ink **3**	Ink **4**	Ink **5**
Ethylene glycol	25	30	35	30	30
PVP	0	0	0	5	5
Polyethylene glycol	0	0	0	0	5
Dye	0.1	0.1	0.1	0.1	0.1
Isopropanol	As required to make up to 100 g	As required to make up to 100 g	As required to make up to 100 g	As required to make up to 100 g	As required to make up to 100 g
Ink properties	Viscosity 1.75 cP, surface tension 27.5 mN m^{-1}	Viscosity 2 cP, surface tension 28 mN m^{-1}	Viscosity 2.14 cP, surface tension 27 mN m^{-1}	Viscosity 4.46 cP, surface tension 27.5 mN m^{-1}	Viscosity 5 cP, surface tension 29 mN m^{-1}
Observations	Viscosity and surface tension lower than required	Viscosity too low, surface tension acceptable	Viscosity and surface tension lower than required	Viscosity acceptable, surface tension too low	Optimum viscosity and surface tension

recommended for the printhead. It was envisaged that this may contribute towards achieving the required viscosity without the need to use a high level of polyvinylpyrrolidone. This in turn may eliminate the need to use 2-pyrrolidone to improve the solubility of polyvinylpyrrolidone. Elimination of the use of 2-pyrrolidone, which has a low surface tension, may compensate for the expected lower surface tension of the ink using isopropanol as an alternative to dichloromethane, given its lower surface tension, as shown in Table 4 [18].

Another factor in selecting isopropanol is its higher boiling point compared with that of dichloromethane, and therefore a slower evaporation rate at room temperature, which in turn provides improved control of the proportional amounts of the materials in the ink formulations. In addition, isopropanol is a significantly less hazardous solvent than dichloromethane [19].

The investigations of isopropanol-based ink formulation and application to polyester fabric by inkjet printing were carried out using dye **2**. In the first attempt, a simple formulation consisting of ethylene glycol 25%, dye 0.1%, and isopropanol as required to make up to 100% was used, referred to as ink **1** in Table 5. Both the viscosity and the surface tension of this ink were lower than the required values, as shown in Table 5.

When the amount of ethylene glycol was increased to 30%, the viscosity and surface tension increased to 2 cP and 28 mN m^{-1} respectively, but the viscosity remained lower than the required range, as shown for ink **2** in Table 5. Consequently, the amount of ethylene glycol was further increased to 35% in an attempt to improve the viscosity of the ink, as shown for ink **3** in Table 5. The result was a slight increase in viscosity to 2.14 cP, accompanied with a decrease in surface tension to 27 mN m^{-1}. To address the undesirable decrease in surface tension, the amount of ethylene glycol was fixed at 30% for further investigations. Thus, ink **4** was formulated using 30% ethylene glycol, 5% polyvinylpyrrolidone (PVP), 0.1% dye, and isopropanol as required, as shown in Table 5. The formulated ink showed a significant increase in viscosity to 4.46 cP, which is within the recommended range (4–7 cP), and a slight increase in surface tension to 27.5 mN m^{-1}, which is still less than the minimum value recommended for the printhead (28 mN m^{-1}). Further improvement was achieved by adding 5% polyethylene glycol to the ink formulation, which resulted in an increase in the viscosity and surface tension of the ink to levels within the recommended ranges for the two parameters, as shown for ink **5** in Table 5.

On the basis of the results of this investigation, the ink formulated according to the last recipe, referred to as ink **5** in Table 5, was selected as optimum, and was thus used in the investigation of the application of photochromic dyes **1** to **6** to polyester fabric by inkjet printing. Thus, six inks were prepared according to this formulation, using the photochromic dyes **1** to **6**. These inks were applied to polyester fabrics by the inkjet printing method described in this study.

