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The use of dendrimers to modify the dyeing behaviour of reactive dyes on cotton

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Abstract

Cotton fabric which had been pretreated with a dendrimer displayed markedly enhanced colour strength with reactive dyes, even when dyeing had been carried out in the absence of both electrolyte and alkali. Competitive dyeing of untreated and dendrimer pretreated cotton suggests that the dendrimers offer the potential for differential-dyeing patterning possibilities. When non-competitively dyed, dendrimer pretreatment also enhances colour strength. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

For their reaction with cellulosic fibres, reactive dyes typically rely on an elevated pH (commonly over 10.5) and large amounts of electrolyte (NaCl or Na_2SO_4) to achieve satisfactory results. As typically used, however, a significant proportion of the dye is not fixed on the fibre at the end of the dyeing process. A portion of the unfixed dye may be hydrolysed and thus be unavailable for recovery or reuse. Processes to destroy this dye and recover the electrolyte have been developed, indicating the high amounts used [1,2].

A major driving force in the research for reactive dyes and processes for their application has been to make the dyeing process more efficient. This has been sought in a number of ways. Machinery of low liquor ratio is advised [3,4], in which context, continuous or semi-continuous processes offer the lowest liquor ratios as well as the opportunity to achieve dyeings in the absence of salt [5]. Dyers seem reluctant to adopt such methods, possibly due to the difficulty in correcting off-shade dyeings. Hetero- and homobifunctional dyes have been developed to achieve higher dye fixation [6,7] and “low-salt” dyes of higher substantivity have been commercialised [8]. Despite this, the application of reactive dyes to cellulosic fibres continues to be costly for the dyehouse in terms of dye wasted, electrolyte and alkali used and, in addition, presents a large pollution load for the environment.

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An alternative approach to increase dye uptake and dye fixation is by the modification of cellulosic fibres themselves. While the modification of cellulose for improved dyeability dates back to the 19th century, recent chemical modifications offer possibilities to increase both the substantivity and the reactivity of the dye–fibre system, allowing the dyeing process to be carried out with lower amounts of electrolyte and less waste of dye. The modification of cellulosic fibres, mostly cotton, to enhance their dyeability with reactive dyes has received considerable attention in recent years [9]. In essence, attention has focussed on the introduction of cationic groups by means of pre-treatment, commonly via quaternised amino groups, to which the anionic reactive dyes are attracted and so enhance dye–fibre substantivity. Such enhanced dye–fibre substantivity can result in reduced electrolyte usage and, potentially at least, lead to "salt-free″ dyeings. In addition, if the cationic pre-treatment compound also contained nucleophilic groups, such as primary amine or thiol, it is possible that the reactive dye could react with such added nucleophiles at lower pH values than are normally needed for cellulosic fibre dyeing; this, in turn, could, theoretically, lead to reduced dye hydrolysis. Despite the availability of apparently feasible systems for the cationisation of cellulosic fibres since 1974 [10], these have not been widely adopted. It has been suggested that there are difficulties associated in applying such compounds in a level manner [11].

Dendrimeric chemistry was developed as a 'spin-off'' from conventional polymer chemistry and dendrimers are gaining importance due to their versatility. In contrast to linear polymers, dendrimers are highly branched, fractal-like macromolecules of well-defined, three-dimensional structure, shape and topology. From their shapes are derived names such as *arborols*, *cascade*, or *star-burst* polymers. The preparation, properties and end uses of dendrimers have been extensively reviewed [12,13]. Dendrimers can be prepared with a M_r and very narrow size distribution, via any of the common polymerisation techniques. The synthesis typically proceeds in stages or *generations* in which both the extent of branching and the size of the dendrimer increase; synthesis can be closely controlled to achieve a given size, shape and internal structure. Dendrimers cannot engage in chain entanglements as do linear polymers and thus are not useful in mechanical applications as are conventional linear polymers; generally, dendrimers are viscous liquids at room temperature. Functional end groups impart to the dendrimer characteristic physical and chemical properties, such as solubility, compatibility with plastics, uptake of guest molecules and surface activity.

