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**Article:**

Burkinshaw, SM [orcid.org/0000-0001-9940-1354](http://orcid.org/0000-0001-9940-1354) and Salihu, G (2019) The role of auxiliaries in the immersion dyeing of textile fibres: Part 9 practical aspects of the role of inorganic electrolytes in dyeing cellulosic fibres with pure reactive dyes. *Dyes and Pigments*, 161. pp. 628-641. ISSN 0143-7208

<https://doi.org/10.1016/j.dyepig.2017.10.014>

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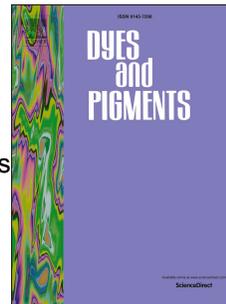


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# Accepted Manuscript

The role of auxiliaries in the immersion dyeing of textile fibres: Part 9 practical aspects of the role of inorganic electrolytes in dyeing cellulosic fibres with pure reactive dyes

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PII: S0143-7208(17)31800-4

DOI: [10.1016/j.dyepig.2017.10.014](https://doi.org/10.1016/j.dyepig.2017.10.014)

Reference: DYPI 6312

To appear in: *Dyes and Pigments*

Received Date: 23 August 2017

Revised Date: 10 October 2017

Accepted Date: 10 October 2017

Please cite this article as: Burkinshaw SM, Salihu G, The role of auxiliaries in the immersion dyeing of textile fibres: Part 9 practical aspects of the role of inorganic electrolytes in dyeing cellulosic fibres with pure reactive dyes, *Dyes and Pigments* (2017), doi: 10.1016/j.dyepig.2017.10.014.

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1 **The role of auxiliaries in the immersion dyeing of textile fibres: Part 9**  
2 **practical aspects of the role of inorganic electrolytes in dyeing cellulosic**  
3 **fibres with pure reactive dyes**

4  
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9  
10 **Abstract**

11 The colour strength, as well as the extents of both exhaustion and fixation, achieved for three pure  
12 reactive dyes on cotton were promoted by the addition of 50 g l<sup>-1</sup> NaCl at each of seven liquor ratios  
13 employed (1:50, 1:20, 1:10, 1:6, 1:3, 1:2 and 1:1.5). The depth of shade of dyeings obtained in the  
14 absence of added electrolyte using a 1:1.5 liquor ratio were of similar magnitude to those secured  
15 using 1:10 – 1:20 liquor ratios in the presence of 50 g l<sup>-1</sup> NaCl. The promotional effect on dye uptake  
16 imparted by both added electrolyte and reduced liquor ratio was interpreted in terms of their effects  
17 on the substantivity of the reactive dyes towards the cotton substrate. The two, seemingly different  
18 actions of adding electrolyte such as NaCl or Na<sub>2</sub>SO<sub>4</sub> to the reactive dye dyebath and reducing the  
19 liquor ratio used for immersion dyeing have the same result, namely that of encouraging dye  
20 aggregation in the dyebath, which reduces the solubility of the direct dye in the dyebath, which, in  
21 turn, shifts the inherent preference of the dye to favour the aqueous phase towards the fibre phase.  
22 It is thus possible to dye cotton using pure reactive dyes in the complete (ie 100%) absence of  
23 added inorganic electrolyte. The ensuing dyeings were of realistic depths of shade and displayed  
24 excellent levels of wash fastness.

25  
26 **Highlights**

- 27
- the role of electrolyte in dyeing with pure reactive dyes is investigated

- 28 • added electrolyte reduces dye solubility and increases dye aggregation
- 29 • use of low liquor ratio enables dyeing in the absence of added electrolyte

30

31 **keywords:** dyeing cotton; dyeing auxiliaries; electrolyte; pure reactive dyes; salt-free dyeing

