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New methods of obtaining patterned dyeings on cellulosic fibres with anionic dyes: photo-modification using a methacryloyl quaternary ammonium compound

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Abstract

Cotton fabric was modified through the introduction of quaternary groups by UV irradiation of a methacryloyl compound. The modified substrate displayed enhanced dyeability towards anionic dyes because of the presence of the introduced quaternary groups; ζ-potential measurements confirmed the cationicity of the modified fabric. The colour yield of the dyeings increased with increasing energy of irradiation and also varied with the amount of quaternary compound adsorbed on the substrate. The results clearly show that the dyeability of the cellulosic fibre can be controlled through the UV induced modification and, therefore, that patterned dyeing effects could be achieved through the exhaustion dyeing of fabric which has been exposed to patterned photo-modification. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cotton; Enhanced dyeing; Chemical modification; Quaternary compounds

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1. Introduction

Various methods have been developed for producing patterned dyeings on textile fabrics, such as roller printing, ink-jet printing, thermal printing and screen-printing. While each of these methods possess meritorious features, demand for new printing methods has recently developed as a result of moves towards more environmentally friendly processes, reduced dependence on expensive chemicals as well as the use of less complex, mechanical or electronic devices [1,2].

This paper describes a method for obtaining patterned dyeings on cellulosic fibres using a conventional exhaustion dyeing method by means of photo-induced modification of the substrate.

The chemical modification of cellulosic fibres in order to improve dyeability is a well-known area. Pre-treatment of cotton has been used to introduce a variety of functional compounds in the form of secondary, tertiary and quaternary amino residues [3–5]. Wu et al. have used cationic monomers to improve the dyeability of cellulosic substrates [6–8]. In such cases, the main objective was to improve the dyeability of cellulosic fibres (especially cotton) so as to obviate the need for inorganic electrolyte in dyeing with anionic (e.g.

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reactive dyes, direct dyes) dyes. The approach described herein is an extension of this earlier work, insofar as when cotton is chemically modified using a methacryloyl quaternary compound by means of UV irradiation, a patterned dyeing should be achievable by subsequent exhaustion dyeing.

2. Experimental

2.1. Materials

A sample of scoured and bleached, unmercerised, fluorescent brightener-free cotton fabric (40 count; 122 g m^{-2}) obtained from Shikisensha was used. The fabric was treated for 30 min at 98°C (100:1 liquor ratio) in distilled water prior to UV-irradiation in order to remove any impurities from the fabric surface and also to stabilise the structure of the fabric.

Two dyes were used, namely C.I. Direct Red 28 and C.I. Acid Orange 7, both of which were of reagent grade purity and obtained from Tokyo Kasei Kogyo. Methacryloyloxyethyltrimethylammonium chloride (MOETMAC) (I) was obtained from Nitto Chemical Industry Co. and was used without further purification. All other reagents were of general-purpose grade purity.

2.2. Procedures

2.2.1. Modification of cotton with MOETMAC

Aqueous solutions of MOEMTAC ranging from 0.1 to 1.0 mol dm^{-3}, were prepared using distilled water. Samples of cotton fabric each measuring 2.5 cm × 5 cm were impregnated with these solutions at 80% pick-up and the impregnated samples then dried. The fabric samples were then irradiated for various times at ambient temperature using the apparatus shown schematically in Fig. 1. The UV light source employed was a low-pressure, 40 Watt mercury lamp (UVB-40) obtained from Sen Light Source Inc. Irradiation was carried out with the UV light source positioned at a distance of 4.5 cm from the fabric surface for various times up to 30 min. The UV light source used radiates particularly 184.5 and 253.7 nm light, which corresponds in energy to that of a covalent bond of an organic compound. After UV-irradiation, the fabric was treated in boiling water for 30 min (100:1 liquor ratio) to remove from the fabric any ozone that may have been formed during irradiation.

2.2.2. Measurement of the amount of MOEMTAC adsorbed on cotton

This was carried out by measuring the mass of the fabrics at 110°C using a Chyo MC-30MB high temperature electronic balance.