Dendrimers were described for the first time some 30 years ago. Initial applications for the compounds were restrained by the lack of reliable and practical methods for dendrimer preparation. The later introduction of so-called *convergent* and *divergent* methods of preparation allowed the materials to become available on an industrial scale; dendrimer chemistry is now expanding rapidly. Along with novel dendrimer structures come novel physical, chiral, electrochemical, optical, photophisycal/photochemical, biological and catalytic properties and thus new applications in many fields. So far, however, they seem to have had enjoyed limited application in the textile field.

The purpose of the present work was to determine whether the pre-treatment of cotton with a dendrimer could enhance the dyeability of the fibre with reactive dyes. The dendrimer contains primary amino groups, with which theoretically, a reactive dye should be able to react under neutral/acidic pH conditions. It was also decided to examine whether or not the dendrimer could, under appropriate pH conditions, assume a positive charge and so permit "salt-free" dyeing.

2. Experimental

2.1. Dyes

Six commercial *Procion MX* (BASF) dyes were used (Table 1). This particular type of reactive dyes was chosen because of the low temperature required for its application to cellulosic fibres that accrues from its high reactivity. The majority of experiments were carried out using C.I Reactive Blue 163.

Table 1
Dyes used

Commercial name	C.I. generic name
Procion Blue MX-G	C.I. Reactive Blue 163
Procion Blue MX-2G 125	C.I. Reactive Blue 109
Procion Red MX-8B	C.I Reactive Red 11
Procion Yellow MX-G	No C.I. generic name
Procion Brown MX-5BR	C.I. Reactive Brown 10
Procion Turquoise MX-G	C.I. Reactive Blue 140

2.2. Dendrimer

The dendrimer used was a derivative of *Am*$_{16}$*decanamide*$_8$, an example of the *Astramol*™ range of dendrimers, provided by DSM New Business Development. The preparation of the dendrimer is described in the literature [14]. The structure shown in Fig. 1 is only one of the isomers present in the product [14].

2.3. Fabric

Woven, bleached, scoured cotton fabric (150 g m^{-2}) free of fluorescent brightening agents was obtained from Whaleys.

2.4. Buffer

The pH 4 buffer used comprised acetic acid (9.60 g dm^{-3})/sodium acetate (3.56 g dm^{-3}) and the pH 7.4 buffer comprised disodium hydrogen phosphate (5.0 g dm^{-3})/potassium dihydrogen phosphate (1.0 g dm^{-3}). pH 9.2 buffer tablets were obtained from BDH

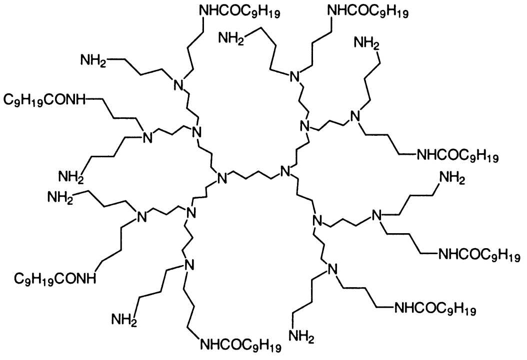

Fig. 1. Dendrimer used.

2.5. Levelling agent

As preliminary trials using dendrimer pretreated fabric revealed that dyeings were unlevel, a commercial levelling agent, *Dyapol PT*, supplied by Yorkshire Chemicals plc, was used at a concentrations of half that of the concentration of dendrimer.

2.6. Application of dendrimer

Samples of cotton were treated with the dendrimer at 90°C at three different pH values (4, 7 and 9) and at four different concentrations (0.25, 0.5, 1.0 and 1.5% omf), using a 15:1 liquor ratio. The application profile is shown in Fig. 2.

2.7. Dyeing

To highlight differences in dye uptake between the pretreated and untreated cotton samples, the majority of dyeings were carried out using a competitive dyeing method (Fig. 3) in which a sample of dendrimer-treated cotton and a sample of untreated cotton were dyed competitively in the same dyebath. All dyeings were carried out using a liquor ratio of 20:1. After dyeing, the samples were washed-off using the method depicted in Fig. 4. In addition, a modified method of dye application was used (Fig. 5) to investigate the application of dye without salt and/or alkali. Accordingly, these modified dyeing processes were carried out both unbuffered as well as at a buffered pH of 4 and 7.4.

3. Results and discussion

Fig. 6 shows the effect of pretreatment of the cotton with 1% omf dendrimer on 1% omf competitive dyeings of C.I. Reactive Blue 163. It is obvious that for each of the three pH values used for dendrimer application, the colour strength of the pretreated cotton was considerably higher than that of the corresponding untreated cotton.

