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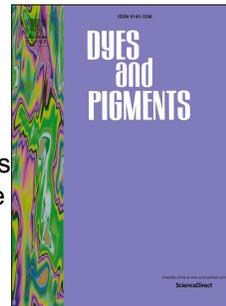


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# Accepted Manuscript

The role of auxiliaries in the immersion dyeing of textile fibres: Part 8 practical aspects of the role of inorganic electrolytes in dyeing cellulosic fibres with commercial reactive dyes

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1 **The role of auxiliaries in the immersion dyeing of textile fibres: Part 8**  
2 **practical aspects of the role of inorganic electrolytes in dyeing cellulosic**  
3 **fibres with commercial reactive dyes**

4  
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9

10 **Abstract**

11 The colour strength of 2% omf dyeings, as well as the extents of both exhaustion and fixation,  
12 achieved for three commercial grade reactive dyes on cotton, were promoted by the addition of 50  
13  $\text{gl}^{-1}$  NaCl at each of seven liquor ratios (1:50, 1:20, 1:10, 1:6, 1:3, 1:2 and 1:1.5). The depth of shade  
14 of dyeings obtained in the absence of added electrolyte using a 1:1.5 liquor ratio were of similar  
15 magnitude to those secured using a 1:10 liquor ratio in the presence of 50  $\text{gl}^{-1}$  NaCl. The promotion  
16 of dye uptake imparted by both added electrolyte and reduced liquor ratio was interpreted in terms  
17 of their effects on the substantivity of the reactive dyes towards the cotton substrate. It was  
18 concluded that the two, ostensibly different actions of adding electrolyte such as NaCl or  $\text{Na}_2\text{SO}_4$  to  
19 a reactive dye dyebath and reducing the liquor ratio used for dyeing have the same result, namely  
20 that of promoting dye aggregation in the dyebath which reduces the aqueous solubility of the anionic  
21 dye, which, in turn, results in the inherent preference of the dye to favour the aqueous phase shifting  
22 towards the fibre phase. The results show that it is possible to dye cotton using commercial grade  
23 reactive dyes in the complete (ie 100%) absence of added inorganic electrolyte. The dyeings  
24 obtained were of realistic depths of shade and displayed excellent levels of wash fastness.

25

26

27 **Highlights**

- 28 • the role of inorganic electrolyte in reactive dyeing is investigated experimentally
- 29 • added electrolyte reduces dye solubility and increases dye aggregation
- 30 • use of low liquor ratio enables dyeing in the absence of added electrolyte

31

32 **keywords:** dyeing cotton; dyeing auxiliaries; electrolyte; commercial reactive dyes; salt-free dyeing

33

## 34 1 Introduction

35 Although various types of auxiliary are available that provide assistance to immersion dyeing  
36 processes, the manner by which many dyeing auxiliaries function is unclear (1). Previous parts of  
37 the paper concerned the role of the most important auxiliary utilised in the exhaust dyeing of  
38 cellulosic fibres with direct dyes, namely inorganic electrolyte, in the form of either NaCl or Na<sub>2</sub>SO<sub>4</sub>.  
39 As an analysis of published work relating to current views of the mechanism by which added  
40 inorganic electrolyte influences direct dye uptake (2), revealed that conventional theoretical  
41 approaches were unable to satisfactorily account for the inherently low uptake on cellulosic fibres  
42 displayed by direct dyes in the absence of added inorganic electrolyte, nor why NaCl or Na<sub>2</sub>SO<sub>4</sub> are  
43 so effective in promoting dye uptake, a theoretical model was devised (3), based on the concept of  
44 interstitial water, to explain the promotional effect imparted by adding NaCl or Na<sub>2</sub>SO<sub>4</sub> to a direct  
45 dye dyebath. In this approach, the inherent low dye-fibre substantivity displayed by direct dyes when  
46 applied in the absence of added inorganic electrolyte was attributed to the dye's high aqueous  
47 solubility and the ensuing preference of the water soluble dye to remain within the aqueous dyebath  
48 phase rather than transfer to the solid fibre phase. By adding inorganic electrolyte to the direct  
49 dyebath, dye aggregation is induced which reduces the solubility of the dye, so that the  
50 characteristic preference of the previously highly soluble dye to favour the aqueous phase shifts  
51 towards the fibre phase and dye uptake is therefore promoted. It was later shown (4) that the same  
52 theoretical model could be used to account for the promotional effect which reducing the liquor ratio  
53 used for dyeing has on the uptake of direct dyes on cellulosic fibres. Equations were derived to  
54 interpret this theoretical model of direct dye adsorption; the equations differed in terms of both the

55 particular stages of the immersion dyeing process to which they applied and the nature of the  
56 experimental data required for their solution. The theoretical model was subsequently (5) utilised to  
57 interpret the results obtained for a series of dyeings on cotton using commercial grade direct dyes,  
58 employing different liquor ratios in both the absence and presence of added NaCl. It was concluded  
59 that because reducing the liquor ratio and adding Na<sub>2</sub>SO<sub>4</sub> or NaCl to a direct dye dyebath  
60 accomplish the same outcome, namely dye uptake promotion, cotton can be dyed satisfactorily  
61 using direct dyes without the addition of added inorganic electrolyte so long as low liquor ratios are  
62 used (5).

63

64 Because reactive dyes are structurally very similar to direct dyes, in that both dye types are  
65 essentially long, planar, anionic molecules solubilised by one or more ionised sulfonate groups, the  
66 adsorption of reactive dyes on cellulosic fibres is assumed to occur in a manner analogous to that of  
67 direct dyes prior to the reactive dye forming a covalent reaction with the substrate (6). In this  
68 context, added inorganic electrolyte is the most important auxiliary utilised in the immersion  
69 application of reactive dyes to cellulosic fibres; indeed, very large quantities of NaCl or Na<sub>2</sub>SO<sub>4</sub> are  
70 habitually employed to promote reactive dye uptake. As the result of a review of current views of the  
71 manner by which inorganic electrolyte promotes reactive dye uptake (7), a theoretical model was  
72 proposed (8), based on that developed for direct dyes (3, 4), to explain the promotional effects of  
73 both added inorganic electrolyte and reduced liquor ratio on the uptake of reactive dyes on cellulosic  
74 fibres.

75

76 This part of the paper concerns the role of inorganic electrolyte in the exhaust application of  
77 commercial grade reactive dyes. The results obtained for a series of dyeings on cotton, carried out  
78 using three commercial grade reactive dyes, employing different liquor ratios in both the absence  
79 and presence of added NaCl, are interpreted in terms of the above mentioned theoretical model (8)  
80 of reactive dye uptake. These findings are then used to explain why it is possible to dye cotton to  
81 realistic depths of shade using commercial grade reactive dyes in the absence of added inorganic  
82 electrolyte.

83

84 Subsequent parts of the paper will consider the role of auxiliaries that are utilised in the application  
85 of pure (ie diluent-free) reactive dyes to cotton using different liquor ratios in both the absence and  
86 presence of added inorganic electrolyte, as well as the beneficial impacts on the wash-off of reactive  
87 dyes that derive from being able to dye cotton in the absence of added electrolyte.

88

### 89 *1.1 reactive dyes*

90 By way of brief introduction, reactive dyes currently dominate the global usage of dyes on cotton  
91 and other types of cellulosic fibre, accounting for ~55-60% of global dye consumption on such fibres  
92 (2). In the immersion application of reactive dyes to cellulosic fibres, inorganic electrolyte (NaCl or  
93 Na<sub>2</sub>SO<sub>4</sub>) is added to the aqueous dyebath to promote dye uptake. The amount of electrolyte that is  
94 used in the immersion application of reactive dyes, which varies according to the type of dye and  
95 amount of dye applied, can be as high as 100 gl<sup>-1</sup> in the case of dark shades (7); indeed, it was  
96 estimated (7) that in 2015, if the ~50-55% (ie ~15 x 10<sup>6</sup> T) of global cellulosic fibre production that  
97 had been dyed using reactive dyes, was carried out in the presence of 50 gl<sup>-1</sup> added NaCl or  
98 Na<sub>2</sub>SO<sub>4</sub>, some 6 x 10<sup>6</sup> T of added inorganic electrolyte would have been consumed. Such routine  
99 usage of very high amounts of added inorganic electrolyte has both major economic consequences  
100 and poses severe environmental challenges. Despite the abundant research that has attended  
101 reactive dyes and their application to cellulosic fibres since their commercial introduction some six  
102 or so decades ago, remarkably very little of this voluminous output has been directed to establishing  
103 the fundamental nature of the role of added inorganic electrolyte in the exhaust application of the  
104 dyes to cotton and other cellulosic fibres (7).

105

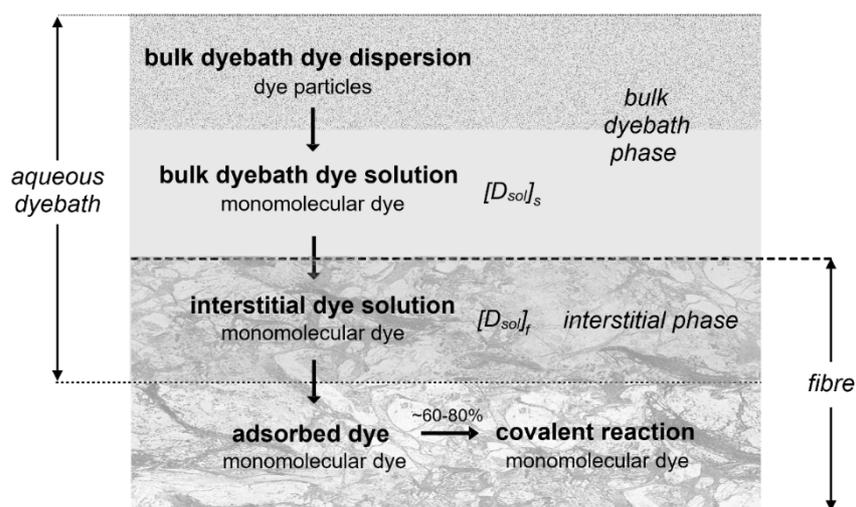
106 Clearly, if it were possible to apply reactive dyes to cellulosic fibres in the absence of added  
107 inorganic electrolyte, substantial environmental and economic savings should be achievable.

108

109 1.2 a model to describe the role of added electrolyte in the dyeing of cellulosic fibres using reactive  
 110 dyes

111 Because of the close structural resemblance of reactive dyes to direct dyes and the fact that the  
 112 adsorptive behaviour of reactive dyes prior to their covalent reaction with the cellulosic fibre is  
 113 analogous to that of direct dyes, the mechanism by which both added inorganic electrolyte and  
 114 reduced liquor ratio promote reactive dye uptake can be described (8) in terms of the notion that dye  
 115 adsorption proceeds from interstitial dye solution present within the substrate, as previously utilised  
 116 in the case of direct dye uptake (3). This approach, which in the case of reactive dyes is depicted in  
 117 Figure 1 (8), assumes that a very small amount of the water that is used in immersion dyeing  
 118 processes is located within the interstices of the fibrous substrate. As interstitial water is considered  
 119 to be that required to saturate the substrate and impart fibre wetting and swelling, the volume of  
 120 interstitial water present in a fibre corresponds to the moisture regain of the substrate at 100%  
 121 relative humidity ( $RH$ ) (3, 4) ( $\sim 0.22 \text{ l kg}^{-1}$  in the case of cotton); the remaining water that is used in  
 122 immersion dyeing (ie the vast majority) is present within the bulk dyebath that surrounds the water-  
 123 swollen fibre and provides functions such as heating, dye dissolution, mechanical agitation, etc. (3,  
 124 8).

125  
 126 By invoking the concept of free and bound sorbed water molecules in porous materials and current  
 127 views of electric double-layer theory, it is envisaged that the properties of the interstitial water differ  
 128 to that of the water that resides within the surrounding bulk aqueous dyebath, from the viewpoint of  
 129 the distribution of sorbed ions/molecules (3, 8). As the interstitial water within the wetted, swollen  
 130 fibre comprises dyebath solution, the transfer of dye molecules from the dyebath to the fibre takes  
 131 place from within this interstitial water (Figure 1).



137

138

139

140

Figure 1 representation of reactive dyeing mechanism (8)

141

142 This approach is expressed in terms of Eq 1 and Eq 2, where  $[D]$  is the total amount of dye within  
 143 the immersion dyeing system, which comprises dye that is present in the interstitial dye solution  
 144 within the fibre phase,  $[D_{sol}]_f$  together with that present in the bulk dyebath dye solution in the  
 145 dyebath phase,  $[D_{sol}]_s$ ,  $S$  is the substantivity coefficient, and  $L$  the fractional liquor ratio.

146

$$147 \quad S = \frac{[D_{sol}]_f}{[D_{sol}]_s} = \left( \frac{[D] - [D_{sol}]_s}{[D_{sol}]_s} \right) \quad 1$$

148

$$149 \quad S = \frac{[D_{sol}]_f}{\frac{[D_{sol}]_s}{L}} = \left( \frac{[D] - \frac{[D_{sol}]_s}{L}}{\frac{[D_{sol}]_s}{L}} \right) \quad 2$$

150

151 According to Eq 1, the partition of the reactive dye between the fibre and dyebath phases depends  
 152 on the concentration of dye within the bulk dyebath solution phase,  $[D_{sol}]_s$ . Adding either NaCl or  
 153  $\text{Na}_2\text{SO}_4$  to an aqueous reactive dyebath is considered to be a dilution effect insofar as the inorganic  
 154 electrolyte induces dye self-association, which reduces the solubility of the dye and, as a result, the  
 155 amount of dye in solution within the dyebath phase,  $[D_{sol}]_s$ , is reduced. The driving force for the  
 156 transfer of dye molecules from the aqueous phase (dyebath) to the solid phase (fibre) is the  
 157 concentration gradient,  $[D_{sol}]_f/[D_{sol}]_s$ , between the amount of dye in the dye solution within the bulk  
 158 dyebath,  $[D_{sol}]_s$ , and the amount of dye in the interstitial dye solution within the fibre phase,  $[D_{sol}]_f$ . It  
 159 therefore follows that in the presence of added inorganic electrolyte, as  $[D_{sol}]_s$  is lowered then the  
 160 term  $([D] - [D_{sol}]_s/[D_{sol}]_s)$  will increase, so that the dye concentration gradient (ie  $[D_{sol}]_f/[D_{sol}]_s$ ) must  
 161 increase, with the result that a higher driving force for dyeing accrues. Eq 1 therefore shows that the  
 162 substantivity of the reactive dye, as expressed by  $S$ , increases in the presence of added NaCl or

163  $\text{Na}_2\text{SO}_4$  because the amount of dye in the dye solution within the bulk dyebath,  $[D_{sol}]_s$ , has been  
164 lowered and, therefore, the amount of dye in the interstitial dye solution within the fibre phase,  $[D_{sol}]_f$ ,  
165 will increase accordingly.