32

### 33 **1 introduction**

34 This paper concerns the mechanism by which some of the auxiliary chemicals that are utilised in the  
35 immersion application of dyes to textile fibres impart their particular effects on dyeing. Various types  
36 of dyeing auxiliary are available that differ in terms of the assistance they provide to exhaust dyeing  
37 processes (1). In recognition of the global significance of cotton and other cellulosic fibres, the focus  
38 of the paper thus far, has been to elucidate the mechanism by which inorganic electrolyte, in the  
39 form of either NaCl or Na<sub>2</sub>SO<sub>4</sub>, promotes the uptake of both direct dyes (2-5) and reactive dyes (6-8)  
40 on cellulosic fibres. Theoretical models were proposed to explain the role of such inorganic  
41 electrolyte in the immersion application of direct dyes (3) and reactive dyes (7), according to which,  
42 the addition of inorganic electrolyte to a direct dye or reactive dye dyebath promotes dye uptake  
43 owing to the combined effects of induced dye aggregation and reduced dye solubility on the  
44 effective concentration of dye in the dyebath. This particular theoretical approach, which invoked the  
45 concept of interstitial water, was also used to explain the promotional effect of reducing the liquor  
46 ratio used for dyeing on the uptake of both direct dyes (4) and reactive dyes (7) on cellulosic fibres.  
47 The theoretical models were used to interpret the results obtained in a series of dyeings of cotton  
48 using commercial grade direct dyes (5) and commercial grade reactive dyes (8). The theoretical  
49 models were able to explain why it was possible to dye cotton in realistic depths of shade using both  
50 direct dyes (5) and reactive dyes (8) in the absence of added inorganic electrolyte using low liquor  
51 ratios. It was therefore concluded (5, 8) that the two, ostensibly different actions, of adding  
52 electrolyte such as NaCl or Na<sub>2</sub>SO<sub>4</sub> to either a direct dye dyebath or reactive dye dyebath and  
53 reducing the liquor ratio used for immersion dyeing have the same result, namely dye aggregation in  
54 the dyebath is promoted, which reduces the solubility of both the direct and reactive dyes in the  
55 dyebath, which, in turn, favours increased dye uptake.

56

57 In this latter two practical studies involving direct dyes (5) and reactive dyes (8) it was observed that  
58 diluent electrolyte present in the commercial dye samples used may have exerted a promotional  
59 effect on dye uptake, although the magnitude of this enhanced dye uptake decreased with  
60 decreasing liquor ratio. In order to resolve the possible influence that diluent NaCl has upon reactive  
61 dye uptake, it was decided to undertake a study of the exhaust application of pure reactive dyes  
62 which do not contain diluent, employing different liquor ratios and in both the absence and presence  
63 of added electrolyte.

64

### 65 1.1 reactive dyes

66 A brief introduction to the chemistry and application of reactive dyes that are utilised for dyeing  
67 cellulosic fibres has been presented (7). Reactive dyes derive their name from the fact that they  
68 comprise a reactive system, containing one or more electrophilic groups, which enable the dyes to  
69 form a covalent bond with nucleophilic hydroxyl groups in the cellulosic substrate. Because the  
70 chromogen is covalently bound to the substrate at the end of the immersion dyeing process, the  
71 ensuing dyeings characteristically display excellent fastness to wet treatments (eg washing,  
72 perspiration, etc.). The dyes are applied to cellulosic fibres under aqueous alkaline (eg NaOH,  
73 Na<sub>2</sub>CO<sub>3</sub>) conditions to deprotonate the cellulosic hydroxyl groups (Cell-OH) and generate the far  
74 more strongly nucleophilic, ionised hydroxyl groups (Cell-O<sup>-</sup>; aka *cellulosate anions*) within the  
75 substrate. However, the aqueous alkaline application conditions not only result in dye fixation (ie  
76 covalent bond formation with the substrate) but also unwanted, alkali-induced hydrolysis of the  
77 reactive dye, which confers inherently low levels of dye-fibre fixation efficiency upon all types of  
78 commercial grade reactive dyes.

79

80 The addition of inorganic electrolyte (either NaCl or Na<sub>2</sub>SO<sub>4</sub>) to a reactive dye dyebath is necessary  
81 in order to increase the inherently low substantivity displayed by the dye anions towards the  
82 substrate and, thereby, promote dye uptake; added inorganic electrolyte also promotes the extent of  
83 covalent fixation of reactive dye to the cellulosic substrate. The amount of electrolyte used in

84 reactive exhaust dyeing varies, typically, between 30 and 100  $\text{gl}^{-1}$  of NaCl or  $\text{Na}_2\text{SO}_4$ ; as such,  
85 outrageously high levels of inorganic electrolyte are habitually used in the immersion application of  
86 reactive dyes to cellulosic fibres. Such usage poses severe environmental and economic difficulties,  
87 not simply because of because of the large amounts of electrolyte that utilised in dyeing but also,  
88 the significant environmental hazards associated with the pronounced salinity of reactive dyeing  
89 wastewater (1, 6).