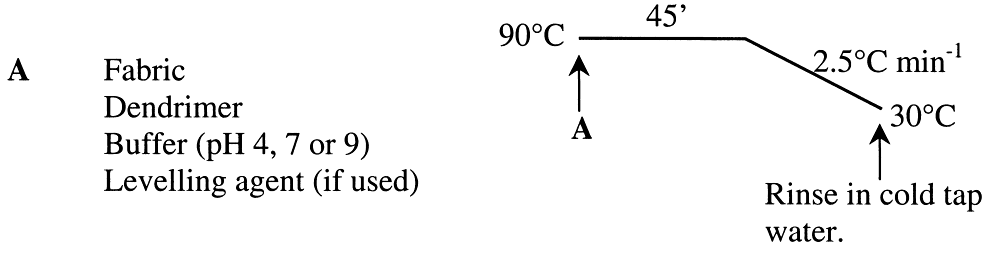

Fig. 2. Dendrimer application profile.

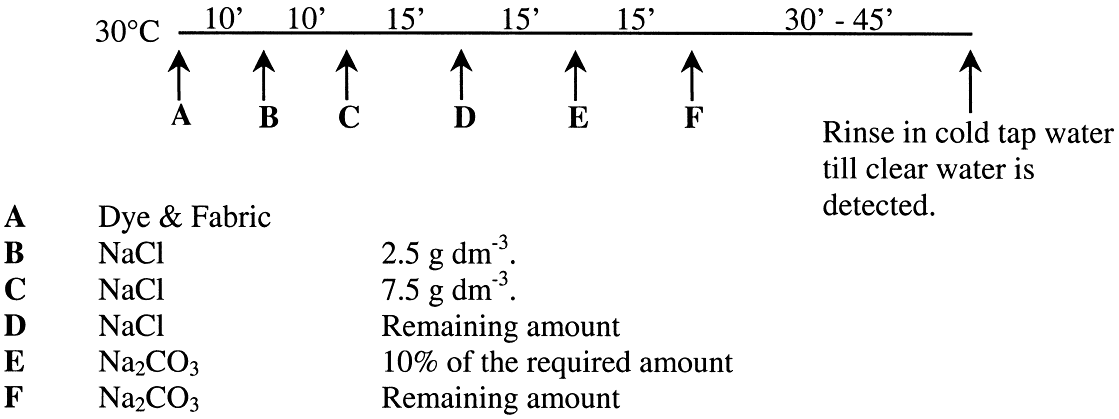

Fig. 3. Dyeing method.

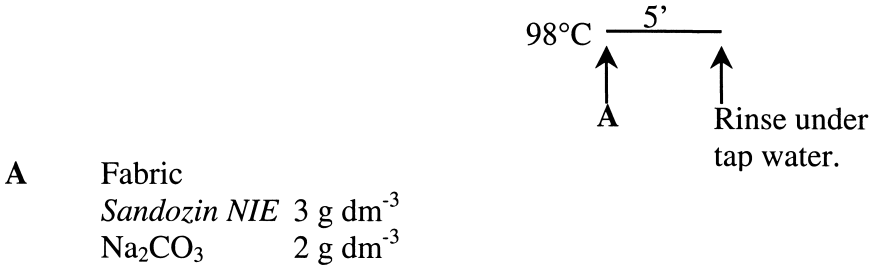

Fig. 4. Wash-off profile.

Fig. 6 also reveals that the application of dendrimer at pH 4 produced dyeings of highest colour strength; consequently, pH 4 was chosen as the pH for all subsequent dendrimer application.

Visual examination of the dyeings featured in Fig. 6 revealed that those of the dendrimer treated material were unlevel, while those of the untreated material were level. This suggested that the dendrimer application itself was unlevel. Subsequent applications of dendrimer were thus made in the presence of the commercial levelling agent *Dyapol PT* at a concentration of half that of the dendrimer. Fig. 7 shows that the use of the levelling agent reduced the colour strength of the dyeing presumably due to a lower amount of dendrimer having been absorbed on the fabric in pre-treatment. However, these and all subsequent dendrimer pretreated dyeings, were level.