Degree of photocoloration and background colours of polyester fabric inkjet printed with photochromic dyes with different numbers of printing passes

The degree of photocoloration (ΔE_1) of dyes **1** to **6** applied to polyester fabric by the digital inkjet printing method

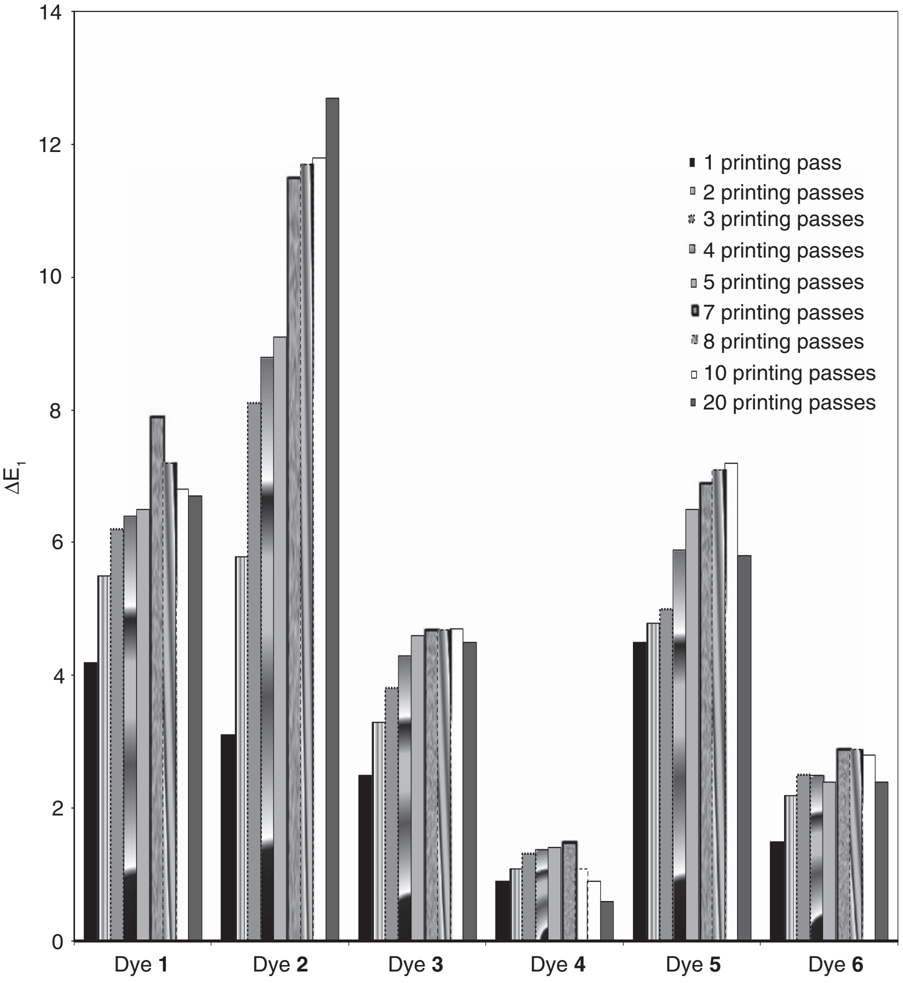


Figure 1 Degree of photocoloration (ΔE_1) of polyester fabric inkjet printed with photochromic dyes **1** to **6** with different numbers of printing passes

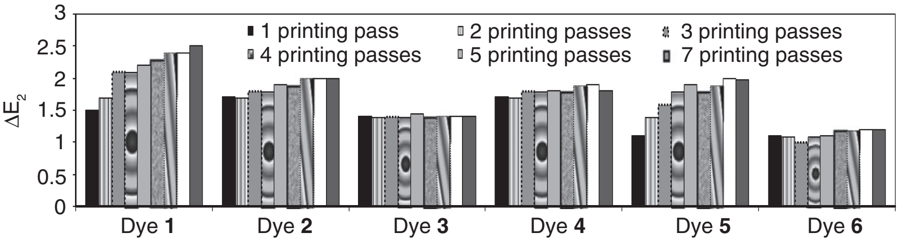


Figure 2 Background colours (ΔE_2) of polyester fabric inkjet printed with photochromic dyes **1** to **6** with different numbers of printing passes

optimised for dye **2** using ink **5** was measured after 4 min of UV light exposure for fabrics inkjet printed with different numbers of printing passes, as shown in Figure 1. Figure 2 illustrates the background colours (ΔE_2) of the same inkjet-printed fabrics.