90

91 In the context of the mechanism of adsorption of reactive dyes on cellulosic fibres, as reactive dyes  
92 bear a close structural resemblance to direct dyes (6), it is assumed that in the absence of dye-fibre  
93 reaction (ie prior to the dye forming a covalent reaction with the cellulosic fibre), the adsorption of  
94 reactive dyes occurs in a manner analogous to that of direct dyes (9). Furthermore, the mechanism  
95 by which added inorganic electrolyte promotes reactive dye uptake prior to dye-fibre fixation is also  
96 assumed to be analogous to that described for direct dye uptake (9).

97

### 98 *1.2 diluent in reactive dyes*

99 Commercial grade samples of all most types of dye often contain quantities of shading components  
100 and diluents, the latter frequently being electrolyte such as NaCl, which are used by the dye maker  
101 as part of the dye standardisation process. This is illustrated by the finding that the amount of  
102 standardising constituents in various commercial grade reactive dyes ranged from 34% to 73% (10-  
103 12). In the case of the three commercial grade reactive dyes employed in the previous part of the  
104 paper (8), the amount of diluent NaCl present in the commercial samples ranged from 11.5% to  
105 12.3%. In this particular study (8), it was found that whilst it is possible to apply commercial grade  
106 reactive dyes to cotton using very low liquor ratios (ie 1:1.5 and 1:1) in the absence of added NaCl,  
107 diluent electrolyte that may have been present in the commercial dye samples may have exerted a  
108 promotional effect on dye uptake, although the magnitude of this enhanced dye uptake decreased  
109 with decreasing liquor ratio used for dyeing.

110

111 As the evidence for such diluent-induced enhancement of dye uptake was not entirely convincing  
 112 (8), it was decided to investigate the exhaust application of diluent-free reactive dyes to cotton using  
 113 different liquor ratios, in both the absence and presence of added electrolyte, so as to determine  
 114 both the possible contribution that diluent electrolyte may exert towards dye promotion whether and,  
 115 also, whether it is possible to dye cotton using reactive dyes in the complete (ie 100%) absence of  
 116 inorganic electrolyte.

117

118 In the latter context, in the absence of public domain reports relating to the application of diluent-free  
 119 reactive dyes to cellulosic fibres, a discussion can be proffered on the application of diluent-free  
 120 direct dyes to such substrates. The findings reported in these particular studies can be considered  
 121 to be of direct relevance to reactive dyes, since, as mentioned, it is assumed that prior to the dye  
 122 forming a covalent reaction with the cellulosic fibre, the nature of adsorption process for reactive  
 123 dyes is analogous to that of direct dyes.

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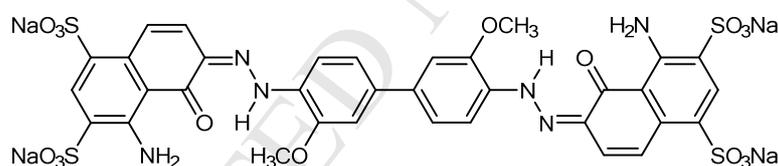
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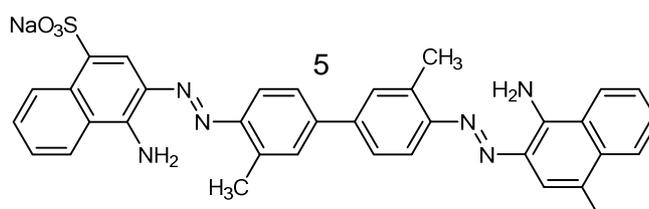
130 It has been observed that diluent-free (ie pure) C.I. Direct Blue 1 was not adsorbed onto cellulosic  
 131 substrates when dyeing had been carried out in the absence of added inorganic electrolyte (13-15).  
 132 These observations were attributed (16-18) to sorption of the dye anions having been prevented  
 133 because of repulsion effects operating between the high negative potential developed at the  
 134 cellulosic fibre surface and the dye anions; it was further proposed (18, 19) that pure (ie diluent-free)  
 135 direct dyes display zero or negligible substantivity towards cellulose because of such repulsive  
 136 interactions.