166

167 This approach therefore considers that the characteristically high aqueous solubility of reactive  
168 dyes, which stems from the presence of sulfonate groups in the dye molecule, is responsible for the  
169 intrinsically low substantivity displayed by the dyes towards cellulosic fibres, when applied in the  
170 absence of added electrolyte; such high aqueous dye solubility was also considered to account for  
171 the remarkable ability of added inorganic electrolyte to promote reactive dye uptake (8).

172

173 The marked influence of dye solubility on reactive dye uptake described by Eq 1 is reflected in the  
174 fact that the liquor ratio used for dyeing exerts a dramatic effect on both the rate and extent of dye  
175 uptake, since liquor ratio influences dye-fibre substantivity. This is because liquor ratio determines  
176 the amount of water in the dyebath available for dye dissolution and, thereby, the amount of dye  
177 available for adsorption on the fibre. Also, as the concentration of both the reactive dye and the  
178 added  $\text{NaCl}$  or  $\text{Na}_2\text{SO}_4$  in the dyebath are dependent upon liquor ratio, the intensity of the dye-  
179 inorganic electrolyte interactions that determine the extent to which electrolyte encourages dye  
180 uptake, are influenced by liquor ratio.

181

182 In this context, it was proposed (4, 8) that the promotional effect on dye adsorption imparted by a  
183 reduction in the liquor ratio used for dyeing could be explained in terms of Eq 1, which accounts for  
184 the manner by which added inorganic electrolyte promotes dye uptake. The ensuing derivative  
185 equation, Eq 2 was derived, according to which, because of the term  $([D_{sol}]_s/L)$ , then liquor ratio, as  
186 described by  $L$ , impacts directly on the amount of dye in solution in the bulk dyebath phase,  $[D_{sol}]_s$ ,  
187 rather than on the amount of dye in the interstitial solution in the fibre,  $[D_{sol}]_f$ . Thus, values of  $[D_{sol}]_s$   
188 will decrease with decreasing liquor ratio and values of  $[D_{sol}]_f$  will therefore increase accordingly, so  
189 that dye uptake is promoted.

190

191 The similarity of Eq 2 and Eq 1 reflects the fact that the mechanism by which added inorganic  
192 electrolyte promotes dye uptake is essentially the same as that which applies in the case of reduced  
193 liquor ratio. Reactive dyes display an intrinsic tendency to aggregate in aqueous solution because of  
194 the characteristic planar structure of the dye anions and the likelihood of  $\pi$ - $\pi$  interactions between  
195 aromatic regions in adjoining dye molecules. Such dye self-association is encouraged at high dye  
196 concentrations, such as those that will exist in dyebaths of low liquor ratio, because of the small  
197 amount of water in the dyebath available for dye dissolution. In such a case, it can be anticipated  
198 that hydrophobic interaction will promote strong dye-dye interactions and suppress ionisation of the  
199 dye molecules so that the aqueous solubility of the ensuing dye aggregates will be lower than that of  
200 their monomolecular reactive dye precursors. Hence, lowering the liquor ratio used for dyeing  
201 reduces the solubility of the dye, which therefore reduces the amount of dye within the dye solution  
202 in the bulk dyebath phase,  $[D_{sol}]_s$  and, therefore, from Eq 1, the substantivity coefficient of the dye  
203 will increase, so that dyeing is promoted. Thus, Eq 1 and Eq 2 both predict that reducing the liquor  
204 ratio employed for reactive dyeing is analogous to that of adding inorganic electrolyte to the dyebath  
205 insofar as both actions lower the concentration of dye in the dye solution within the dyebath phase.

206

207 Since reducing the liquor ratio used for dyeing and adding inorganic electrolyte to a reactive dye  
208 dyebath accomplish the same result (8), namely promoted dye uptake, each of these procedures  
209 can be considered to impart controlled precipitation of the dye within the fibre, as proposed in the  
210 case of direct dyes (4, 5). From this it follows that the use of very liquor ratios should enable reactive  
211 dyeing to be achieved in the absence of added inorganic electrolyte.

212

213 The purpose of the work described in this part of the paper was to interrogate the above  
214 assumptions by interpreting the results obtained for a series of dyeings on cotton, carried out using  
215 three commercial grade reactive dyes, employing different liquor ratios in both the absence and  
216 presence of added NaCl, in terms of the above theoretical models (8) of reactive dye uptake.

217



## 246 2.2 methods

247 2.2.1 Dyeing

248 2% omf dyeings were undertaken using various liquor ratios in both the presence and absence of 50  
 249  $\text{gl}^{-1}$  NaCl. The amount of added electrolyte in dyeing was adjusted to ensure that a concentration of  
 250  $50 \text{ gl}^{-1}$  was employed, regardless of liquor ratio employed; two dyeing methods were used, which  
 251 are described below.

252

253 2.2.1.1 dyeing tubes/dyeing machine

254 Dyeings were carried out according to the dye maker's recommendations, following the procedure  
 255 shown in Figure 2, employing liquor ratios of 1:50, 1:20, 1:10, 1:6 and 1:3, in sealed,  $300 \text{ cm}^3$   
 256 capacity, stainless steel dyepots housed in a *Roaches Pyrotec S* dyeing machine.

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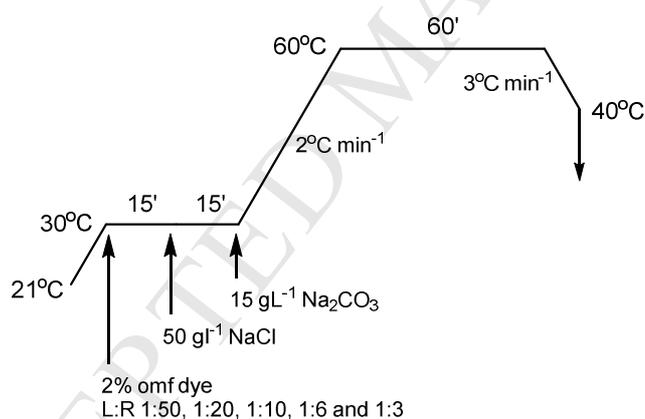
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265 Figure 2 dyeing tubes/dyeing machine method

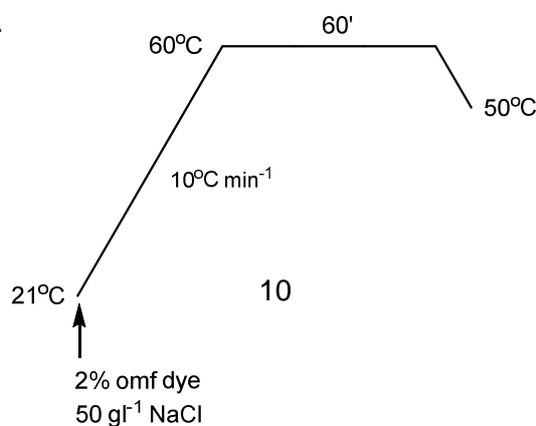
267 2.2.1.2 PP bags/tumble dryer

268 Dyeings were undertaken, employing liquor ratios of 1:3, 1:2, 1:1.5 and 1:1, in sealed,  $1000 \text{ cm}^3$   
 269 capacity, polypropylene plastic bags housed in a *Miele PT8257* tumble dryer, following the  
 270 procedure shown in Figure 3.

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Figure 3 PP bags/tumble dryer dyeing method

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280 2.2.1.3 wash-off

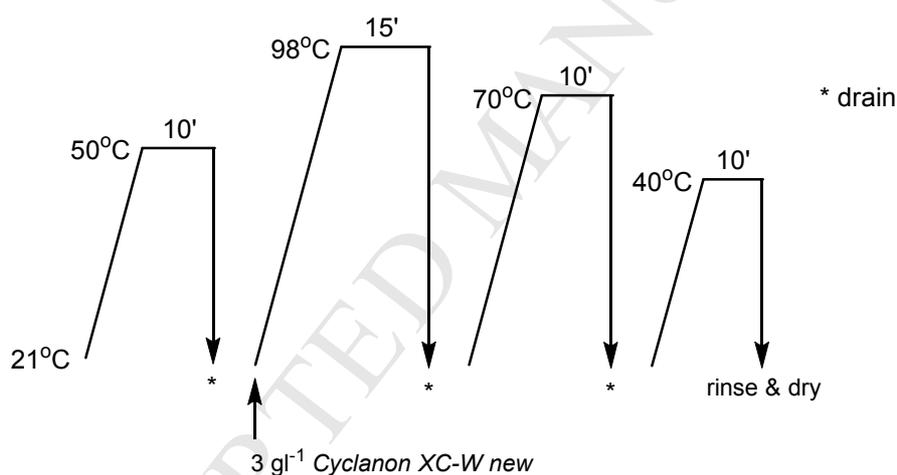
281 At the end of dyeing, the sample was removed from the dyebath, squeezed to remove surplus dye

282 liquor and then subjected to the wash-off procedure shown in Figure 4, using a 10:1 L:R for each

283 stage; the washed-off dyeing was allowed to dry in the open air.

284

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293

Figure 4 wash-off method

294

295 2.2.2 Colour measurement296 The CIE colorimetric co-ordinates and colour strength ( $f_k$  values) of the dyeings were determined for297 each dyeing from measurements made using a *Datacolour Spectroflash 60* reflectance298 spectrophotometer from 400 nm to 700 nm using  $D_{65}$  illuminant,  $10^\circ$  standard observer with UV

299 component included and specular component excluded. Samples were folded so as to realise two

300 thicknesses and the average of four measurements was taken for each sample.

301

302 2.2.3 Measurement of dye exhaustion

303 The absorbance at  $\lambda_{\max}$  of a suitably diluted (distilled water) sample of dye liquor taken both before  
 304 and after dyeing was determined using a 1 cm path quartz cell housed in a Perkin-Elmer *Lambda 9*  
 305 UV/Visible/NIR spectrophotometer in the region 400–700 nm. The percentage dyebath exhaustion,  
 306 %E, was calculated using Eq 3 where  $A_0$  and  $A_1$  represent the absorbance of the dye solution  
 307 before and after dyeing, respectively.

308

$$309 \quad \%E = 100 \times \left(1 - \frac{A_1}{A_0}\right) \quad 3$$

310

311 2.2.4 Determination of dye fixation

312 The extent of reactive dye fixation, %F, is commonly determined by firstly removing unfixed dye (ie  
 313 both unreacted reactive dye and/or hydrolysed dye) using an appropriate method, such as that  
 314 employed in this work, namely the commercially recommended wash-off process depicted in Figure  
 315 3, and calculating the extent of dye fixation, %F, using Eq 4, where  $f_{k1}$  and  $f_{k2}$  represent the colour  
 316 strength of the dyeing before and after wash off, respectively.

$$317 \quad \%F = \frac{f_{k2}}{f_{k1}} \times 100 \quad 4$$

318 The extent of total reactive dye fixation, %T, describes the overall efficiency of the reactive dyeing  
 319 process, insofar as it is the proportion of the reactive dye applied to the fibre which is covalently  
 320 bound to that fibre. As such, using Eq 5, total dye fixation describes the amount of the exhausted  
 321 reactive dye, %E, which has been fixed to the cellulosic substrate, %F.

$$322 \quad \%T = \frac{\%E \times \%F}{100} \quad 5$$

323 2.2.5 Wash fastness

324 Washed-off dyeings were subjected to the ISO 105:C06/C2S (60°C) wash fastness test.

325

### 326 **3 Results and Discussion**

327 As mentioned, this part of the paper concerns the exhaust application of commercial grade reactive  
328 dyes to cotton and the role of the most fundamentally important dyeing auxiliary utilised in this  
329 dyeing system, namely added inorganic electrolyte, in the guise of sodium chloride. The results of  
330 dyeings on cotton carried out using commercial grade reactive dyes, at various liquor ratios and in  
331 both the absence and presence of added NaCl, are interpreted in terms of the previously derived  
332 theoretical model (8) by which inorganic electrolytes such as NaCl and Na<sub>2</sub>SO<sub>4</sub> promote the uptake  
333 of reactive dyes on cellulosic fibres during immersion dyeing.

334

#### 335 *3.1 the use of two dyeing methods*

336 Dyeings were carried out using two methods, namely one that employed 300 cm<sup>3</sup> capacity, stainless  
337 steel dyepots housed in a *Roaches Pyrotec S* dyeing machine, following the procedure recounted in  
338 2.2.1 as well one that employed sealed, 1000 cm<sup>3</sup> capacity, polypropylene plastic bags housed in a  
339 *Miele PT8257* tumble dryer, as described in section 2.2.2. These two particular dyeing methods  
340 were the same as those utilised in the previous part of the paper that described the dyeing of cotton  
341 using direct dyes (5), although the application conditions employed in the previous study were  
342 different to those used here.

343

344 Trials revealed that both the shape of the 300 cm<sup>3</sup> stainless steel dyepots and the particular  
345 agitation mechanism employed in the *Roaches Pyrotec S* dyeing machine enabled consistently level  
346 dyeings to be obtained at liquor ratios of 1:50, 1:20, 1:10, 1:6 and 1:3. However, inconsistently level  
347 dyeings were secured using liquor ratios of 1:2 and 1:1.5. An alternative dyeing vessel/agitation  
348 method, described earlier (5), was used which provided consistently level dyeings at liquor ratios of  
349 1:2 and 1:1.5, namely, one in which sealed, 1000 cm<sup>3</sup> capacity, polypropylene bags were housed in  
350 a *Miele PT8257* tumble dryer. It was considered that level dyeings could be achieved at these two  
351 low liquor ratios because of enhanced fabric:dye liquor interchange that stemmed from the use of  
352 the larger capacity container and the random, tumbling action provided by the tumble dryer.  
353 However, whilst dyeings were secured at a 1:1 liquor ratio using the PP bag/tumble dryer method,

354 since the uniformity of these dyeings was not always perfect, especially in the case of dyeings  
 355 carried out in the presence of added NaCl, it was decided that the results obtained for the 1:1 liquor  
 356 ratio dyeings would not be included in this part of the paper.