As mentioned, for their reaction with cellulosic fibres, reactive dyes typically rely on an elevated

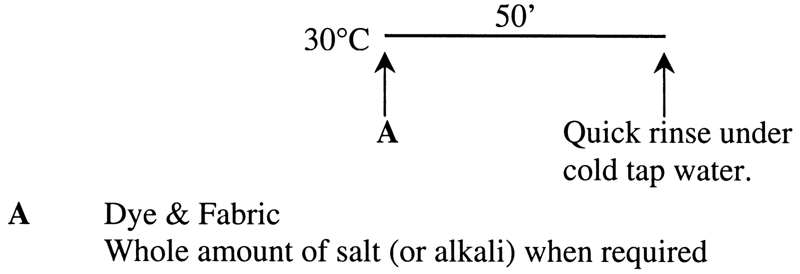

Fig. 5. Modified dyeing method.

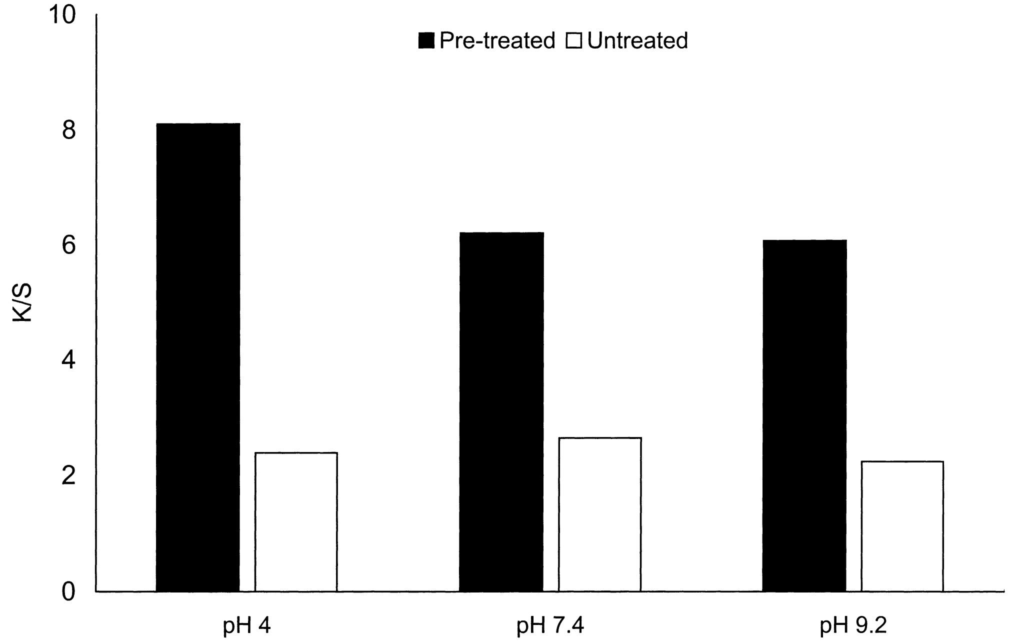

Fig. 6. Effect of pH of dendrimer application on colour strength achieved using 1% omf C.I. Reactive Blue 163.

pH (commonly over 10.5) and large amounts of electrolyte (NaCl or Na_2SO_4) to achieve satisfactory results. It was decided to determine if the pretreatment of cotton with the dendrimer would permit salt-free and/or alkali-free dyeing to be achieved. Fig. 8 reveals that for untreated cotton, a reduction in colour strength occurred when alkali (Na_2CO) was not used and also when NaCl was not used; lowest colour strength was achieved when both electrolyte and alkali were absent. These findings were expected and clearly demonstrate the importance of using a high pH and electrolyte in the dyeing of cotton with the reactive dye used. Fig. 8 also shows that identical behaviour was obtained for the dyeing of pretreated cotton insofar as a reduction in colour strength occurred when both alkali and electrolyte were not used; lowest colour strength was achieved when both electrolyte and alkali were absent. However, Fig. 8 clearly shows that the colour strength achieved for the dendrimer pretreated cotton was much larger than that obtained for the corresponding dyeing of untreated material. The *K*/*S* values displayed in Fig. 8 show that the colour strength of both electrolyte-free and alkali-free dyeings of pretreated cotton were higher than