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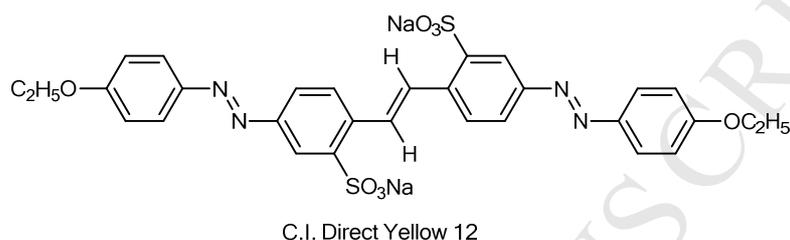
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C.I. Direct Blue 1



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However, as dye uptake was observed in the absence of added electrolyte in the case of the diluent-free dibasic dyes C.I. Direct Red 2 (13, 20) and C.I. Direct Yellow 12 (21), it was concluded that if repulsion interactions were responsible for the observed lack of dye uptake in the absence of added electrolyte then dye basicity should be important (15, 20) insofar the effect should be greatest for dye anions of high basicity and low substantivity (ie as is the case for the tetrasulfonated C.I. Direct Blue 1) but dye uptake should still occur in the absence of added electrolyte for dyes of low charge and high substantivity (ie as observed for the dibasic C.I. Direct Red 2 and C.I. Direct Yellow 12).

Alternatively, it was suggested (9) that the extent of diluent-free direct dye uptake achieved in the absence of added inorganic electrolyte should be related to the aqueous solubility of the dyes and their aggregation behaviour in solution, in that highly soluble direct dyes such as the tetrasulfonated C.I. Direct Blue 1 will display a low tendency to aggregate in solution and, therefore, should exhibit lower uptake than dyes of lower solubility, such as the dibasic C.I. Direct Red 2 and C.I. Direct Yellow 12.

167 It therefore appears that whilst some diluent-free direct dyes may exhibit little if any substantivity  
 168 towards cellulosic fibres when applied in the absence of added electrolyte, other diluent-free dyes  
 169 may display significant levels of uptake. This situation may apply to reactive dyes, bearing in mind  
 170 that the adsorption of reactive dyes on cellulosic fibre prior to covalent reaction with the substrate is  
 171 assumed to occur in a manner analogous to that of direct dyes.

172

### 173 1.3 proposed theory of the role of added electrolyte in the dyeing of cellulosic fibres using reactive 174 dyes

175 As recounted above, the mechanism by which reactive dyes are adsorbed on cellulosic fibres in the  
 176 presence of added inorganic electrolyte prior to the covalent reaction with the substrate, can be  
 177 described using a theoretical model (7) that invokes the concept of interstitial water (22-26) and  
 178 assumes that the aqueous dyebath comprises both interstitial water located within the swollen  
 179 fibrous substrate as well as bulk dyebath water that surrounds the swollen fibre.

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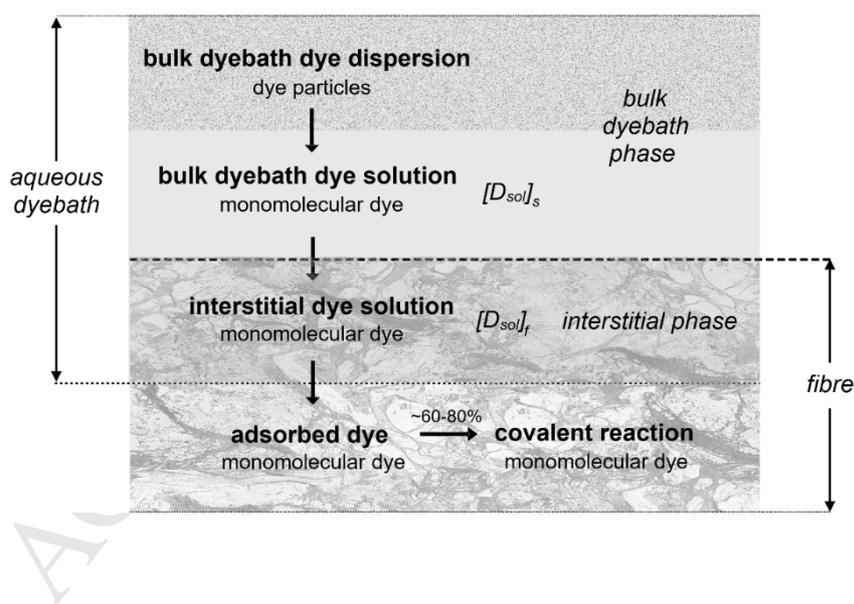
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191