357

358 To determine the compatibility of the two dyeing methods, as previously described in the case of  
 359 direct dyes (5), dyeings which had been carried out in both the absence and presence of  $50 \text{ g l}^{-1}$   
 360 added NaCl, employing both dyeing tube/ dyeing machine and PP bag/tumble dryer methods, using  
 361 a 1:3 liquor ratio, were analysed. A 1:3 liquor ratio was selected because consistently level dyeings  
 362 were achieved using this particular liquor ratio for both dyeing methods.

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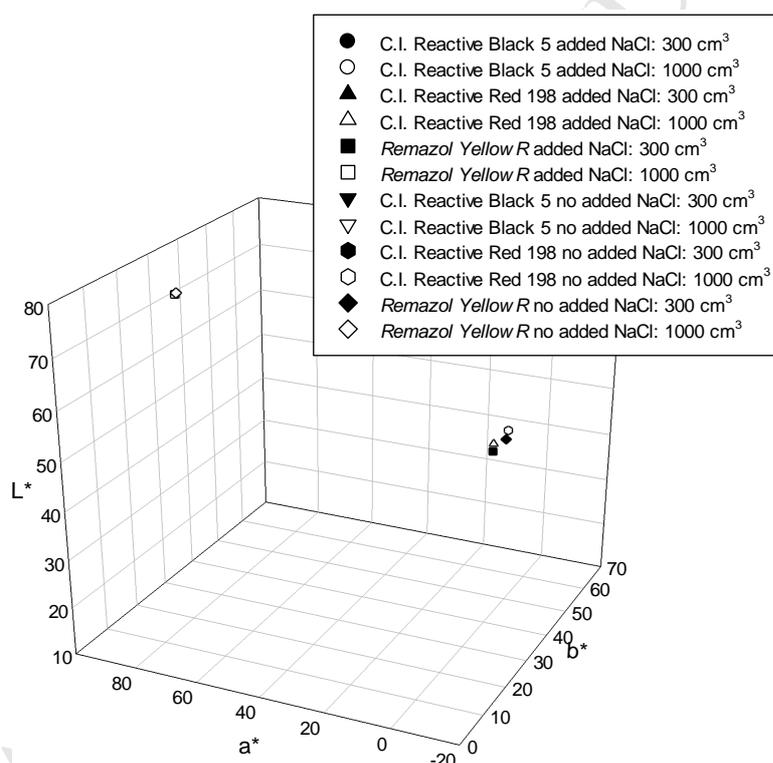
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376



377 Figure 5 comparison of dyeings achieved using dyeing tube/ dyeing machine and PP bag/tumble dryer dyeing  
 378 methods; absence and presence of  $50 \text{ g l}^{-1}$  NaCl; 1:3 liquor ratio

379

380 Figure 5 reveals that only small colorimetric differences were observed between the dyeings carried  
 381 out using the two dyeing methods, as demonstrated by the L\*, a\* and b\* data. Furthermore, the

382  $\Delta E_{\text{CIELAB}}$  values between corresponding dyeings were  $\ll 1.0$  and the colour strength data secured  
 383 for the respective dyeings were very similar. It was thus concluded that the two types of dyeing  
 384 vessel/agitation system were compatible in terms of the quality (depth of shade, hue and chroma) of  
 385 the dyeings produced.

386

387 In summary, the results presented below were obtained using the two dyeings methods discussed  
 388 above, insofar as those displayed over the range of liquor ratio 1:50 to 1:3 were secured using the  
 389 dyeing tubes/dyeing machine and those at liquor ratios of 1:2 and 1:1.5 were generated using the  
 390 PP bags/tumble dryer.

391

### 392 3.2 colour strength

393 Figure 6 shows the effect of reducing the liquor ratio from 1:50 to 1:1.5 on the colour strength ( $f_k$   
 394 values) of 2% omf dyeings obtained using the three reactive dyes on woven cotton fabric, in both  
 395 the absence and presence of  $50 \text{ gl}^{-1}$  added NaCl.

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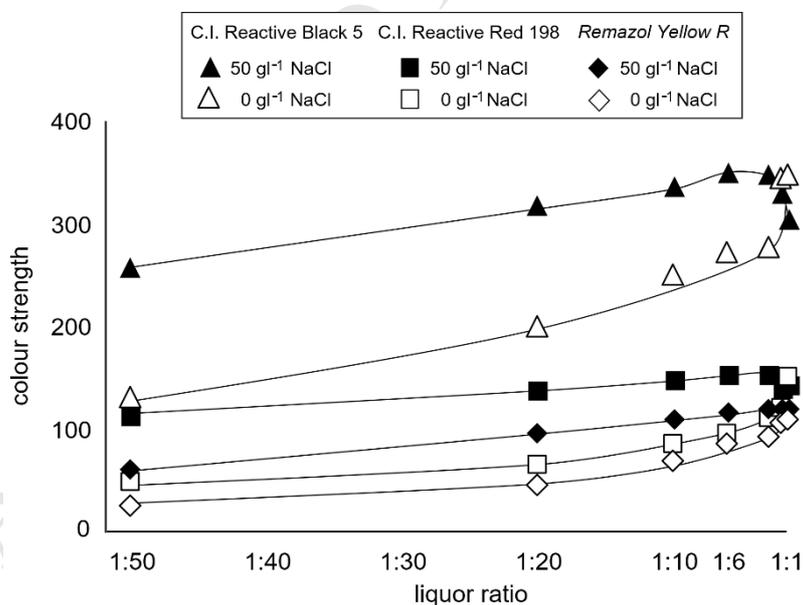


Figure 6 Effect of liquor ratio on colour strength; absence and presence of  $50 \text{ gl}^{-1}$  NaCl

408 The corresponding colorimetric data obtained for the dyeings are displayed in Table 1 which reveal  
 409 that the colour of the dyeings did not change, as expected, as the liquor ratio used for dyeing was

410 reduced from 1:50 to 1:1.5. Also, dyeing in the presence or absence of added sodium chloride did  
 411 not affect the colour of the samples, again, as expected.

412

413 From Figure 6 it is apparent that the effect of liquor ratio on colour yield differed for dyeings which  
 414 had been carried out in the presence and absence of added NaCl. For each of the three dyes used,  
 415 colour yield increased with decreasing liquor ratio over the range 1:50 to 1:6, in the case of the  
 416 dyeings carried out in the presence of added electrolyte; the  $f_k$  values then gradually decreased with  
 417 further reduction in liquor ratio. In the case of dyeings that were carried out in the absence of added  
 418 NaCl, colour yield increased with decreasing liquor ratio over the complete range of liquor ratios  
 419 examined, for each of the three dyes studied (Figure 6).

420

421

Table 1 Colorimetric parameters for 2% omf dyeings; absence and presence of 50  $\text{gl}^{-1}$  NaCl

| liquor ratio | dye      | NaCl/ $\text{gl}^{-1}$ | L*   | a*   | b*    | C*   | $h^\circ$ | $\lambda_{\text{max}}$ |
|--------------|----------|------------------------|------|------|-------|------|-----------|------------------------|
| 1:50         | Black 5  | 50                     | 21.0 | -2.7 | -14.4 | 14.6 | 259.4     | 600                    |
|              |          | 0                      | 30.3 | -5.6 | -17.5 | 18.4 | 252.4     |                        |
|              | Red 198  | 50                     | 41.0 | 57.8 | 5.9   | 58.1 | 5.8       | 520                    |
|              |          | 0                      | 49.7 | 56.1 | -0.1  | 56.1 | 359.9     |                        |
|              | Yellow R | 50                     | 76.9 | 19.3 | 80.5  | 82.8 | 76.5      | 440                    |
|              |          | 0                      | 80.0 | 11.7 | 64.9  | 66.0 | 79.8      |                        |
| 1:20         | Black 5  | 50                     | 18.1 | -1.4 | -11.6 | 11.7 | 263.0     | 600                    |
|              |          | 0                      | 24.4 | -3.9 | -15.9 | 16.3 | 256.3     |                        |
|              | Red 198  | 50                     | 39.8 | 59.4 | 9.7   | 60.2 | 9.2       | 520                    |
|              |          | 0                      | 46.7 | 57.7 | 2.1   | 57.7 | 2.1       |                        |
|              | Yellow R | 50                     | 74.8 | 24.8 | 87.0  | 90.5 | 74.1      | 440                    |
|              |          | 0                      | 78.3 | 18.7 | 76.4  | 78.7 | 76.3      |                        |

|      |          |    |      |      |       |      |       |     |
|------|----------|----|------|------|-------|------|-------|-----|
| 1:10 | Black 5  | 50 | 17.4 | -0.9 | -10.7 | 10.7 | 265.0 | 600 |
|      |          | 0  | 21.4 | -2.8 | -14.4 | 14.7 | 258.8 |     |
|      | Red 198  | 50 | 39.5 | 59.6 | 10.9  | 60.6 | 10.4  | 520 |
|      |          | 0  | 44.5 | 59.4 | 5.0   | 59.6 | 4.8   |     |
|      | Yellow R | 50 | 73.8 | 27.7 | 88.1  | 92.4 | 72.6  | 440 |
|      |          | 0  | 76.2 | 23.3 | 82.3  | 85.5 | 74.2  |     |
| 1:6  | Black 5  | 50 | 16.9 | -0.7 | -10.3 | 10.3 | 266.2 | 600 |
|      |          | 0  | 20.2 | -2.1 | -13.2 | 13.4 | 260.9 |     |
|      | Red 198  | 50 | 39.4 | 59.9 | 11.4  | 60.9 | 10.8  | 520 |
|      |          | 0  | 43.5 | 59.5 | 5.7   | 59.7 | 5.4   |     |
|      | Yellow R | 50 | 73.4 | 28.6 | 88.6  | 93.1 | 72.1  | 440 |
|      |          | 0  | 75.3 | 25.6 | 85.5  | 89.2 | 73.3  |     |
| 1:3  | Black 5  | 50 | 16.9 | -0.7 | -10.5 | 10.5 | 266.1 | 600 |
|      |          | 0  | 20.3 | -2.4 | -13.5 | 13.7 | 260.0 |     |
|      | Red 198  | 50 | 39.1 | 59.0 | 11.0  | 60.0 | 10.5  | 520 |
|      |          | 0  | 42.5 | 59.1 | 6.4   | 59.5 | 6.2   |     |
|      | Yellow R | 50 | 73.8 | 27.6 | 89.3  | 93.4 | 72.8  | 440 |
|      |          | 0  | 75.2 | 25.0 | 86.2  | 89.7 | 73.8  |     |
| 1:2  | Black 5  | 50 | 17.6 | -0.8 | -10.9 | 10.9 | 265.7 | 600 |
|      |          | 0  | 17.0 | -0.5 | -10.9 | 10.9 | 267.4 |     |
|      | Red 198  | 50 | 39.1 | 58.0 | 9.0   | 58.7 | 8.8   | 520 |
|      |          | 0  | 40.2 | 57.5 | 7.0   | 57.9 | 6.9   |     |
|      | Yellow R | 50 | 73.0 | 27.2 | 88.4  | 92.5 | 72.9  | 440 |

|       |          |    |      |      |       |      |       |     |
|-------|----------|----|------|------|-------|------|-------|-----|
|       |          | 0  | 73.7 | 26.1 | 87.3  | 91.1 | 73.3  |     |
|       | Black 5  | 50 | 19.6 | -0.7 | -13.2 | 13.3 | 262.7 | 600 |
|       |          | 0  | 16.9 | -0.5 | -10.6 | 10.6 | 267.4 |     |
| 1:1.5 | Red 198  | 50 | 38.6 | 57.3 | 8.9   | 58.0 | 8.8   | 520 |
|       |          | 0  | 38.7 | 58.3 | 10.6  | 59.3 | 10.3  |     |
|       | Yellow R | 50 | 73.1 | 27.8 | 88.7  | 93.0 | 72.6  | 440 |
|       |          | 0  | 74.2 | 26.5 | 88.6  | 92.5 | 73.4  |     |

422

## 423 3.3 dye exhaustion

424 When the variation in dye exhaustion as a function of liquor ratio displayed in Figure 7 is compared  
 425 to the corresponding values recorded for colour strength shown in Figure 6, it is apparent that when  
 426 each of the three dyes had been applied in the absence of added NaCl, the observed increase in  
 427 colour strength that accompanied a reduction in liquor ratio over the range 1:50 to 1:1.5 (Figure 6)  
 428 can be attributed to a corresponding increase in dye exhaustion over the same liquor ratio range.