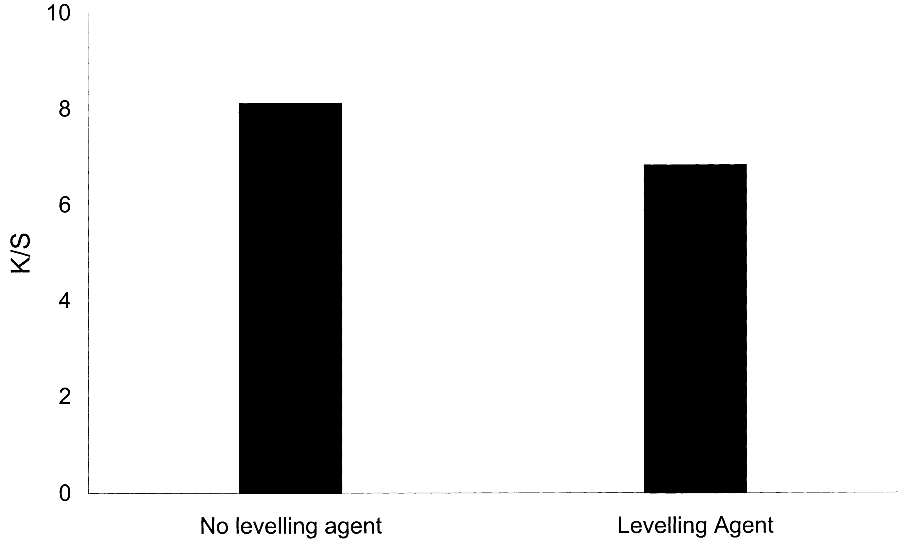

Fig. 7. Effect of levelling agent on colour strength achieved using 1% omf C.I. Reactive Blue 163.

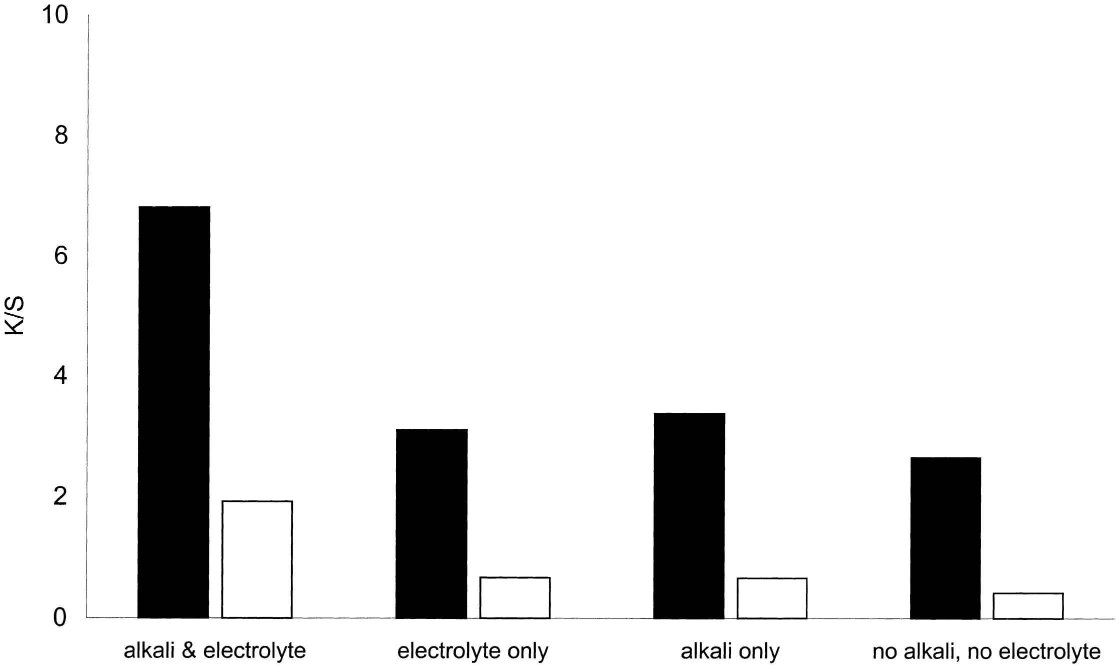

Fig. 8. The colour strength of 1% omf C.I. Reactive Blue 163 dyeings produced in the absence and presence of electrolyte and alkali.

those of the conventional dyeing (i.e. with alkali and electrolyte present).