192 This approach, which is depicted in Scheme 1 (7), assumes that a very small proportion of the water  
 193 that is used in immersion dyeing processes resides within the interstices of the fibrous substrate.  
 194 Interstitial water is considered to constitute that which is required to impart fibre wetting and



Scheme 1 representation of reactive dyeing mechanism (7)

195 swelling; as such, the volume of interstitial water is assumed to correspond to the moisture regain of  
196 the substrate at 100% relative humidity ( $RH$ ) (3, 4) ( $\sim 0.22 \text{ l kg}^{-1}$  in the case of cotton). It is  
197 presumed that because of the presence of different types of sorbed water molecules in porous  
198 materials such as textile fibres and based on current views of electric double-layer theory, the  
199 properties of interstitial water will differ to that of the water that is located within the surrounding bulk  
200 aqueous dyebath in terms of the distribution of sorbed ions/molecules (3, 7). The remaining, much  
201 greater proportion of the water that is utilised in immersion dyeing resides within the bulk dyebath  
202 that surrounds the water-swollen fibre and provides functions such as heating, dye dissolution, etc.  
203 (3, 7).

204

205 Owing to the proclivity of reactive dye molecules to self-associate in solution, which is promoted by  
206 the presence of added inorganic electrolyte and low liquor ratio, a proportion of the dye will likely be  
207 present in the form of particles that comprise a bulk dyebath dye dispersion within the bulk dyebath  
208 phase (scheme 1). Dissolved dye molecules/ions will also be present that make up a bulk dyebath  
209 dye solution; dissolved dye molecules will also populate the interstitial dye solution within the  
210 interstitial phase in the fibre. Dissolved dye molecules are therefore considered to be present within  
211 both an interstitial dye solution that resides in the fibre phase and also, within a bulk dye solution  
212 that is present in the dyebath phase. Dyeing proceeds by means of the transfer of dye molecules  
213 from the bulk dye solution in the dyebath phase to the interstitial dye solution within the fibre phase  
214 and thence adsorption on the solid fibre (scheme 1). As the adsorption of reactive dye molecules  
215 from the interstitial dye solution can result in covalent bond formation with ionised hydroxyl groups in  
216 the substrate, Scheme 1 includes this important stage of the immersion dyeing process.

217

218 In terms of the notion that dye adsorption proceeds from interstitial dye solution present within the  
219 substrate, the primary contributor to reactive dye-cellulosic fibre substantivity was presumed (7) to  
220 be the solubility of the dye in the aqueous dyebath, as proposed in the case of direct dyes (2).  
221 Indeed, the characteristic low substantivity displayed by reactive dyes towards cellulosic fibres in the  
222 absence of added  $\text{NaCl}$  or  $\text{Na}_2\text{SO}_4$  can be attributed to the dye's high aqueous solubility. In this

223 context, the promotion of reactive dye uptake on cellulosic fibres imparted by added inorganic  
224 electrolyte was attributed to an increase in dye-fibre substantivity that resulted from a corresponding  
225 reduction in the aqueous solubility of the dye (7); this occurs because adding inorganic electrolyte to  
226 a reactive dye dyebath encourages dye aggregation which reduces dye solubility. Consequently, the  
227 concentration gradient between the amount of dye in the dyebath and the amount of dye in the fibre  
228 is increased, so that the distribution of the dye between the dyebath and the fibre favours the latter.  
229 Thus, the amount of dye adsorbed onto the fibre is determined by the effect of the added inorganic  
230 electrolyte on the concentration of dye in the dyebath.

231

232 This mechanism was also invoked (7) to describe the promotional effect of reducing the liquor ratio  
233 used for dyeing on the uptake of reactive dyes on cellulosic fibres in both the presence and absence  
234 of added electrolyte.