The degree of photocoloration of dyes **1** to **6** increased gradually when the number of printing passes increased from 1 to 7. However, the results of further passes were inconsistent, except for dye 2, which continued to show an increase, as shown in Figure 1. A possible explanation for this trend may be the negative effect on the degree of photocoloration that was brought about by the increase in the background colour of printed fabrics when the number of printing passes was increased to 10 or 20, as shown in Figure 2. This negative effect may be due to two factors. The first factor involves minimising the difference between background colour and developed colour as a result of increase in the background colour. The second factor is the increase in the number of ring-opened permanently coloured dye molecules associated with increase in the background colour, as discussed in our previous series of publications [3], which in turn leads to a relative decrease in the number of ring-closed molecules that are responsible for the photocoloration process of photochromic dyes under UV light exposure. As a result of this discussion, the optimum number of printing passes for applying dyes **1** to **6** was selected as 7 owing to the reasonably high degree of photocoloration and reasonable background colours given by samples printed at this number of printing passes, as shown in Figures 1 and 2. Thus, all further investigations of

Table 6 Degree of photocoloration and background colours of photochromic dyes **1** to **6** applied to polyester fabric by different dyeing and inkjet printing methods

	ΔE_1			ΔE_2		
Dye	Inkjet printing (isopropanol)	Aqueous-based dyeing	Solvent-based dyeing (dichloromethane)	Inkjet printing (isopropanol)	Aqueous-based dyeing	Solvent-based dyeing (dichloromethane)
1	7.9	9.1	12.4	2.3	16.8	9.7
2	11.5	27.1	27.7	1.9	10.0	8.9
3	4.7	3.4	7.1	1.4	32.0	7.0
4	1.5	3.5	8.0	1.9	8.5	15.3
5	6.9	8.8	8.0	1.8	18.1	11.5
6	2.9	14.7	13.3	1.2	15.5	7.9

the application of photochromic dyes **1** to **6** to polyester fabric by inkjet printing were carried out using seven printing passes.

A comparison between the background colours and degree of photocoloration of dyes **1** to **6** applied by the inkjet printing method and those of the same dyes applied by dyeing methods [2,3] shows that, in general, both parameters are lower for each dye applied by inkjet printing, as shown in Table 6. The first factor that may be important in determining this trend is the relatively low concentration of the dyes in isopropanol, which was used as the solvent in the ink formulation, owing to the low solubility of the dyes in this solvent, which in turn leads to a relatively low amount of dye delivered to the fabric. A second factor that may be important in relation to dyeing from dichloromethane is the larger difference between the solubility parameter of polyester (45 $\mathrm{J}^{0.5}\ \mathrm{cm}^{-1.5}$) and isopropanol (36.8 $\mathrm{J}^{0.5}\ \mathrm{cm}^{-1.5}$) compared with that between polyester and dichloromethane (40.8 $\mathrm{J}^{0.5}\ \mathrm{cm}^{-1.5}$) [20,21]. It has been reported that matching of the solubility parameters of solvent and fibre is required to facilitate dye penetration into fibre [21–23]. The effect of the relatively significant difference between the solubility parameter of water (97.9 $\mathrm{J}^{0.5}\ \mathrm{cm}^{-1.5}$) and polyester (45 $\mathrm{J}^{0.5}\ \mathrm{cm}^{-1.5}$) was not taken into account in the comparison based on the second possible factor, because the aqueous-based dyeing was carried out at a high temperature and for a relatively long time, as discussed in our previous series of publications [2]. Thus, isopropanol may be less active than dichloromethane in facilitating dye diffusion into polyester fabric during dyeing or printing processes. A third factor may be the application of the dyes only on the surface of one side of the fabric in the case of inkjet printing, compared with complete impregnation of the fabric in the