2.2.3. Dyeing

C I Acid Orange 7 dyed samples of cotton which had been UV-irradiated, as well as samples which had not undergone this treatment, were dyed using 300 cm^3 capacity stainless steel dyepots housed in a Mini-Color (Texam Co.) laboratory dyeing machine, for 12 h at 25°C at pH 3.5 using a

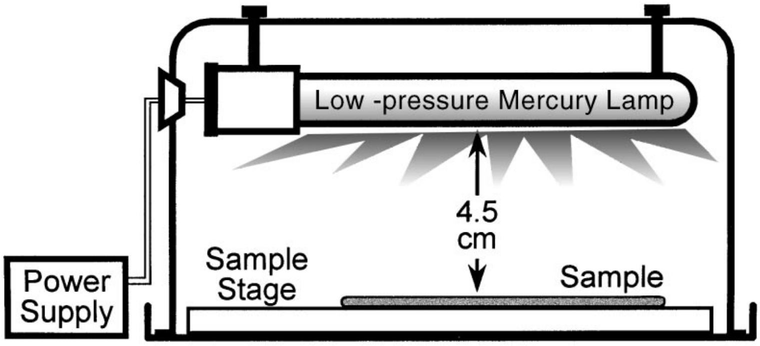


Fig. 1. Apparatus used.

liquor ratio of 1000:1 and a dye concentration of 3×10^{-4} mol dm^{-3}. A further set of dyeings was produced using C I Direct Red 28 at 70% for 12 h. The equipment described above was used, dyeings being carried out with a concentration of dye of 1×10^{-4} mol dm^{-3}, liquor ratio 3000:1 and NaCl concentrations ranging from 0 to 1 mol dm^{-3}.

2.2.4. *Colour measurement*

The reflectance of the dyed fabrics was measured using a Minolta CM-1000 reflectance spectrophotometer under illuminant D_{65} using a 10° standard observer with UV component included and specular component excluded. The corresponding K/S values were calculated from the reflectance data at the λ_{max} of the dyeing.

2.2.5. *Measurement of zeta potential*

The ζ-potential of the fabric samples was measured using a Shimadzu ZP-10B instrument and calculated by the Helmholtz-Smoluchowski equation [Eq. (1)] where H is streaming potential, P pressure, η viscosity, k relative conductivity and D dielectric constant.

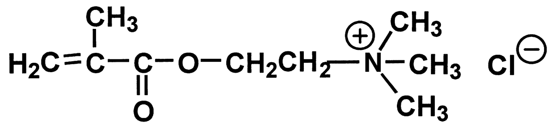
$$\zeta = \frac{\mathbf{H}}{\mathbf{P}}\cdot\frac{\mathbf{4\pi\eta k}}{\mathbf{D}} \qquad (1)$$

Throughout the work, pH was varied using aqueous solutions of hydrochloric acid and sodium hydroxide in order to maintain the ionic strength at 0.001. The pressure of the stream was maintained within 3–12 Torr (0.4–1.6 kPa); all measurements were carried out at 25°C.

3. Results and discussion

3.1. *Adsorption of MOEMTAC on cotton*

Fig. 2 reveals that after 1 min irradiation, a linear relationship existed between the amount of the quaternary compound adsorbed on the cotton substrate and the amount of MOETMAC applied.