The effect of pretreatment with varying amounts of dendrimer on colour strength is shown in Fig. 9. Generally, colour strength increased with increasing amount of dendrimer applied, although the observed increase in colour strength was small.

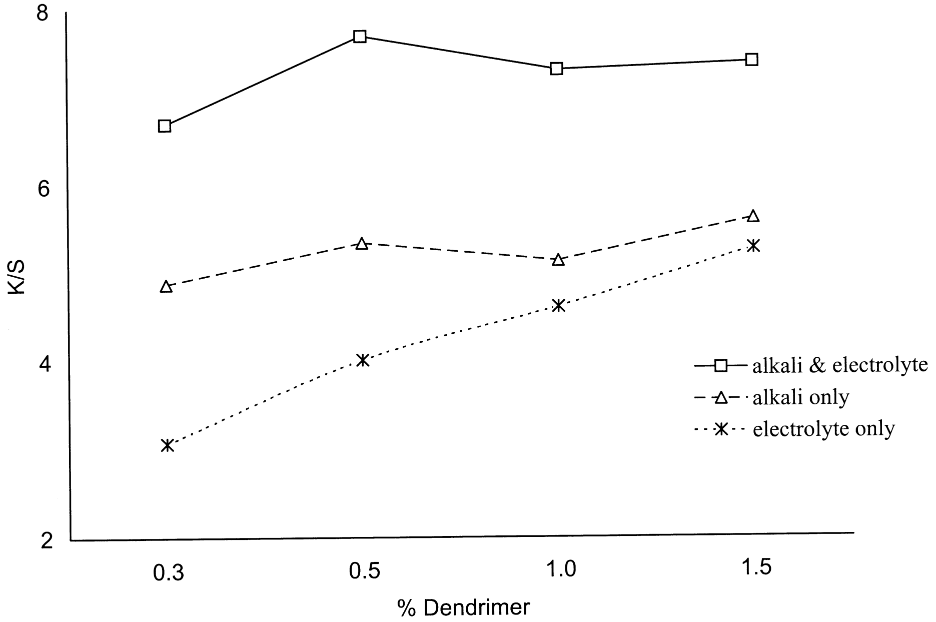

Fig. 9. The effect of the amount of dendrimer pretreatment concentration on the colour strength of 1% omf dyeings of C.I. Reactive Blue 163.

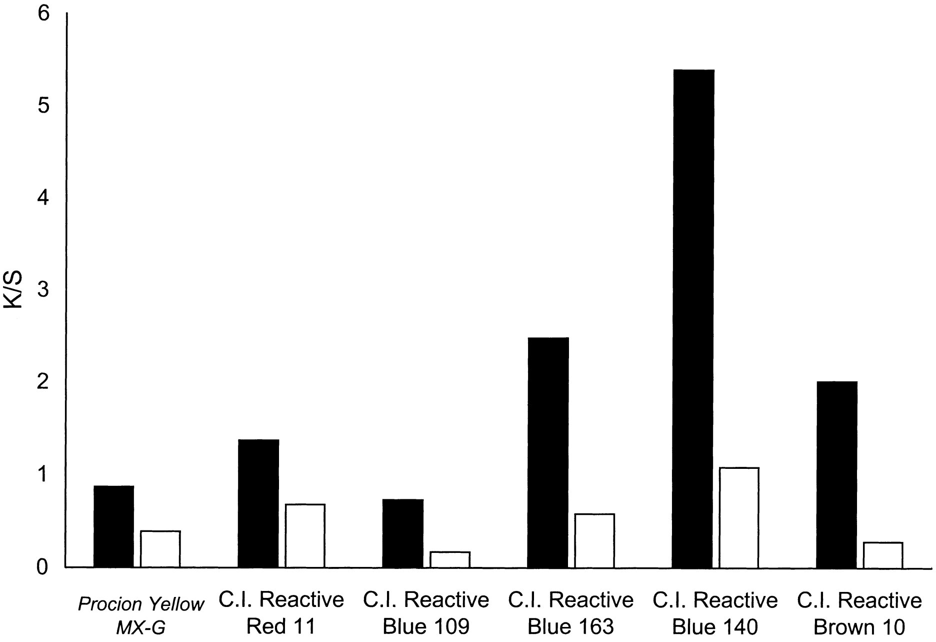

Fig. 10. Electrolyte-free dyeings at pH 7.4.