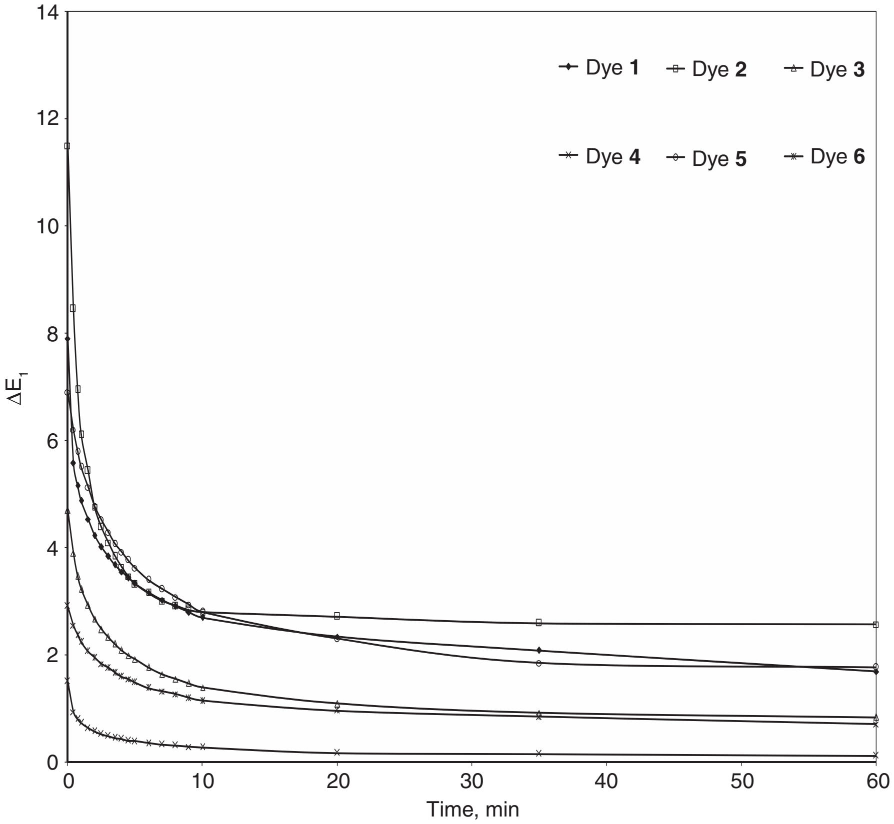


Figure 3 Fading curves for photochromic dyes **1** to **6** applied to polyester fabric by an inkjet printing method

Table 7 Half-life of fading of dyes **1** to **6** applied to polyester fabric by different dyeing and inkjet printing methods

	Half-life of fading, min		
Dye	Inkjet printing (isopropanol)	Solvent-based dyeing (dichloromethane)	Aqueous-base dyeing
1	2.7	4.5	7.6
2	1.3	3.1	4.2
3	2.9	4.5	7.1
4	1.0	4.2	3.1
5	5.8	11.5	18.1
6	5.1	14.1	19.8

dye solutions in the case of dyeing methods. Thus, the dye uptake by fabric in the case of inkjet printing may be lower than that in the case of dyeing methods owing to the application of the dye to only one side of the fabric, and also at the surface, so that it is relatively easy to remove dye by the reduction clearing that follows the printing process.

Fading time of photochromic dyes applied to polyester fabric by an inkjet printing method

Samples of polyester fabric inkjet printed with dyes **1** to **6** at the optimum number of printing passes by using the optimised printing procedure were irradiated with UV light for 4 min, followed by measuring their degree of photocoloration immediately after irradiation and over 60 min of fading in the dark. The fading curves show that the dyes start to fade immediately after removal of the UV light source, as shown in Figure 3. Although the fading rates were different, they all reached low values at which the fading curves levelled, indicating slow fading of all dyes after a relatively long fading time, as shown in Figure 3.

The time required by photochromic dyes **1** to **6** on polyester to fade in the dark to half of the original values of ΔE_1 recorded immediately after UV light exposure was measured and referred to as the half-life of fading. Comparison of the half-lives of fading of dyes **1** to **6** indicates differences in the fading rates of the dyes applied to polyester fabric. Thus, as shown in Table 7, the naphthopyran-based dyes (dyes **5** and **6**) showed relatively low fading rates, expressed by higher half-lives of fading, compared with the spironaphthooxazines (dyes **1** to **4**). In this respect, these results are consistent with the half-lives of fading of the same dyes applied to polyester fabric by dyeing methods, as discussed in our previous series of publications [2,3]. This trend has also been observed in a previous study of photochromic dyes applied to polyester fabric by a screen printing method [24].