MOETMAC

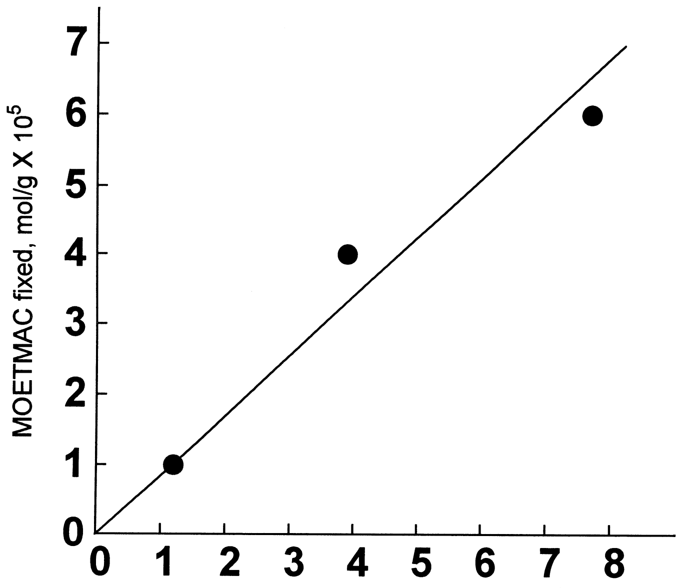


Fig. 2. Amount of MOETMAC adsorbed as a function of MOETMAC applied.

3.2. *Effect of MOETMAC on uptake of C I Acid Orange 7*

Fig. 3 shows the colour yield (K/S value) obtained as a function of the amount of MOETMAC that was applied after 1 min UV irradiation. From this it is evident that after an initial marked increase in K/S value, colour strength reached a constant level at about $3.5\times10^{-4}\,\text{mol}\,\text{g}^{-3}$ of the quaternary compound. This finding is not consistent with that displayed in Fig. 2 which clearly demonstrates that no such plateau was achieved in the amount of MOETMAC adsorbed on the cotton substrate. The conclusions suggested by these findings are that the plateau region in Fig. 3 represents, in effect, that ion-ion interaction operating between the anionic dye and the cationic MOETMAC on the fibre reached a saturation value and, therefore, that further enhancement of dye uptake may not be possible through the introduction of further MOETMAC in the substrate.

3.3. *Effect of UV irradiation on adsorption of MOETMAC*

When colour yield achieved using C I Acid Orange 7 is plotted as a function of irradiation energy for a constant concentration of $3.9\times 10^{-4}\,\text{mol}\,\text{g}^{-1}$ of MOETMAC applied (Fig. 4), it is evident that colour yield reached a maximum value at about $3\,\text{J}\,\text{cm}^{-2}$, and thereafter decreased gradually with increasing irradiation energy. This result implies that no more than $3\,\text{J}\,\text{cm}^{-2}$ is needed for the UV initiated fixation of the quaternary compound. Indeed, it can be argued that UV radiation in excess of this level could impart photo degradation to the cotton substrate, which may decrease the dyeability of the fabric [12].

3.4. *Electrolyte substitution*

Comparison of the results shown in Fig. 5 and Fig. 6 reveals that the colour yield obtained using C I Direct Red 28 in the absence of NaCl on the modified fabric was greater than that achieved for the dyeing of unmodified fabric in the presence of electrolyte in the dyebath. It can thus be concluded that the modification of the cotton fabric enables dyeings of deep shade to be obtained in the absence of electrolyte.

3.5. *ζ-potential of modified cotton.*

Fig. 7 shows the surface charge of fabrics that had been irradiated for one, and for 5 min, compared to

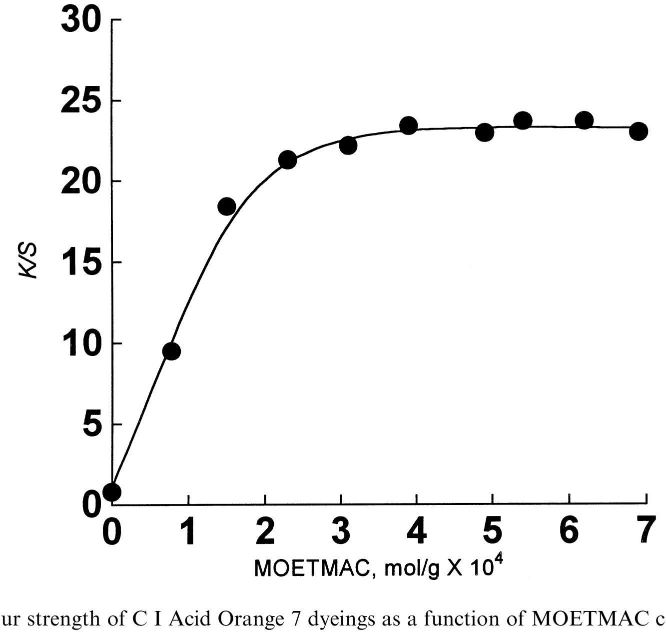


Fig. 3. Colour strength of C I Acid Orange 7 dyeings as a function of MOETMAC concentration.