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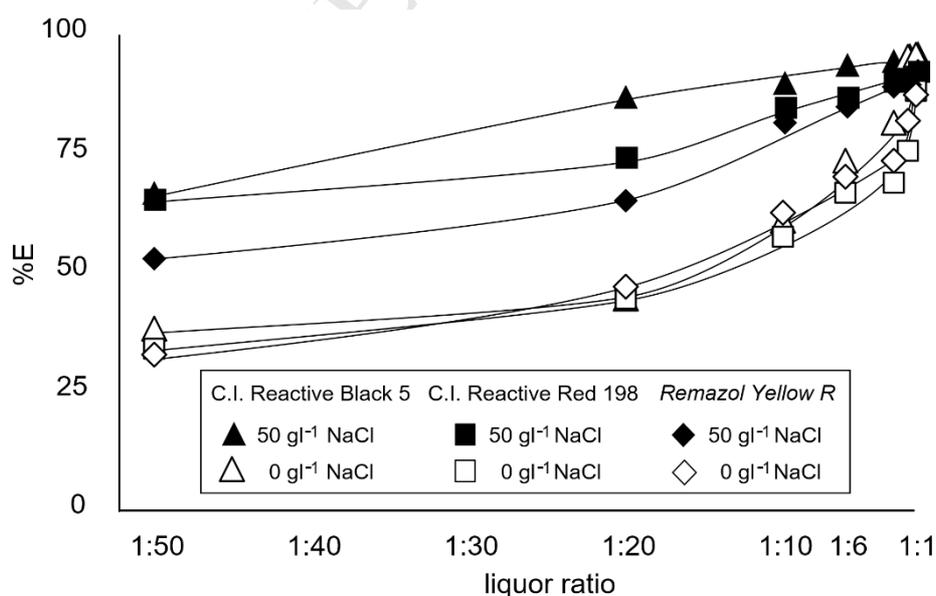
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440 Figure 7 Effect of liquor ratio on dye exhaustion; absence and presence of 50 gl<sup>-1</sup> NaCl

441

(legend as for Figure 6)

442

443 However, for dyeings which had been carried out in the presence of  $50 \text{ gl}^{-1}$  added electrolyte, dye  
444 exhaustion increased with decreasing liquor ratio over the range 1:50 to 1:3 and thereafter remained  
445 largely unchanged with further reduction in liquor ratio to 1:1.5. Hence, the findings shown in Figure  
446 6 that the  $f_k$  values of dyeings carried out in the presence of added electrolyte increased with  
447 decreasing liquor ratio over the range 1:50 to 1:6 and, thereafter, decreased with further reduction in  
448 liquor ratio, do not correlate with the corresponding values of dye exhaustion secured for the  
449 dyeings (Figure 7).

450

451 Instead, as discussed below, the trends in colour yield that accompanied a decrease in liquor ratio  
452 observed for dyeings undertaken in the presence of added NaCl (Figure 6) reflect the total dye  
453 fixation (%T) achieved for the dyeings.

454

455 The promotional effect of decreasing liquor ratio on the extent of dye exhaustion (Figure 7) was less  
456 pronounced in the case of dyeings undertaken in the presence of  $50 \text{ gl}^{-1}$  added electrolyte at liquor  
457 ratios  $\leq 1:6$ . In this context, it is apparent that the increase in dye uptake that accompanied a  
458 reduction in the liquor ratio employed for dyeing was more modest in the case of dyeings carried out  
459 in the presence of  $50 \text{ gl}^{-1}$  added electrolyte. In order to explain these findings, the arguments  
460 proposed in a previous part (5) of the paper to explain the observed effects of liquor ratio on direct  
461 dye uptake on cotton can be employed.

462

463 The finding (Figure 7) that in the absence of added NaCl, dye exhaustion increased with decreasing  
464 liquor ratio over the complete range of liquor ratios studied (ie 1:50 to 1:1.5), can be attributed to the  
465 combined effects which increased dye aggregation and reduced dye solubility had upon the  
466 effective concentration gradient between the amount of dye in the dyebath and the amount of dye in  
467 the fibre phase. According to the theoretical model outlined in section 1.2.1, as liquor ratio is  
468 reduced, the amount of water in the dyebath available for dye dissolution decreases, with the result  
469 that the concentration of dye in the dye solution within the bulk dyebath,  $[D_{sol}]_s$ , is lowered. Because

470  $[D_{sol}]_s$  decreases with decreasing liquor ratio then because of the term  $([D] - [D_{sol}]_s/[D_{sol}]_s)$  in Eq 2,  
471 the substantivity coefficient of the dye,  $S$ , will increase so that the driving force for dyeing increases  
472 and the partition of dye between the aqueous phase and the fibre phase shifts towards the fibre  
473 phase. Accordingly, dye uptake should increase with decreasing liquor ratio, as was indeed  
474 observed for each of the three dyes used in this work.

475

476 As discussed, this particular model was developed to describe the manner by which reduced liquor  
477 ratio promotes the uptake of direct dyes on cotton and other cellulosic fibres (3) and was also shown  
478 to be identical to that which explained the promotional effect of added inorganic electrolyte on direct  
479 dye uptake. Indeed, both a reduction in the liquor ratio utilised in dyeing and the addition of  
480 inorganic electrolyte to the dyebath were presumed (3) to impart the same promotional effect on  
481 direct dye uptake insofar as both actions encourage dye aggregation in the dyebath, which reduces  
482 the solubility of the dye in the dyebath, which, in turn, favours increased direct dye uptake. As  
483 mentioned, such an argument can be assumed to operate in the case of reactive dyes on cotton,  
484 since it is assumed that prior to dye-fibre fixation, the adsorption of reactive dyes on cellulosic fibres  
485 occurs in a manner analogous to that of direct dyes.

486

487 According to the notion that the promotion of reactive dye uptake imparted by both added electrolyte  
488 and lowered liquor ratio is each the result of a shift in the preference of the highly soluble dye to  
489 favour the fibre phase rather than the aqueous dyebath phase that is a consequence of increased  
490 dye aggregation and reduced dye solubility, it follows that the extent to which dye uptake is  
491 enhanced will be greatest when the promotional impacts of reduced liquor ratio and added NaCl are  
492 maximised, as is the case when low liquor ratio dyeings are carried out in the presence of added  
493 electrolyte and will be lowest when the promotional impacts of reduced liquor ratio and added  
494 electrolyte are minimised, as is the case when high liquor ratio dyeings are undertaken in the  
495 absence of added electrolyte. Thus, because the actions of adding electrolyte and reducing liquor  
496 ratio have the same outcome in terms of promoting dye uptake, the promotion of reactive dye

497 exhaustion imparted by the added inorganic electrolyte should decrease with decreasing liquor ratio,  
 498 as was observed (Figure 7).

499

500 Hence, in effect, adjustment of the liquor ratio used for dyeing and regulation of the amount of  
 501 inorganic electrolyte that is added to a reactive dye dyebath determine the level of substantivity  
 502 displayed by the reactive dye towards the cellulosic substrate.

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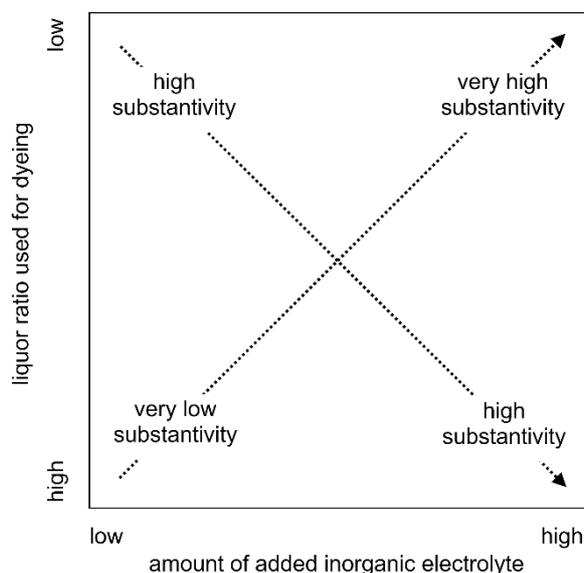
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514 Figure 8 simple representation of the combinatorial effects of added inorganic electrolyte and liquor ratio on  
 515 the reactive dye-cellulosic fibre substantivity

516

517 A corollary of this is that the adoption of very high liquor ratios (eg >1:100) in conjunction with the  
 518 complete absence of added electrolyte during dyeing results in very low dye-fibre substantivity,  
 519 whereas, in contrast, the use of very low liquor ratios (eg <1:1) coupled with large amounts of added  
 520 electrolyte in dyeing (eg >100  $\text{gl}^{-1}$ ) results in very high dye-fibre substantivity, as observed in  
 521 practice. This is illustrated by the relationship between liquor ratio and inorganic electrolyte on dye-  
 522 fibre substantivity depicted in Figure 8.

523

524 The use of application conditions that create such extremes of dye-fibre substantivity are  
525 commercially unrealistic, since the ensuing dyeings will be either of unacceptably low colour  
526 strength in the case of very low levels of dye-fibre substantivity or grossly unlevel owing to dye  
527 precipitation caused by excessive dye aggregation in the case of very high levels of dye-fibre  
528 substantivity. Instead, all commercial immersion dyeing processes used for applying reactive dyes  
529 to cellulosic fibres seek to achieve a level of dye-fibre substantivity that enables uniform dyeings to  
530 be secured which are of the desired colour strength. As mentioned, this is achieved by balancing  
531 the relative contributions that liquor ratio and added electrolyte make towards dye-fibre substantivity,  
532 insofar as a given amount of added electrolyte is used in conjunction with a particular liquor ratio. As  
533 such, commercial dyeing recipes for applying reactive dyes to cellulosic fibres typically specify  
534 different electrolyte (and alkali) requirements for different liquor ratios [eg (9, 10)].

535

536 Accordingly, when dyeing had been carried out in the absence of added electrolyte, the low extent  
537 of dye exhaustion observed for high liquor ratio dyeings (ie 1:50, 1:20, 1:10) was the result of the  
538 inherently low dye-fibre substantivity generated at such high liquor ratios. In contrast, the high %E  
539 values secured at low liquor ratios (ie 1:2 and 1:1.5) resulted from the intrinsically high dye-fibre  
540 substantivity that prevailed at such low liquor ratios.

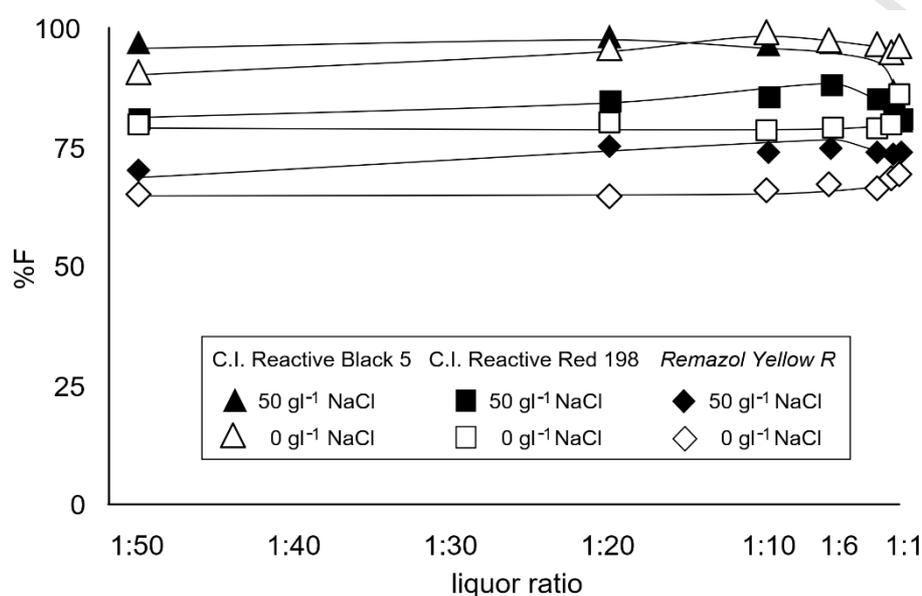
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542 However, the finding (Figure 7) that the impact of lowering liquor ratio on the extent of dye  
543 exhaustion was less pronounced for dyeings which had been undertaken in the presence of  $50 \text{ g l}^{-1}$   
544 NaCl requires attention. Because higher values of %E were obtained when dyeings had been  
545 carried out in the presence of added electrolyte (Figure 7), it follows that in the presence of added  
546 NaCl, the prevailing level of dye-fibre substantivity was greater than that when dyeing had been  
547 undertaken in the absence of added inorganic electrolyte. In effect, such was the inherently high  
548 dye-fibre substantivity provided by the  $50 \text{ g l}^{-1}$  added electrolyte, that the promotional effect of  
549 reduced liquor ratio on dye exhaustion was restricted to higher liquor ratios (ie 1:50 to 1:6); indeed,  
550 values of E% were essentially constant over the range of liquor ratios 1:3 to 1:1.5.

551

## 552 3.4 dye fixation

553 Figure 9 shows the effect which reducing the liquor ratio used in dyeing from 1:50 to 1:1.5 had upon  
 554 the extent of dye fixation, %F, achieved for 2% omf dyeings of the three reactive dyes on woven  
 555 cotton fabric, in both the absence and presence of 50 gl<sup>-1</sup> added NaCl. It is apparent that at each  
 556 liquor ratio used, the level of fixation achieved differed for the three different dyes, which was not  
 557 unexpected.



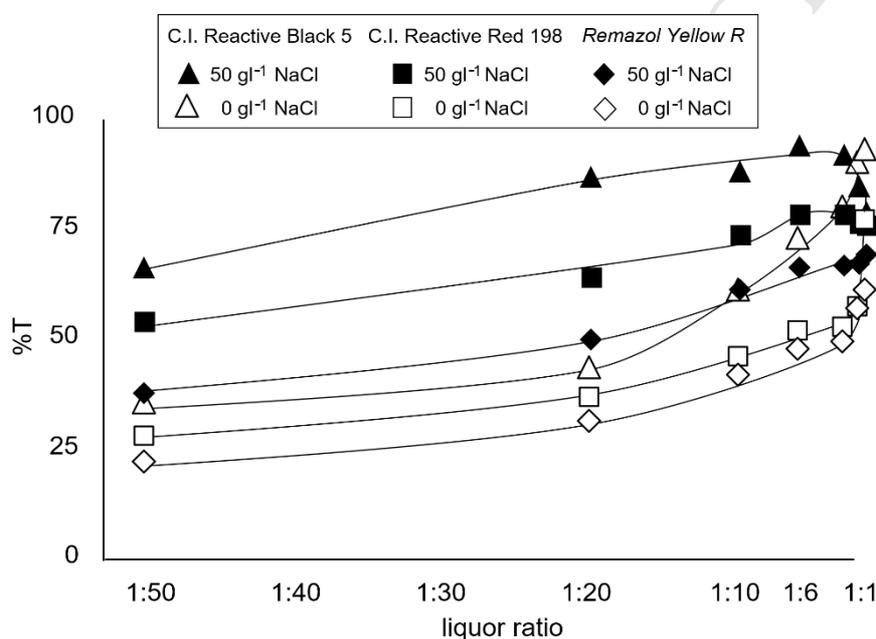
568 Figure 9 Effect of liquor ratio on dye fixation; absence and presence of 50 gl<sup>-1</sup> NaCl

569 (legend as for Figure 6)

570  
 571 The effect of decreasing the liquor ratio used for dyeing on dye fixation differed for dyeings which  
 572 had been carried out in the presence and absence of added electrolyte (Figure 9). For dyeings  
 573 carried out in the presence of added NaCl, values of %F increased gradually with decreasing liquor  
 574 ratio over the range 1:50 to 1:6, for each of the three dyes used, and thereafter decreased with  
 575 decreasing liquor. In the case of dyeings that were carried out in the absence of added NaCl, Figure  
 576 9 reveals that the extent of dye fixation generally increased with decreasing liquor ratio over the  
 577 complete range of liquor ratios examined, for each of the three dyes studied.