Table 8 Residual colours after fading of photochromic dyes **1** to **6** applied to polyester fabric by different inkjet printing and dyeing methods

	Residual colour after 60 min of fading in the dark as a percentage of the degree of photocoloration		
Dye	Inkjet printing	Solvent-based dyeing	Aqueous-based dyeing
1	21	18	24
2	22	11	4
3	18	18	21
4	7	15	9
5	26	30	32
6	24	37	29

A notable observation in Table 7 is the relatively low values of the half-life of fading of dyes applied by inkjet printing compared with those for the same dyes applied by dyeing methods. This trend may be due to the lower penetration of the dyes into polyester fabric when they are applied by inkjet printing compared with when they are applied by dyeing methods. Thus, inkjet-printed dyes may have less restriction applied to molecular ring closure, leading to the colourless ring-closed form due to their presence close to the surface of the fabric, compared with more deeply penetrating dyes, which may be in a more restricted environment, when applied by dyeing methods.

In another respect, all inkjet-printed fabrics retained residual colours after fading for 60 min in the dark. The retained colours were significantly higher in the cases of the naphthopyran-based dyes (dyes **5** and **6**) than with the other four dyes, which are spironaphthooxazines, as shown in Table 8. This observation may simply be due to the kinetics of fading of these particular dyes. However, it has also been reported that certain naphthopyran-based photochromic dyes may form two different stable, coloured isomers on irradiation: the major component, a short-lived, strongly coloured species, which is the *transoid-cis* isomer, and the minor component, a long-lived, paler-coloured *transoid-trans* isomer [2,25,26].

A comparison between the residual colours retained by photochromic dyes **1** to **6** applied to polyester fabric by inkjet printing and dyeing methods shows no apparent consistency between the order of magnitude of values of residual colours of dyes applied by the inkjet printing and dyeing methods, although in all cases the naphthopyran dyes show the strongest residual colours, as indicated in Table 8. In addition, the values of the residual colours of each dye applied by the different inkjet printing and dyeing methods vary. These trends are difficult to explain and may be due to differences in the interaction between polyester fabric and the different printing or dyeing solvent at the different application conditions used, and the interaction between each dye and the application solvent, as determined essentially by the specific chemical structure of the dye.

Fatigue resistance of photochromic dyes applied to polyester fabric by an inkjet printing method

Assessment of the fatigue resistance of photochromic dyes applied to polyester fabric by inkjet printing was carried out by repeating 20 times the cycle of UV exposure and fading for 2 h of the optimally printed samples. The degrees of photocoloration of each sample after first and last exposure were compared (Figure 4).

Results showed, that after 20 cycles of UV exposure of fabrics inkjet printed with dyes **1** to **6**, the dyes retained different proportions of their original degree of photocoloration recorded after the first UV exposure. The retention values ranged between 71 and 46%, with the highest value