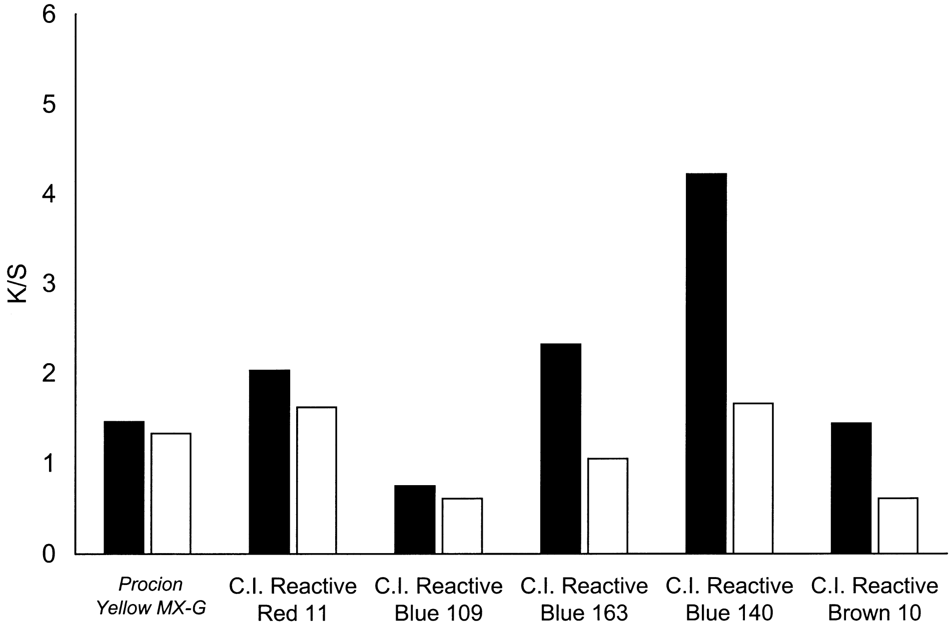

Fig. 11. Electrolyte-free, non-competitive dyeings.

The results so far were obtained using one dye, namely C.I. Reactive Blue 163. Electrolyte-free dyeings at pH 7.4 were conducted using this same dye together with five other *Procion MX* dyes. Fig. 10 shows that for each of the six dyes used, dendrimer pre-treatment resulted in enhanced colour strength. Interestingly, the effect of pretreatment on colour strength was especially marked in the case of C.I. Reactive Blue 140.

The effectivity of the added dendrimer in improving the dyeing process can be explained in terms of the pH-behaviour of the constituent amine groups. At low pH, the primary and tertiary amine groups of the dendrimer are protonated [15]. The ensuing local high positive charge density should act as a primary point of attraction for the anionic dye molecules. When the pH is subsequently increased during the dyeing process, the amines are deprotonated and the liberated primary amine groups can serve as highly reactive nucleophilic sites for the dyes.

The data presented so far was obtained using competitive dyeings in which pretreated and untreated fabrics were dyed in the same dyebath. Non-competitive dyeings, were also carried out using six dyes in the absence of electrolyte, but in the presence of alkali. Fig. 11 shows that dendrimer pretreatment increased colour strength for each dye used.

4. Conclusions

Dendrimer pretreated cotton displayed markedly enhanced colour strength, even when dyeing had been carried out In the absence of both electrolyte and alkali. Their use as a pretreatment of cellulosic fibres might thus offer considerable savings of electrolyte and alkali and may allow unfixed reactive dye to be reused.

When competitively dyed, the difference in colour strength obtained suggests that the dendrimers offer the potential for differential-dyeing patterning possibilities, either in fabric woven from treated and untreated yarns, or printed with dendrimer prior to dyeing. When non-competitively dyed, dendrimer pretreatment also enhances colour strength.

The use of dendrimers as textile dyeing auxiliaries is hitherto unexplored and their application is still to be optimised; in this context, their application by padding is worthy of exploration. The application of dendrimer is straightforward and doesn't involve a reaction with the substrate. The effectiveness of the commercial levelling agent used suggests that there is the possibility of correction in the event of unlevel application of dendrimer and thus seems to offer an advantage over the reactive-type, cellulosic pretreatment compounds that have been developed.

While no formal fastness tests were conducted, rinsing and wash-off treatments were used to remove unfixed dye.

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