578

579 From Figure 10, it is apparent that at each liquor ratio used, the extent of total fixation, %T, secured  
 580 differed for the three different dyes, which was not unexpected. For dyeings carried out in the  
 581 presence of added electrolyte, values of %T increased with decreasing liquor ratio over the range  
 582 1:50 to 1:6, for each of the three dyes used, and thereafter decreased with decreasing liquor to  
 583 1:1.5. In the case of dyeings that were carried out in the absence of added NaCl, total dye fixation  
 584 increased with decreasing liquor ratio over the complete range of liquor ratios examined (ie 1:50 to  
 585 1:1.5), for each of the three dyes studied.



597 Figure 10 Effect of liquor ratio on total fixation; absence and presence of 50 gl<sup>-1</sup> NaCl  
 598 (legend as for Figure 6)

600 The observed general increase in %T that accompanied a reduction in liquor ratio when dyeing had  
 601 been carried out in both the presence and absence of added NaCl (Figure 10) can be attributed to a  
 602 corresponding increase in dye exhaustion over the same liquor ratio range (Figure 10).

603

## 604 3.5 promotional effect of added NaCl on dye uptake

605 The data presented in Figures 6 to 10 describe the enhancement of colour strength, dye exhaustion  
 606 and dye fixation achieved by reducing the liquor ratio used for dyeing, in both the absence and  
 607 presence of 50 gl<sup>-1</sup> added NaCl.

608

609 The effect of added inorganic electrolyte on direct dye uptake and its variation as a function of liquor  
 610 ratio was described by the *promotional effect*, via Eq 6 (5), which expresses the proportional  
 611 contribution that added NaCl made to the extent of dye exhaustion achieved at a particular liquor  
 612 ratio as a percentage.

613

$$614 \quad \% \text{ promotional effect} = \frac{\%E \text{ in presence of added NaCl} - \%E \text{ in absence of added NaCl}}{\%E \text{ in presence of added NaCl}} \times 100 \quad 6$$

615

616 Figure 11 shows the promotion of colour strength imparted by adding 50 gl<sup>-1</sup> NaCl to the dyebath, as  
 617 a function of liquor ratio, for each of the three dyes used. It is apparent that the ability of the added  
 618 electrolyte to promote colour strength diminished with decreasing liquor ratio, as previously  
 619 observed in the case of direct dyes on cotton (5).

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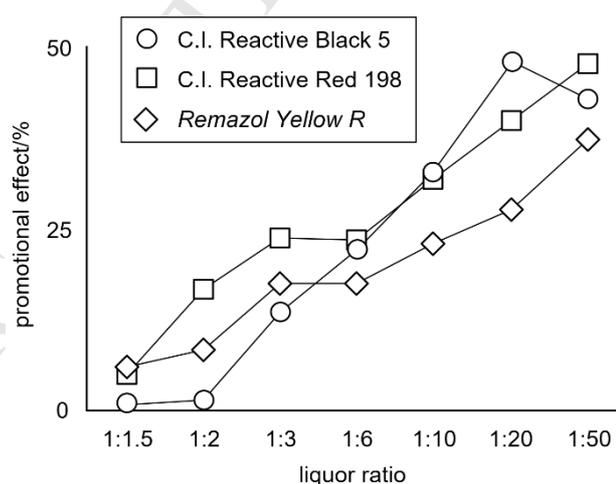
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627

628 Figure 11 Promotion effect imparted by added electrolyte as a function of liquor ratio; absence and presence  
 629 of 50 gl<sup>-1</sup> NaCl

630



631 This implies that the added electrolyte was more effective in promoting colour strength, and thus  
632 dye uptake, at longer liquor ratios (ie 1:50) than at shorter liquor ratios (ie 1:15), even though a  
633 constant concentration (ie  $50 \text{ gl}^{-1}$ ) of added NaCl had been employed at each of the seven liquor  
634 ratios examined. This diminution in the ability of the added electrolyte to promote colour strength  
635 that accompanied a decrease in liquor ratio (Figure 11) requires explanation.

636

637 If the manner by which reduced liquor ratio promotes the uptake of the three commercial grade  
638 reactive dyes is the same as that by which dye uptake is encouraged by adding NaCl, then reducing  
639 the liquor ratio that is used in dyeing and adding electrolyte to the dyebath will have the same effect  
640 on dye uptake: the preference for the dye to remain within the aqueous dyebath is reduced because  
641 of the effects of increased dye aggregation and reduced dye solubility. Accordingly, the extent to  
642 which dye uptake is enhanced by added NaCl should be greatest when the promotional impact of  
643 reduced liquor ratio is lowest, which will occur in the case of high liquor ratio dyeings, and will be  
644 lowest when the promotional impact of reduced liquor ratio is greatest, as will arise when low liquor  
645 ratio dyeings are undertaken. Thus, the promotional effect of the added  $50 \text{ gl}^{-1}$  NaCl on the uptake of  
646 the three reactive dyes should decrease with decreasing liquor ratio, as was indeed observed  
647 (Figure 11).

648

#### 649 3.5.1 interpretation of results using the theoretical model

650 Although both Eq 5 and Eq 6 provide explanations for the promotional effect imparted by added  
651 inorganic electrolyte on reactive dye adsorption, insofar as they predict that dye solubility, via  $[D_{so}]_s$ ,  
652 is the controlling influence on the transfer of the dye molecules from the dyebath to the fibre phase  
653 during dyeing, both equations require knowledge of the aqueous solubility of the dye in the bulk  
654 dyebath solution. Whilst such data can be obtained, it is not readily available nor is it especially easy  
655 to determine accurately owing to practical difficulties of separating the dissolved solute from the  
656 saturated solution. An alternative approach can be adopted to the use of Eq 5 and Eq 6, which  
657 offers an experimentally more accessible solution that entails the use of equations which describe  
658 the distribution of the reactive dye between the dyebath phase and the fibre phase at the end of the

659 dye adsorption process, and which require knowledge of the far more easily experimentally  
 660 measurable amounts of dye that are present in the residual dyebath and the solid fibre at the end of  
 661 dyeing (8).

662

$$663 \quad K = \frac{[D]_f}{[D]_s} \quad 7$$

664

665 As discussed (3, 7), Eq 7 (and equations based upon it), where  $[D]_f$  is the amount of dye present in  
 666 the fibre phase (ie the substrate) relative to the amount of fibre and  $[D]_s$  is the amount of dye in  
 667 solution (ie the dyebath) relative to the amount of solution and the equilibrium partition coefficient,  $K$ ,  
 668 describes the distribution of the dye between the dyebath,  $s$  and fibre,  $f$ , phases, is often used to  
 669 describe the partition of a dye between the fibre phase and the solution (dyebath) phase when  
 670 equilibrium dye uptake has been achieved.

671

672 Although equations based on Eq 7 are often used in studies that seek to determine the mechanism  
 673 by which dye adsorption proceeds when equilibrium dye uptake has been achieved and to  
 674 determine the thermodynamic standard affinity of dye adsorption, it was shown that the effects of  
 675 induced aggregation and reduced dye solubility on both direct dye (3, 4) and reactive dye (7) uptake  
 676 onto cellulosic fibres can be interpreted in terms of the relationship depicted in Eq 7, via Eq 8 in the  
 677 case of added inorganic electrolyte and Eq 9 in the case of liquor ratio, where  $S$  is the substantivity  
 678 coefficient and  $L$  the fractional liquor ratio, even though equilibrium dye uptake was not achieved.

679

$$680 \quad S = \frac{[D]_f}{[D]_s} = \left( \frac{[D] - [D]_s}{[D]_s} \right) \quad 8$$

681

$$682 \quad S = \frac{[D]_f}{\frac{[D]_s}{L}} = \left( \frac{[D] - \frac{[D]_s}{L}}{\frac{[D]_s}{L}} \right) \quad 9$$

683

684 In Eq 9, the ratio  $[D]_f/[D]_s/L$  describes the relative partition of the dye between the fibre and dyebath  
685 phases and, therefore, represents the substantivity exhibited by the reactive dye towards the  
686 cellulosic fibre, as expressed in terms of the substantivity coefficient,  $S$ , of the dye at the end of the  
687 immersion dyeing process: the higher the value of this ratio then the greater is the partition of the  
688 dye in favour of the fibre phase (ie  $[D]_f > [D]_s/L$ ) and the greater is dye uptake. Owing to the term  
689  $[D]_s/L$  liquor ratio impacts directly on the amount of dye in solution rather than on the amount of dye  
690 in the fibre. As such, Eq 9 predicts that because values of  $L$  decrease with increasing liquor ratio (eg  
691 value of  $L$  @ a given liquor ratio: 0.2 @ 1:5; 0.02 @ 1:50) then values of  $[D]_s$  will fall as liquor ratio  
692 decreases and, therefore, values of  $[D]_f$  will increase accordingly. Eq 9 therefore predicts that the  
693 extent of dye uptake achieved at the end of the immersion dyeing process will be determined by the  
694 effect of liquor ratio on the amount of dye in solution,  $[D]_s$ .

695

696 Because of the term  $([D]-[D]_s/L / [D]_s/L)$  in Eq 9, dye-fibre substantivity, as represented by  $S$ ,  
697 depends on the amount of dye in the bulk dyebath dye solution,  $[D]_s$  relative to the total amount of  
698 dye within the dyeing system,  $[D]$ ; the greater this difference, then the higher is dye-fibre  
699 substantivity, and, therefore, the greater is dye uptake. Eq 9 therefore suggests that the solubility of  
700 the reactive dye in the dyebath markedly effects the substantivity coefficient of the dye, in that  
701 substantivity will increase with decreasing liquor ratio (ie increasing values of  $L$ ), as is observed in  
702 practice, because the amount of dye in solution,  $[D]_s$ , decreases with decreasing liquor ratio owing to  
703 the relationship  $([D]_s/L)$ ; hence, the partition of the dye will shift towards the fibre phase,  $[D]_f$ .

704

705 As such, Eq 9 relates the degree of substantivity displayed by the reactive dye towards the fibre and  
706 the corresponding extent of dye uptake achieved, to the solubility of the dye in the dyebath.

707

708 As a constant concentration of added NaCl was employed in this work (ie 50  $\text{gl}^{-1}$ ), then the  
709 promotional effect on dye uptake imparted by the added NaCl was constant, regardless of the  
710 particular liquor ratio used for dyeing. It follows therefore that in this case, liquor ratio must be the  
711 primary determinant of dye-fibre substantivity. Hence, the influence of liquor ratio on the

712 substantivity coefficient,  $S$ , and, therefore, on dye uptake, will be much lower at high liquor ratios (eg  
 713 1:50, 1:20) than at low liquor ratios (eg 1:3, 1:2).

714

715 The plot of substantivity coefficient as a function of liquor ratio presented in Figure 12 clearly shows  
 716 that this was indeed observed, insofar as  $S$  decreases markedly with increasing liquor ratio in the  
 717 case of dyeings undertaken in the presence of added NaCl. Figure 12 also reveals that in the case  
 718 of dyeings which had been carried out in the absence of added NaCl, a decrease in the liquor ratio  
 719 used for dyeing induced a similar reduction in substantivity coefficient. The results presented in  
 720 Figure 18 therefore show that the promotional effect of reduced liquor ratio on dye-fibre  
 721 substantivity, as predicted by Eq 9, decreases, exponentially, with increasing liquor ratio, regardless  
 722 of the presence or absence of added inorganic electrolyte. Furthermore, Eq 8 and Eq 9 predict that  
 723 reduced liquor ratio and added inorganic electrolyte exert a combinatorial effect on dye uptake. In  
 724 this context, the plots in Figure 12 clearly show that at a particular liquor ratio, the addition of  $50 \text{ gl}^{-1}$   
 725 NaCl to the dyebath enhanced dye-fibre substantivity and, that this combinatorial promotional effect  
 726 decreased with decreasing liquor ratio, as was depicted by the plots shown in Figure 11.

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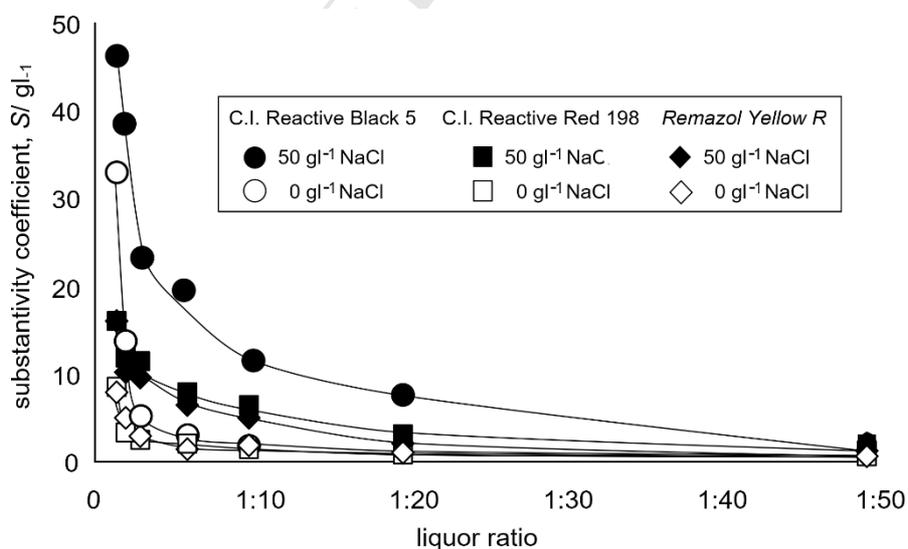
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Figure 12 substantivity coefficient as a function of liquor ratio; absence and presence of  $50 \text{ gl}^{-1}$  NaCl

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738 The behaviour of C.I. Reactive Black deserves mention insofar as the findings (Figure 12) that for  
 739 this dye,  $S$  increased markedly at liquor ratios of 1:2 and 1:1.5 in both the presence and absence of

740 added electrolyte, imply that this particular dye is more responsive to changes in liquor ratio and/or  
 741 the addition of electrolyte than are the other two dyes studied.