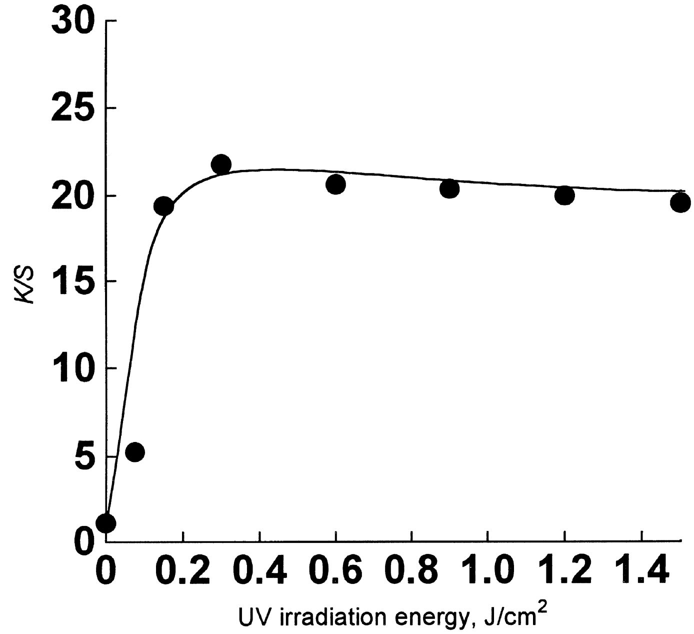


Fig. 4. Colour strength of C I Acid Orange 7 dyeings as a function of irradiation energy.

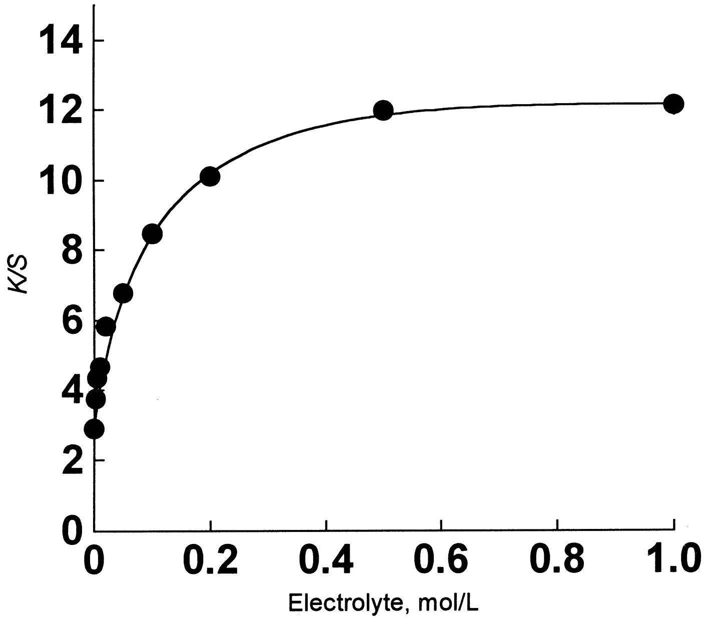


Fig. 5. Colour strength of C I Direct Red 28 dyeings as a function of electrolyte concentration.