235

236 As mentioned, this part of the paper concerns the exhaust application of diluent-free reactive dyes  
237 to cotton using different liquor ratios in both the absence and presence of added electrolyte. The  
238 results of these dyeings are interpreted in terms of the theoretical model of the mechanism (7) by  
239 which both inorganic electrolytes and reduced liquor ratio promote the uptake of direct dyes on  
240 cellulosic fibres. These findings are then used to explain why it is possible to dye cotton to realistic  
241 depths of shade using diluent-free (ie pure) reactive dyes in the complete (ie 100%) absence of  
242 added inorganic electrolyte.

243

## 244 **2. experimental**

### 245 **2.1 Materials**

246 Scoured, bleached and mercerised woven cotton fabric (180 gm<sup>-2</sup>) was obtained from Whaleys  
247 (Bradford, UK). Samples of three diluent-free reactive dyes, namely *Novacron Blue FNR*, *Novacron*  
248 *Red FN2BL* and *Novacron Yellow FN-2R* (no Colour Index Generic Names available) were  
249 generously supplied by Huntsman. All other chemicals were of general purpose grade except for a  
250 commercial sample of the wash-off auxiliary *Cyclanon XCW* which was kindly supplied by BASF.

251

252 The three dyes used were chosen arbitrarily as being representative of modern reactive dyes. A 2%  
 253 omf depth of shade was used for each of the three dyes as this provided typical pale/medium depth  
 254 dyeings.

255

256 As discussed above, commercial grade reactive dyes normally contain various amounts of diluent,  
 257 such as NaCl, which are added to the dye sample as part of the standardisation process. Thus,  
 258 unlike the pure (diluent-free) grade dye samples utilised in this study, commercial grade samples of  
 259 reactive dyes will commonly contain less than 100% pure (aka active) dye. The tinctorial strength of  
 260 a commercial grade sample of a given reactive dye will therefore be lower than that of a pure  
 261 sample of the same dye. Consequently, the depth of shade of the 2% omf dyeings that were  
 262 obtained in this study (as expressed by colour strength), can be expected to be greater than that  
 263 obtained by applying 2% omf of a commercial grade sample of the same dyes. As discussed in  
 264 section 3.7, this has implications in terms of the wash fastness of the ensuing dyeings, since it is  
 265 generally accepted that the level of wash fastness displayed by dyed materials generally decreases  
 266 with increasing depth of shade.

## 267 2.2 Dyeing

268 2% omf dyeings were carried out using various liquor ratios in both the presence and absence of 50  
 269  $\text{gl}^{-1}$  NaCl. The amount of added electrolyte in dyeing was adjusted to ensure that a concentration of  
 270  $50 \text{ gl}^{-1}$  was employed, regardless of liquor ratio employed; two dyeing methods were used, which  
 271 are described below.

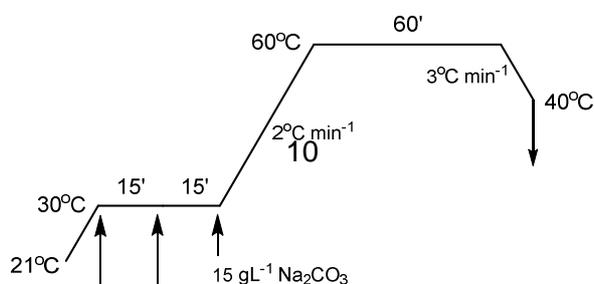
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### 273 2.2.1 dyeing tubes/dyeing machine

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

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Figure 1 dyeing tubes/dyeing machine method

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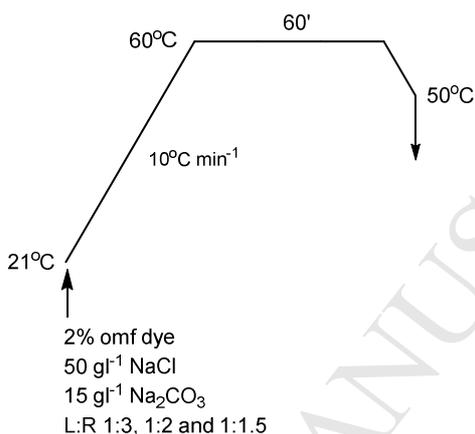
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291

Figure 2 PP bags/tumble dryer method

292

### 293 2.2.2 PP bags/tumble dryer

294 Dyeings were undertaken, employing liquor ratios of 1:3, 1:2 and 1:1.5, in sealed, 1000 cm<sup>3</sup>  
 295 capacity, polypropylene plastic bags housed in a *Miele PT8257* tumble dryer, following the  
 296 procedure shown in Figure 2.