742

743 If the proposal (8) that electrolyte-induced dye aggregation in the dyebath is the cause of the  
 744 reduced solubility of the dye in the dyebath, this situation will be favoured under conditions in which  
 745 dye self-association into dimers, trimers, etc. can occur, such as will be secured when dyeing is  
 746 undertaken at low liquor ratio. Essentially, lowering the liquor ratio exploits the inherent tendency of  
 747 the reactive dyes to aggregate in the dyebath, so that the solubility of the dye in the dyebath is  
 748 reduced and dye uptake is increased. Accordingly, the substantivity coefficient should increase as a  
 749 function of reduced liquor ratio, as illustrated by the data presented in Figure 12, which reveals that  
 750 the magnitude of the coefficient obtained for the three dyes increased markedly with decreasing  
 751 liquor ratio when a constant concentration of added NaCl had been used for dyeing.

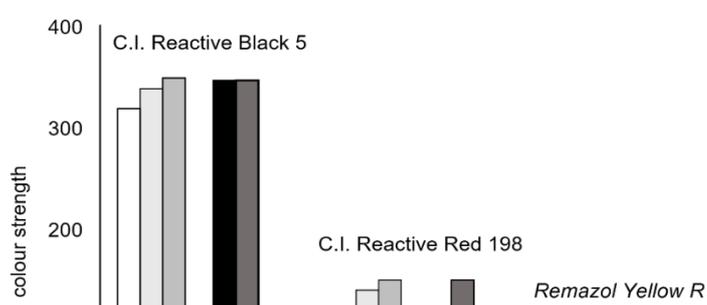
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### 753 3.5.2 comparison of low liquor ratio/zero added electrolyte and high liquor ratio/added electrolyte 754 dyeing

755 The results shown in Figure 6 reveal that the colour strength of dyeings obtained in the absence of  
 756 added electrolyte using liquor ratios of 1:2 and 1:1.5 were similar to those of dyeings secured using  
 757 higher liquor ratios in the presence of 50  $\text{gl}^{-1}$  added NaCl. Indeed, as the data presented in Figure  
 758 13 clearly reveal, in the case of C.I. Reactive Black 5, the colour strength obtained for 1:2 and 1:1.5  
 759 liquor ratio dyeings undertaken in the absence of added NaCl were similar to that achieved using a  
 760 1:6 liquor ratio in the presence of added electrolyte, and were greater than those achieved at liquor  
 761 ratios of 1:10 and 1:20 in the presence of added NaCl. For the other two commercial grade dyes  
 762 used in this work, Figure 13 shows that the  $f_k$  values of 1:1.5 liquor ratios dyeings carried out in the  
 763 absence of added electrolyte were similar to those secured using a 1:10 liquor ratio in the presence  
 764 of NaCl, which, again, were greater than those achieved at liquor ratios of 1:20 and 1:50 in the  
 765 presence of added NaCl.

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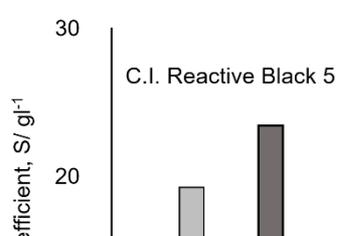


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Figure 13 colour strength as a function of liquor ratio; absence and presence of 20  $\text{gl}^{-1}$  NaCl

The above findings can be explained by recalling that, as recounted above, commercial immersion dyeing processes for applying reactive dyes to cotton and other cellulosic fibres aim to regulate the level of dye-fibre substantivity within the dyebath so that uniform dyeings of the required colour strength are obtained. This is achieved by employing a given amount of added electrolyte in conjunction with a particular liquor ratio, so as to manipulate the relative contributions that liquor ratio and added inorganic electrolyte make to dye-fibre substantivity. Thus, the results in Figure 13 clearly show that for each of the three dyes used, the level of dye-fibre substantivity can be manipulated so that level dyeings are obtained in the complete absence of added NaCl by employing very low liquor ratios (ie 1:2 and 1:1.5). From this it follows that a plot of substantivity coefficient as a function of liquor ratio for the particular dyeings displayed in Figure 13 should display similar trends to those in Figure 15, as indeed was observed (Figure 14).

Significantly, Figure 13 shows that the depth of shade of the ensuing electrolyte-free dyeings secured using low liquor ratios (1:1.5 and 1:2) in the absence of added NaCl were comparable to those achieved using higher liquor ratios in the presence of added electrolyte. Hence, dyeings of realistic depths of shade can be produced on cotton using commercial grade reactive dyes employing an immersion process in the absence of added electrolyte so long as low liquor ratios are employed.



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Figure 14 Substantivity coefficient as a function of liquor ratio; absence and presence of 20  $\text{gl}^{-1}$  NaCl

These findings demonstrate that the addition of NaCl and reduction of liquor ratio increase the substantivity of the reactive dyes towards the cellulosic substrate, which implies that the mechanism by which dye-fibre substantivity is promoted is essentially the same for both electrolyte addition and reduced liquor ratio, namely, increased dye aggregation and consequent reduced dye solubility. As such, because the contribution that dye self-association will make towards increased dye-fibre substantivity (via reduced dye solubility) will vary according to the particular amount of inorganic electrolyte and liquor ratio used, then a given amount of added electrolyte (eg 50  $\text{gl}^{-1}$  NaCl as was employed in this work) will be more effective in promoting dye uptake at higher liquor ratios, as was indeed observed (Figures 11 and 12).

Although the three dyes used in this work varied, in absolute terms, from the viewpoints of colour strength, level of dye exhaustion and fixation obtained, as expected, since the three dyes had been chosen arbitrarily as being representative of modern commercial grade reactive dyes. Nonetheless, the three dyes displayed notable similarity in their response to liquor ratio variation, as exemplified by the results shown in Figures 6 to 10.

### 823 3.6 effect of diluent electrolyte

824 Commercial grade reactive dyes were used in this work so as to reflect commercial dyeing practice.  
825 Such dyes usually contain quantities of shading components and diluents, the latter often being  
826 electrolyte (eg NaCl), which are included in commercial dye samples by the manufacturer as part of  
827 the dye standardisation process. For example, the amount of standardising constituents in six  
828 commercial grade reactive dyes was found to range from 34% to 65% (11) and 44% to 73% (12),  
829 whilst a commercial sample of C.I. Reactive Black 5 was 55% pure (13). In terms of the three  
830 reactive dyes utilised in this work, the amount of diluent NaCl present in the commercial samples  
831 was: C.I. Reactive Black 5 11.6%, C.I. Reactive Red 198 11.5% and Remazol Yellow R 12.3%, as  
832 revealed using two methods of determination which are discussed in a subsequent part of the  
833 paper.

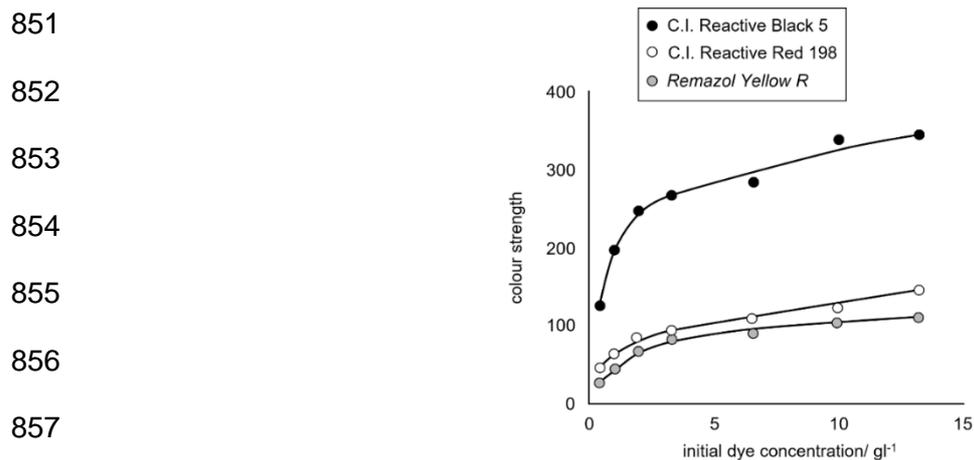
834

835 In this work, whilst a constant amount of each of the three dyes was used in dyeing (ie 2% on mass  
836 of fibre), irrespective of the liquor ratio used, the concentration of each dye in the dyebath at the  
837 start of dyeing of course varied, according to the liquor ratio selected for dyeing. Because the dye  
838 concentration in the dyebath increased by a factor of ~33, based on liquor volume, over the 1:50 to  
839 1:1.5 liquor ratio range used (ie 0.4 g l<sup>-1</sup> @ 1:50; 1 g l<sup>-1</sup> @ 1:20; 2 g l<sup>-1</sup> @ 1:10; 3.3 g l<sup>-1</sup> @ 1:6; 6.6 g l<sup>-1</sup>  
840 @ 1:3; 10 g l<sup>-1</sup> @ 1:2, 13.3 g l<sup>-1</sup> @ 1:1.5) it follows that the concentration of any diluent NaCl in the  
841 dyebath derived from the commercial grade reactive dye can also be expected to increase over the  
842 same range of liquor ratio, based on liquor volume.

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#### 844 3.6.1 dyeing in the absence of added electrolyte

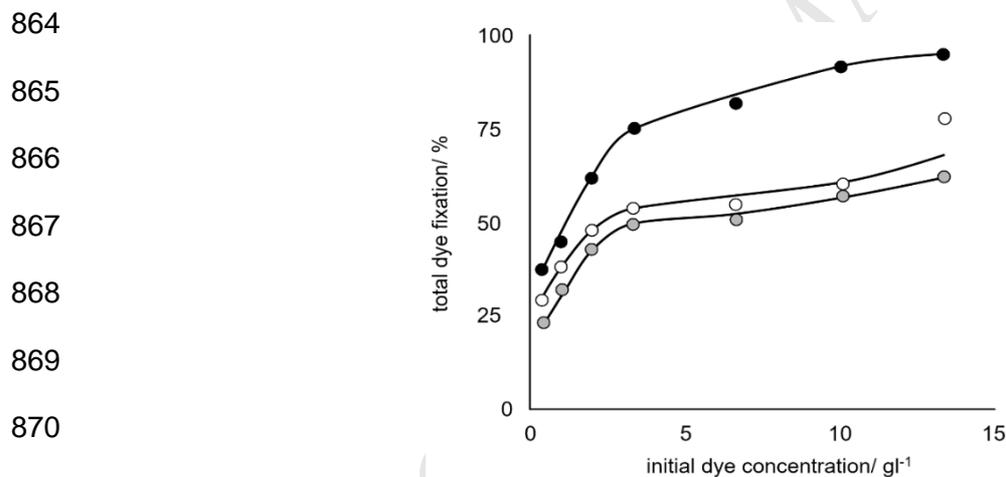
845 Figure 15 shows the colour strength of dyeings achieved at liquor ratios of 1:50 to 1:1.5, as a  
846 function of initial dye concentration in the absence of added NaCl. Although an increase in initial dye  
847 concentration over the range 0.4 to 3.3 g l<sup>-1</sup> (corresponding to liquor ratios of 1:50 to 1:6) resulted in  
848 a sharp increase in colour strength, further increase in initial dye concentration over the range 6.6 to  
849 13.3 g l<sup>-1</sup> (corresponding to liquor ratios of 1:3 to 1:1.5) was accompanied by a more gradual  
850 increase in colour strength.



858 Figure 15 colour strength as a function of initial dye concentration; absence of NaCl

859

860 The results in Figure 15 concur with those displayed in both Figures 6 and 10, which show that in  
 861 the absence of added NaCl, colour yield and total dye fixation, respectively, increased with  
 862 decreasing liquor ratio over the complete range of liquor ratios examined (ie 1:50 to 1:1.5), for each  
 863 of the three dyes studied.



872 Figure 16 total dye fixation as a function of initial dye concentration; absence of NaCl

873 (legend as for Figure 15)

874

875 As mentioned, the observed variation in colour yield as a function of liquor ratio secured for the  
 876 three dyes used in both the presence and absence of  $50 \text{ gl}^{-1}$  added NaCl (Figure 6) reflect the  
 877 observed variation in total dye fixation achieved for the dyeings (Figure 10). It follows therefore, that

878 a plot of %T as a function of initial dye concentration should be similar to that displayed in Figure 15,  
879 as indeed was observed (Figure 16).

880

881 From a comparison of Figures 15 and 16, it is clear that the scales of the vertical axes in the two  
882 graphs differ by a factor of 4; therefore, the three plots in Figure 16 are condensed vertically  
883 compared to those in Figure 17. Nonetheless, Figures 15 and 16 bear strong similarities insofar as,  
884 after an initial, sharp increase in colour strength (Figure 15) or %T (Figure 16) over the initial dye  
885 concentration range 0.4 to 3.3  $\text{gl}^{-1}$  (corresponding to liquor ratios of 1:50 to 1:6), further increase in  
886 initial dye concentration from 6.6 to 13.3  $\text{gl}^{-1}$  (corresponding to liquor ratios of 1:3 to 1:1.5) resulted  
887 in a more gradual increase in either  $f_k$  value (Figure 15) or %T (Figure 16).

888

889 If diluent NaCl present in the commercial dye samples contributed to the promotional effect of  
890 reducing liquor ratio on dye uptake, it follows that when dyeing had been carried out in the absence  
891 of 50  $\text{gl}^{-1}$  added NaCl, both colour strength and total dye fixation should increase with increasing  
892 initial dye concentration, because the amount of diluent electrolyte in the dyebath derived from the  
893 dye, would also increase. Although both %T and colour strength were found to increase as a  
894 function of initial dye concentration (Figures 15 and 16), the curvilinear plots obtained and, in  
895 particular, the marked difference in the rates of increase in colour strength and %T that occurred  
896 prior to and after an initial dye concentration of 3.3  $\text{gl}^{-1}$  (corresponding to a liquor ratio of 1:6),  
897 warrant examination.