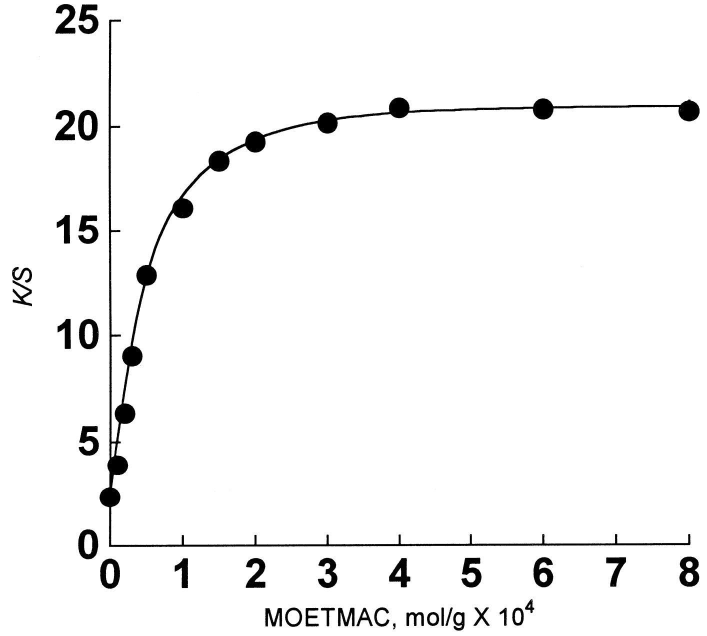


Fig. 6. Colour strength of C I Direct Red 28 dyeings as a function of MOETMAC concentration.

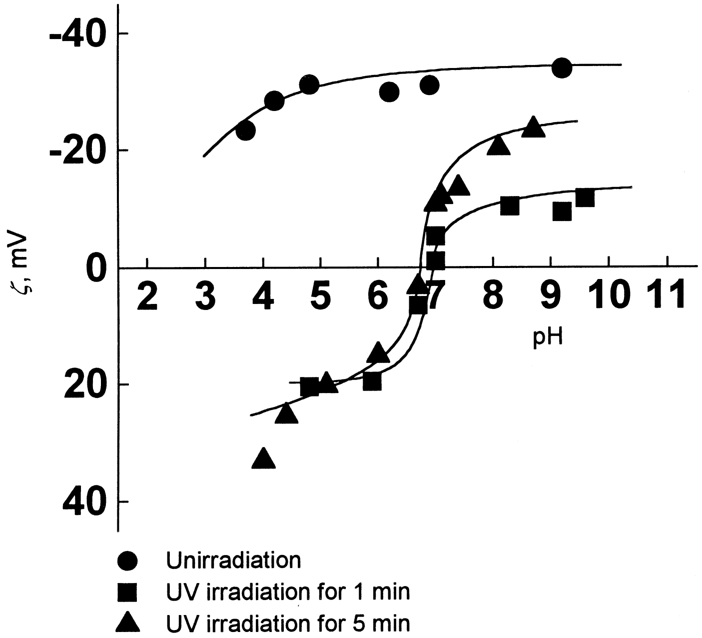


Fig. 7. Zeta potential.

that of the unmodified substrate. The negative potential recorded for the unmodified fabric can be attributed to the presence of carboxyl groups which were formed during the bleaching and other stages involved in the preparation of the material. In contrast, the two modified substrates display marked cationicity in the acidic region, which suggests that the introduced quaternary groups have more than compensated for the carboxyl groups. However, the negative potential observed for the modified substrates under alkaline conditions clearly shows that negative sites in the cotton are present; it seems reasonable to propose that these would probably be ionised hydroxyl groups, bearing in mind the low pK_a of carboxylic acid groups. Fig. 7 also shows that the negative ζ-potential was greater for 5 min exposure than for 1 min irradiation. This difference could be attributed to a difference in the extent of photo-oxidation of the fabric surface insofar as the longer the duration of irradiation, the greater could be the extent of photo-oxidation. If this were the case, it follows that excessive irradiation could have a deleterious effect on fibre modification using MOETMAC.

4. Conclusions

Cotton fabric can be modified through the introduction of quaternary groups by UV irradiation. The modified substrate displayed enhanced dyeability towards anionic dyes because of the presence of the introduced quaternary groups. Hence, the dyeability of the cellulosic fibre can be controlled through the UV induced modification and, therefore, patterned dyeing effects could be achieved through the exhaustion dyeing of fabric which has been exposed to patterned UV modification.

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