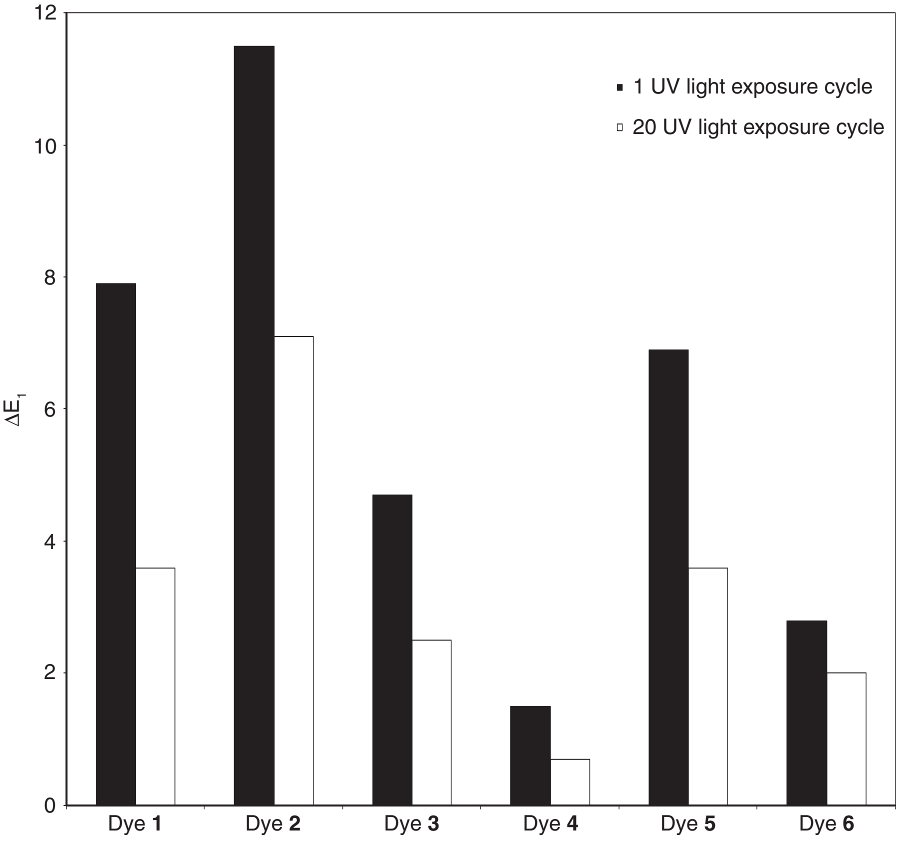


Figure 4 Fatigue resistance of photochromic dyes **1** to **6** applied to polyester fabric by an inkjet printing method

Table 9 Fatigue resistance of photochromic dyes **1** to **6** applied to polyester fabric by different dyeing and inkjet printing methods

	Retention of photochromic response after 20 cycles of UV light exposure, %		
Dye	Inkjet printing	Solvent-based dyeing	Aqueous-based dyeing
1	46	47	70
2	62	75	92
3	53	60	98
4	47	41	28
5	52	95	99
6	71	72	78

recorded by dye **6** and the lowest value given by dye **1**, as shown in Table 9. These values show no obvious correlation with the chemical class of the dye, and may be determined by the specific chemical structure of each dye, possibly also influenced by its interactions with the printing solvent and the fibre under the application conditions.

In addition, the fatigue resistance of dyes **1** to **6** applied to polyester fabric by inkjet printing is mostly lower than that of the same dyes applied by dyeing methods, discussed in our previous series of publications [2,3], as shown in Table 9. This trend may be a result of the location of the dyes near the surface of the fabric when they are applied by inkjet printing, compared with their penetration deeper into the fabric when they are applied by dyeing methods. Thus, in the case of the inkjet-printed fabrics, the dye will be more susceptible to photodegradation as a result of the effect of repeated exposure to UV light.

Storage stability of photochromic dyes applied to polyester fabric by an inkjet printing method

The storage stability of photochromic dyes **1** to **6** applied to polyester fabric by inkjet printing was assessed by measuring the degree of photocoloration of the optimally printed samples 170 days after printing and comparing the results with measurements of the same samples on the day of printing.

Figure 5 shows that the printed samples retained different levels of degree of photocoloration after storage for 170 days, ranging from 62% in the case of dye **5** to 82% in the case of dye **2**. In another respect, it was observed that the storage stability of dyes **1** to **6** applied to polyester fabric by inkjet printing is mostly lower than that of the same dyes applied by dyeing methods, described in our previous series of publications [2,3], as shown in Table 10. However, there is no apparent consistency between the order of magnitude of storage stability of photochromic dyes **1** to **6** applied by inkjet printing and that of the same dyes applied by dyeing methods, as shown by comparing the results in this study with those in our previous series of publications, which are given in Table 10. In addition, the values of storage stability of the same dye applied to polyester fabric by the different application methods were different, with no apparent relation between the application method and the directions of this difference, either an increase or a decrease, in the storage stability of the dyes. Thus, the application method may affect the storage stability of the dye as a result of the interaction between the dye, the application solvent, and