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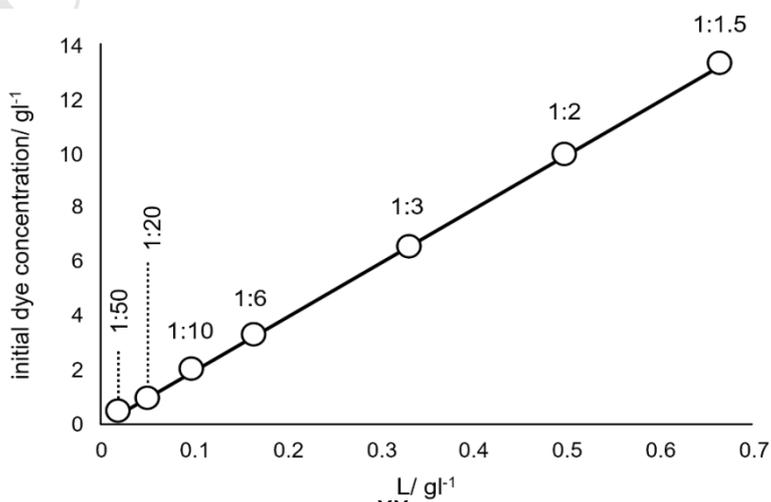
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907 Figure 17 initial dye concentration as a function of fractional liquor ratio (8)

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909 As reported in the case of direct dye uptake on cotton (8), when values of initial dye concentration  
910 are plotted as a function of fractional liquor ratio,  $L$  (given by Eq 9), an essentially linear relationship  
911 is obtained (Figure 17); the various liquor ratios that correspond to the values of  $L$  are displayed in  
912 Figure 17.

913  
914 According to Figure 17, since initial dye concentration increases more or less linearly as a function  
915 of  $L$  then the concentration of diluent NaCl in the dyebath derived from the commercial dye can also  
916 be expected to increase in an identical manner. Thus, if diluent electrolyte present in the dye  
917 contributed to the observed promotion of colour strength (Figure 15) and %T (Figure 16) imparted  
918 by a reduction in liquor ratio, it follows that the magnitude of this contribution should be proportional  
919 to the amount of diluent electrolyte in the dyebath derived from the dye. However, the fact that the  
920 concentration of diluent NaCl derived from the commercial dye is likely to increase linearly as a  
921 function of fractional liquor ratio, as inferred from Figure 17, does not correlate with the curvilinear  
922 relationships observed for the variations in both colour strength (Figure 15) and total dye fixation  
923 (Figure 16) as a function of initial dye concentration.

924  
925 Thus, for dyeings undertaken in the absence of added NaCl, the observed sharp increases in both  
926 colour strength (Figure 15) and %T (Figure 16) that accompanied an increase in initial dye  
927 concentration over the range 0.4 to 3.3  $\text{gl}^{-1}$  and the subsequent more gradual increase in  $f_k$  values  
928 and %T over the initial dye concentration range 6.6 to 13.3  $\text{gl}^{-1}$ , imply that any promotional effect  
929 exerted by diluent electrolyte in the dyebath derived from the dye differed, depending on whether  
930 dyeing had been carried out at high liquor ratios (ie between 1:6 and 1:50) or at low liquor ratios (ie  
931 1:3 to 1:1.5).

932

933 To explain this finding, the idea proposed earlier can be invoked, namely that the extent to which  
934 dye uptake is enhanced by added electrolyte and reduced liquor ratio will be greatest when the  
935 promotional impacts of reduced liquor ratio and added NaCl are maximised (ie when low liquor ratio  
936 dyeings are carried out in the presence of added electrolyte) and will be lowest when the  
937 promotional impacts of reduced liquor ratio and added electrolyte are minimised (ie when high liquor  
938 ratio dyeings are undertaken in the absence of added electrolyte). Accordingly, in the case of the  
939 variation of colour strength as a function of initial dye concentration (Figure 15) [although an  
940 identical argument applies to the variation of total dye fixation as a function of initial dye  
941 concentration depicted in Figure 16], at high liquor ratios (ie between 1:50 and 1:6) and thus low  
942 values of initial dye concentration (ie corresponding to the range between 0.4 and 3.3  $\text{gl}^{-1}$ ), the  
943 observed marked increase in colour strength that accompanied an increase in initial dye  
944 concentration (ie a decrease in liquor ratio) could be attributed to additional enhancement of dye  
945 uptake exerted by increasing diluent electrolyte concentration. In simple terms, the inherently low  
946 substantivity of the dyeing systems that were obtained using high liquor ratios (ie between 1:6 and  
947 1:50) in the absence of added NaCl may have been supplemented by the presence of increasing  
948 concentrations of diluent electrolyte. As such, the presence of diluent electrolyte in the dyebath may  
949 have provided increased dye-fibre substantivity which augmented the intrinsically low dye-fibre  
950 substantivity provided by the use of high liquor ratios in conjunction with zero added NaCl.

951

952 However, when lower liquor ratios of 1:3 to 1:1.5 were employed for dyeing, the far more gradual  
953 increase in colour strength that accompanied an increase in initial dye concentration (ie 6.6 to 13.3  
954  $\text{gl}^{-1}$ ) (Figure 15), suggests that these particular liquor ratios provided higher dye-fibre substantivity  
955 upon which, the presence of increasing concentrations of diluent NaCl may have had comparatively  
956 lower influence. The presence of diluent electrolyte in the dyebath may therefore have imparted  
957 relatively moderate increases to the intrinsically high dye-fibre substantivity dyeing system provided  
958 by the use of low liquor ratios.

959

960 Furthermore, the findings displayed in Figure 15, as well as those presented in Figures 5 to 10,  
 961 suggest that the particular concentration of diluent electrolyte in the dyebath conferred by the  
 962 presence of  $3.3 \text{ gl}^{-1}$  dye (ie corresponding to a 1:6 liquor ratio), may be of significance in terms of  
 963 the combined promotional effects on dye uptake of liquor ratio and added diluent NaCl. The possible  
 964 reasons as to why, at initial dye concentrations  $<3.3 \text{ gl}^{-1}$  (ie from 1:50 to 1:6 liquor ratio) diluent  
 965 electrolyte plays a major role in promoting dye uptake whereas  $>3.3 \text{ gl}^{-1}$  initial dye concentration (ie  
 966 at liquor ratios from 1:6 to 1:1.5), the added diluent present in the dyebath is of much less influence  
 967 than liquor ratio in enhancing dye uptake, are discussed below.

968

### 969 3.6.2 dyeing in the presence of added electrolyte

970 The plot of colour strength as a function of initial dye concentration for dyeings obtained in the  
 971 presence of  $50 \text{ gl}^{-1}$  NaCl (Figure 18) differ in shape to those obtained in the absence of added  
 972 electrolyte (Figure 15) insofar as after an initial sharp increase in colour strength over the initial dye  
 973 concentration of  $0.4$  to  $3.3 \text{ gl}^{-1}$  (corresponding to liquor ratios of 1:50 to 1:6), the  $f_k$  values decrease  
 974 gradually.

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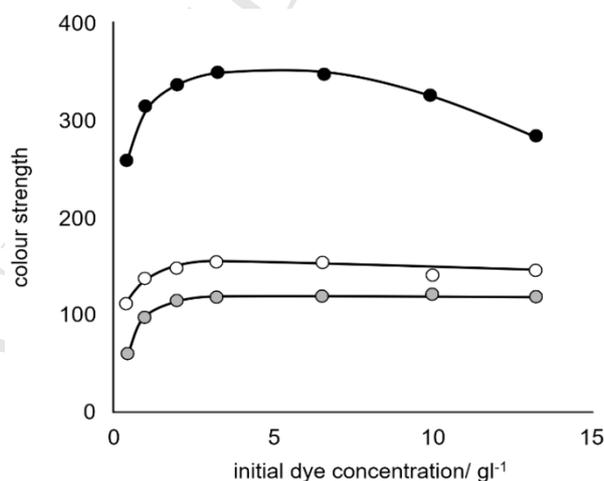
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Figure 18 colour strength as a function of initial dye concentration; presence of  $50 \text{ gl}^{-1}$  NaCl

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(legend as for Figure 15)

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987

The results in Figure 18 concur with those displayed in both Figures 6 and 10, which show that in the presence of  $50 \text{ gl}^{-1}$  added NaCl, both colour yield and total dye fixation, respectively, increased

988 with decreasing liquor ratio over the range 1:50 to 1:6, for each of the three dyes used and then  
 989 decreased with further reduction in liquor ratio to 1:1.5. As the observed variation in colour yield as a  
 990 function of liquor ratio secured for the three dyes used in the presence of added electrolyte (Figure  
 991 6) reflect the observed variation in total dye fixation achieved for the dyeings (Figure 10), then a plot  
 992 of %T as a function of initial dye concentration should be similar to that displayed in Figure 18.

993

994 This was indeed observed (Figure 19) insofar as, despite the three plots in Figure 18 being  
 995 condensed vertically compared with those in Figure 19, because of the different scales used for the  
 996 vertical axes in the two figures, the two graphs bear strong parallels. It is clear that an initial, sharp  
 997 increase in colour strength (Figure 18) or %T (Figure 19) over the initial dye concentration range of  
 998 0.4 to 3.3  $\text{gl}^{-1}$  (corresponding to liquor ratios of 1:50 to 1:6) was followed by a gradual decrease in  
 999 either  $f_k$  value (Figure 18) or %T (Figure 19) with further increase in initial dye concentration from  
 1000 6.6 to 13.3  $\text{gl}^{-1}$  (corresponding to liquor ratios of 1:3 to 1:1.5).

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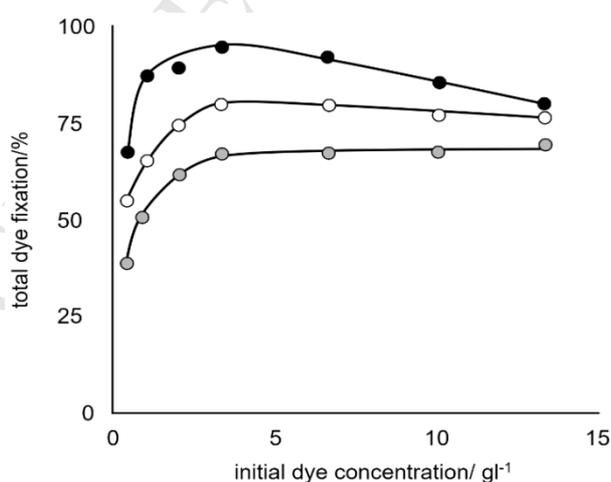


Figure 19 total dye fixation as a function of initial dye concentration; presence of 50  $\text{gl}^{-1}$  NaCl

(legend as for Figure 15)

1015 In view of the above discussions concerning the possible effects of diluent NaCl on values of  $f_k$   
1016 (Figure 15) and %T (Figure 16) obtained in the absence of added NaCl, the sharp increases  
1017 observed for both colour strength and total dye fixation over the initial dye concentration range 0.4  
1018 to  $3.3 \text{ gl}^{-1}$  observed when dyeing had been undertaken in the presence of added electrolyte (Figures  
1019 18 and 19) may be due to the diluent electrolyte present in the dye having contributed towards  
1020 increased dye uptake, because the concentration of diluent NaCl in the dyebath derived from the  
1021 dye also increased upto a particular level conferred by the presence of  $3.3 \text{ gl}^{-1}$  dye (ie at a liquor  
1022 ratio of 1:6). Hence, the sharp increase in  $f_k$  values that accompanied an increase in initial dye  
1023 concentration the range 0.4 to  $3.3 \text{ gl}^{-1}$ , which corresponded to liquor ratios of between 1:50 and 1:6,  
1024 could be attributed to the promotional effect imparted by the increasing diluent electrolyte  
1025 concentration being of greater magnitude than that provided by reduction in liquor ratio. Thus, it  
1026 appears that even in the presence of a constant concentration of added NaCl (ie  $50 \text{ gl}^{-1}$ ), the levels  
1027 of dye-fibre substantivity that prevailed at high liquor ratios (ie between 1:6 and 1:50), may have  
1028 been sufficiently low enough to be enhanced by the presence of diluent electrolyte derived from the  
1029 commercial dye. As such, the presence of diluent electrolyte in the dyebath may thus have provided  
1030 increased dye-fibre substantivity which boosted the intrinsically low dye-fibre substantivity provided  
1031 by the use of high liquor ratios, even in the presence of added NaCl.

1032

1033 However, the ensuing gradual decrease in both colour strength (Figure 18) and %T (Figure 19) that  
1034 was secured for lower liquor ratios, namely 1:3 to 1:1.5, which corresponded to increasing initial dye  
1035 concentrations of  $6.6$  to  $13.3 \text{ gl}^{-1}$  and thus the presence of increasing concentrations of diluent NaCl  
1036 derived from the dye reduce dye uptake, imply that in the presence of added NaCl, the levels of  
1037 dye-fibre substantivity secured at low liquor ratios (ie between 1:3 and 1:1.5) were already very high  
1038 and, in effect, may have been intensified by the presence of (additional) diluent electrolyte, resulting  
1039 in excessive dye aggregation and marked reduced dye solubility that instigated a reduction in dye  
1040 uptake and total dye fixation. As it is assumed that the addition of electrolyte and reduction of liquor  
1041 ratio impart the same promotional effect on reactive dye uptake, since both reducing the liquor ratio  
1042 employed for dyeing and adding electrolyte to the dyebath produce the same outcome, namely the

1043 promotion of dye aggregation in the dyebath, as a result of which, the solubility of the direct dye in  
1044 the dyebath is reduced, then the extent to which diluent electrolyte in the dyebath may have  
1045 enhanced the intrinsically very high dye-fibre substantivity imparted by the use of low liquor ratios in  
1046 conjunction with  $50 \text{ gl}^{-1}$  added NaCl was such that dye uptake reduced, owing to excessive dye  
1047 aggregation and reduced dye solubility.

1048

1049 A comparison of the plots shown in Figures 15, 16, 18 and 19 reveals that similar behaviour was  
1050 obtained in both the absence and presence of added NaCl, insofar as colour strength and total dye  
1051 fixation increased with increasing initial dye concentration over the range  $0.4$  to  $3.3 \text{ gl}^{-1}$  (liquor ratios  
1052  $1:50$  to  $1:1.6$ ) at a rate that was similar for each of the respective pairs of dyes. Furthermore, the  
1053 rate of change in colour strength achieved upto  $3.3 \text{ gl}^{-1}$  initial dye concentration was greater than  
1054 that observed at initial dye concentrations  $>3.3 \text{ gl}^{-1}$  (ie over the range  $6.6$  to  $13.3 \text{ gl}^{-1}$ , corresponding  
1055 to liquor ratios of  $1:3$  to  $1:1.5$ ).

1056

1057 From these findings, it seems reasonable to suggest that irrespective of whether dyeing had been  
1058 carried out in the absence or presence of added electrolyte, diluent NaCl present in the commercial  
1059 dyes used in this work may have exerted a promotional effect on dye uptake, although the  
1060 magnitude of this enhanced dye uptake decreased with decreasing liquor ratio.

1061

1062 In order to clarify the possible influence that diluent electrolyte exerted upon dye uptake, it was  
1063 decided to undertake a study of the exhaust application of pure reactive dyes which do not contain  
1064 diluent, using different liquor ratios and in both the absence and presence of added electrolyte. The  
1065 results of this study are presented in the next part of this paper.

1066

### 1067 *3.7 fastness*

1068 The remarkable commercial success of reactive dyes on cellulosic fibres can be attributed to their  
1069 outstanding wet fastness properties that arise because of the covalent linkage of the dye molecules  
1070 to the cellulosic polymer, as well as the relative simplicity of their application by immersion dyeing

1071 methods (7). However, because dye-fibre fixation is always accompanied by undesirable, alkali-  
1072 induced hydrolysis of the reactive dye. As the presence of unreacted dye and/or hydrolysed dye in  
1073 the dyed material at the end of dyeing will reduce the wet fastness properties of the dyeing, it is  
1074 necessary to subject the dyed material to a stringent wash-off process to remove both hydrolysed  
1075 dye and unreacted dye. Wash-off also reduces the very high levels of residual added electrolyte and  
1076 other dyebath auxiliaries that are adsorbed onto/deposited within the substrate during dyeing (6).

1077

1078 Theoretically, there should be no difference between dyeing cotton with reactive dyes in the  
1079 absence and presence of added electrolyte in terms of the quality (fastness, colour, etc.) of the  
1080 dyeings obtained, since, in an immersion dyeing process carried out in the absence of added  
1081 electrolyte, so long as an acceptable depth of shade (ie colour yield) is obtained by securing an  
1082 adequate level of dye exhaustion and an appropriate level of dye fixation by means of alkali  
1083 addition, then the ensuing dyeing will be no different to one of the same depth of shade and extent  
1084 of fixation produced in the presence of added electrolyte.

1085

1086 This was indeed found to be the case for the 2% omf dyeings obtained in this work. As Figure 20  
1087 shows, there was no difference in the fastness to washing of corresponding dyeings carried out in  
1088 the presence and absence of 50  $\text{gl}^{-1}$  added NaCl. Thus, dyeing cotton with reactive dyes in the  
1089 absence of added electrolyte has no effect on the characteristic excellent wash fastness.

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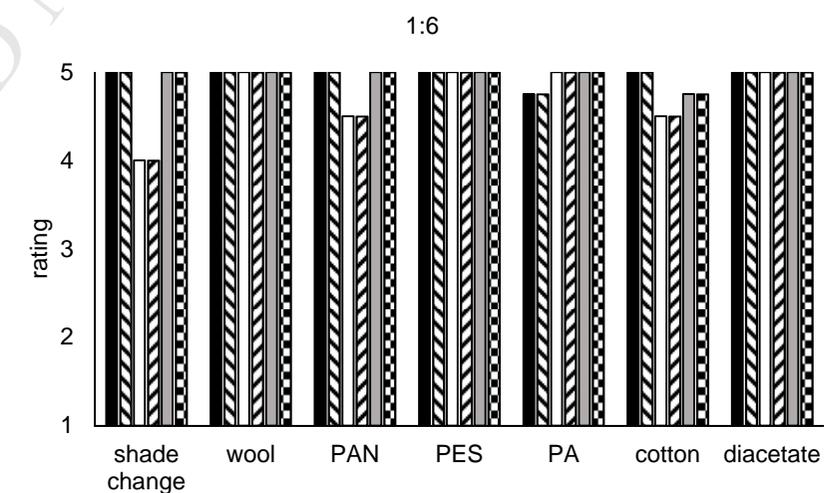
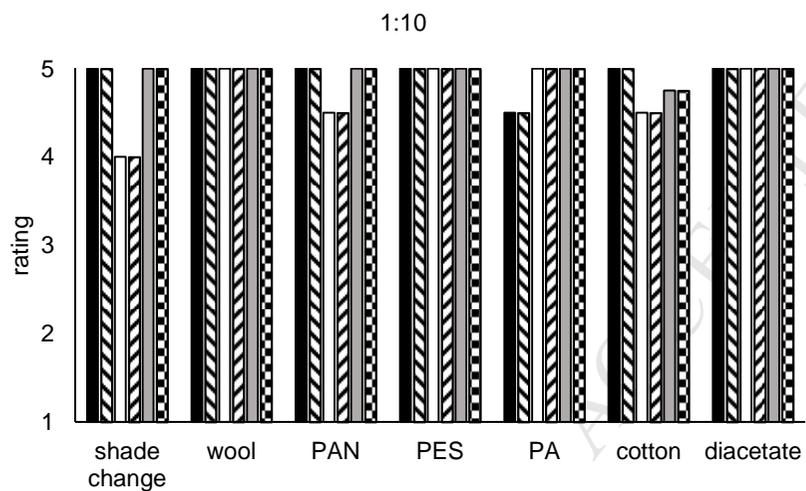
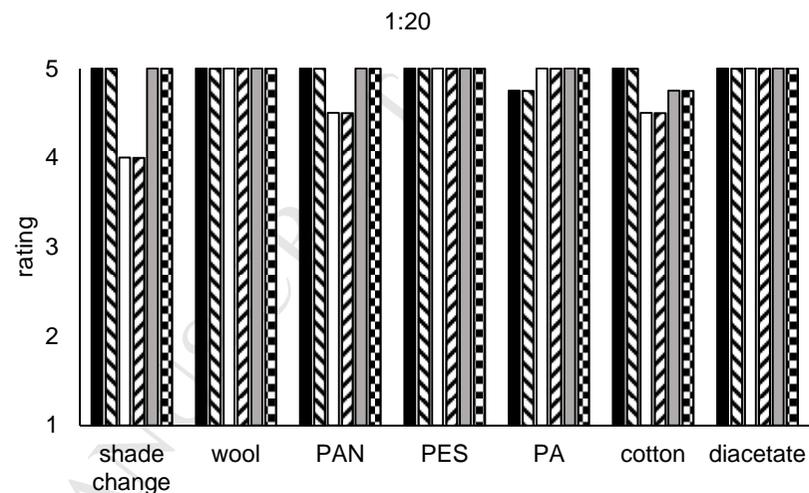
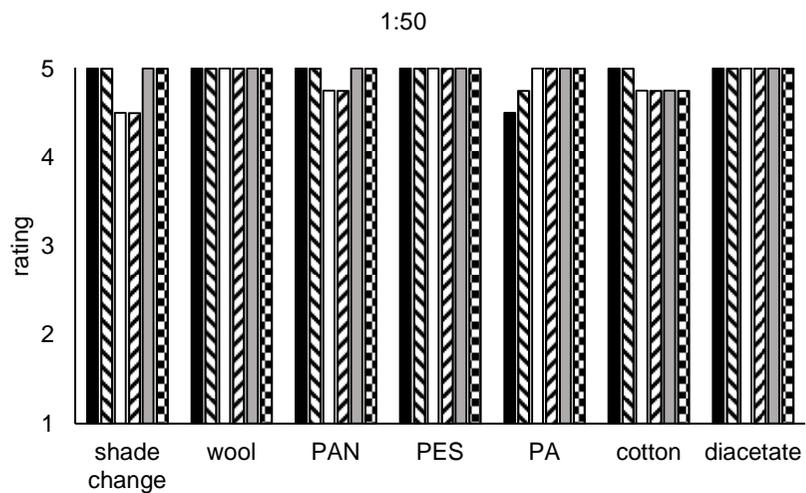
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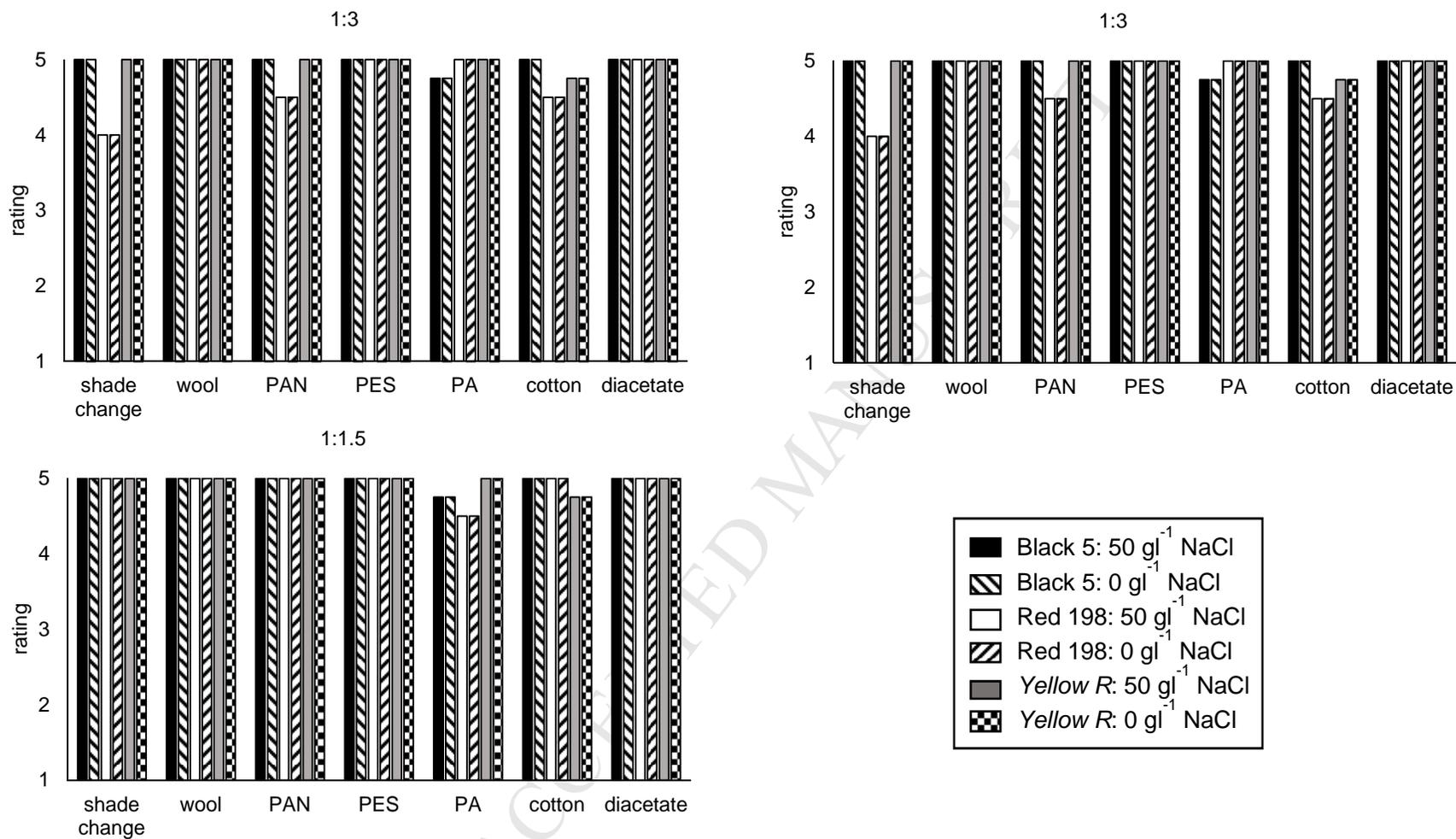


Figure 20 fastness of dyeings to ISO 105:C06/C2S (60°C)

1116 Further studies will compare the fastness of dyeings on cotton, which have been undertaken with  
1117 reactive dyes in the absence of added electrolyte, to a variety of agencies (water, light, perspiration,  
1118 etc.).

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#### 1120 **4 conclusions**

1121 The addition of inorganic electrolyte and reduction of liquor ratio impart the same promoting effect  
1122 on the uptake of commercial grade reactive dyes on cotton. Thus, the two, ostensibly different  
1123 actions of adding electrolyte such as NaCl or Na<sub>2</sub>SO<sub>4</sub> to a reactive dye dyebath and reducing the  
1124 liquor ratio used for immersion dyeing have the same result, namely that of encouraging dye  
1125 aggregation in the dyebath, which reduces the solubility of the direct dye in the dyebath, which, in  
1126 turn, results in the inherent preference of the dye to favour the aqueous phase shifting towards the  
1127 fibre phase.

1128

1129 These findings concur with the theoretical model (3, 4) that was proposed to explain the roles of  
1130 both added NaCl or Na<sub>2</sub>SO<sub>4</sub> and reduced liquor ratio in the application of direct dyes to cotton,  
1131 which invoked the concept of interstitial water within the fibrous substrate. Irrespective of whether  
1132 dyeing was undertaken in the absence or presence of added electrolyte, diluent electrolyte present  
1133 in the commercial grade dyes may have exerted a promotional effect on dye uptake, although the  
1134 magnitude of this enhanced dye uptake decreased with decreasing liquor ratio.

1135

1136 The findings revealed that the theoretical models are able to explain why it is possible to dye cotton  
1137 to realistic depths of shade using reactive dyes in the complete absence of added inorganic  
1138 electrolyte. Dyeing cotton with reactive dyes in the absence of added electrolyte has no effect on the  
1139 characteristic excellent wash fastness displayed by this class of dye.

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