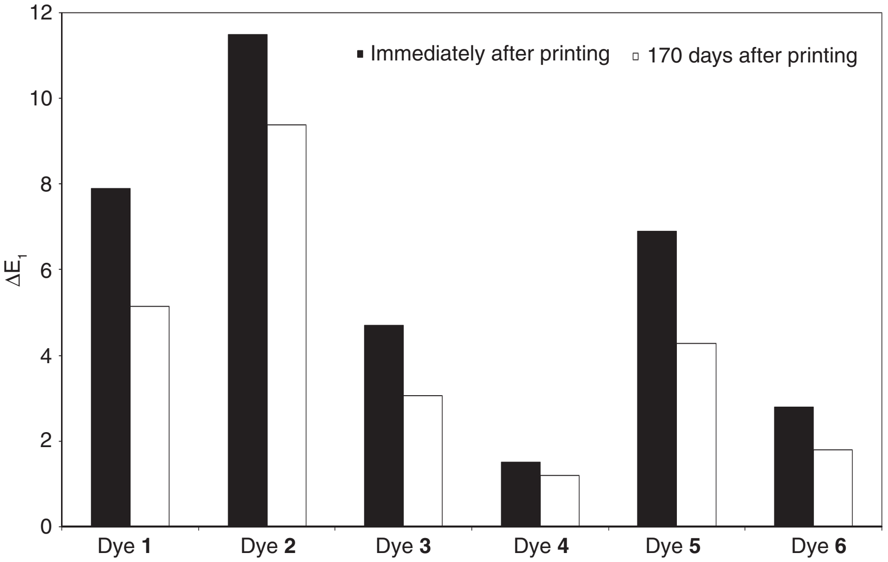


Figure 5 Storage stability of dyes **1** to **6** applied to polyester fabric by an inkjet printing method

Table 10 Storage stability of photochromic dyes **1** to **6** applied to polyester fabric by different dyeing and inkjet printing methods

	Retention of photochromic response after 170 days of storage in the dark, %		
Dye	Inkjet printing	Solvent-based dyeing	Aqueous-based dyeing
1	65	96	84
2	82	71	76
3	65	94	60
4	79	86	83
5	62	87	81
6	64	64	73

the application conditions rather than as a result of the effect of the solvent on the dyed substrate, and therefore this effect is related to the specific chemical structure of each dye. This result is anticipated, because the storage stability represents a property of the dye that is affected by the dye behaviour in the dark rather than its behaviour under UV light exposure. Therefore, this property is not affected by the factors associated with the effect of the application conditions on the fabric, such as geometrical changes in the physical structure of polyester fibres. These geometrical changes affect other properties, such as the fading time and fatigue resistance, by restricting the ring-closure reaction after removing the UV exposure in the former case and shielding the dye molecules from UV exposure in the latter case when the solvent-based dyeing medium is replaced with aqueous-based dyeing, as discussed in our previous series of publications [3].

Thus, the interaction between photochromic dyes **1** to **6** and isopropanol, which was used as a printing solvent, may lead to a decrease in the storage stability of the dyes in most cases when this solvent replaces the solvents used in the other dyeing methods investigated. In the case of dye **2**, the effect of isopropanol on the storage stability of the dye was opposite to its effect on the other dyes, and therefore the specific chemical structure of the dye and the interaction with the solvent may have an effect on its storage stability.

Conclusions

Six photochromic dyes were successfully applied to polyester fabric by digital inkjet printing using a solvent-based ink. The application process was optimised in terms of ink formulation and the number of printing passes required to achieve the maximum degree of photocoloration (ΔE_1) and minimum background colour (ΔE_2) of printed fabrics. The printed fabrics performed differently in terms of their degree of photocoloration and background colours. However, the performance was mostly inferior in terms of degree of photocoloration and superior in terms of background colours compared with that shown by the same dyes applied to polyester fabric by the dyeing methods discussed in our previous series of publications.

Investigation of the fading characteristics and fatigue resistance of printed fabrics demonstrated mostly the higher rate of fading and lower fatigue resistance of these fabrics compared with fabrics dyed with the same dyes by dyeing methods.

Storage stabilities of photochromic dyes applied to polyester fabric by inkjet printing were variable. In addition, comparison between the storage stability of photochromic dyes applied by inkjet printing and that of the same dyes applied by dyeing methods showed no consistent effect of application method on this property for any of the dyes, probably owing to the dependence of this property on the specific chemical structure of each dye.

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