297

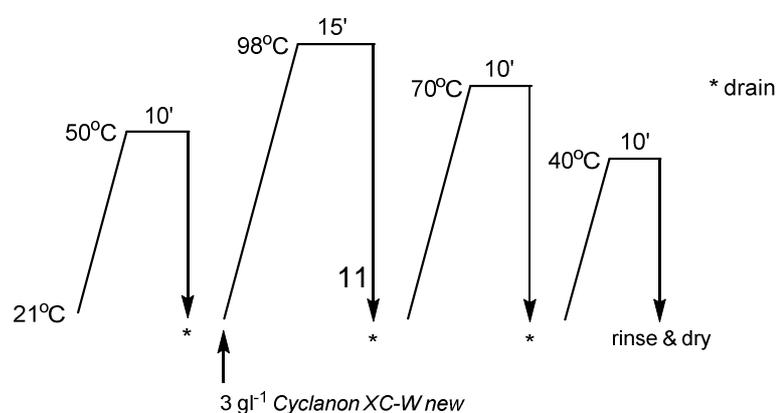
### 298 2.2.3 wash-off

299 At the end of dyeing, the sample was removed from the dyebath, squeezed to remove surplus dye  
 300 liquor and then subjected to the wash-off procedure shown in Figure 3, using a 10:1 L:R for each  
 301 stage; the washed-off dyeing was allowed to dry in the open air.

302

303

304



305

306

307

Figure 3 wash-off method

### 308 2.3 Colour measurement

309 The CIE colorimetric co-ordinates and colour strength ( $f_k$  values) of the dyeings were determined for  
310 each dyeing from measurements made using a *Datacolour Spectroflash 60* reflectance  
311 spectrophotometer from 400 nm to 700 nm using  $D_{65}$  illuminant,  $10^\circ$  standard observer with UV  
312 component included and specular component excluded. Samples were folded so as to realise two  
313 thicknesses and the average of four measurements was taken for each sample.

314

### 315 2.4 Measurement of dye exhaustion

316 The absorbance at  $\lambda_{\max}$  of a suitably diluted (distilled water) sample of dye liquor taken both before  
317 and after dyeing was determined using a 1 cm path quartz cell housed in a Perkin-Elmer *Lambda 9*  
318 UV/Visible/NIR spectrophotometer in the region 400–700 nm. The percentage dyebath exhaustion,  
319 %E, was calculated using Eq 1 where  $A_0$  and  $A_1$  represent the absorbance of the dye solution  
320 before and after dyeing, respectively.

321

$$322 \quad \%E = 100 \times \left(1 - \frac{A_1}{A_0}\right) \quad 1$$

323

### 324 2.5 Determination of dye fixation

325 Unfixed dye was removed using the wash-off process shown in Figure 3 and the extent of fixation  
326 (%F) was calculated using Eq 2, whilst the overall fixation efficiency (%T), which describes the  
327 amount of exhausted dye (%E) that has been fixed (%F), was calculated using Eq 3.

$$328 \quad \%F = \frac{f_{k2}}{f_{k1}} \times 100 \quad 2$$

329

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

3

330 In both Eq 2 and 3, the subscripts  $_1$  and  $_2$  represent the colour strength ( $f_k$ ) values before and after  
331 wash off, respectively.

## 332 **2.8 Wash fastness**

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

334

## 335 **3 Results and Discussion**

336 As mentioned, this part of the paper concerns the exhaust application of diluent-free reactive dyes  
337 to cotton and the role of added inorganic electrolyte, in the guise of sodium chloride. The results of  
338 dyeings on cotton carried out using the three pure reactive dyes, at various liquor ratios and in both  
339 the absence and presence of added NaCl, were interpreted in terms of the previously derived (7)  
340 theoretical model by which inorganic electrolytes such as NaCl and Na<sub>2</sub>SO<sub>4</sub> promote the uptake of  
341 direct dyes on cellulosic fibres during immersion dyeing.

342

### 343 *3.1 the use of two dyeing methods*

344 Two dyeing methods were used to dye cotton, namely one using 300 cm<sup>3</sup> capacity, stainless steel  
345 dyepots housed in a *Roaches Pyrotec S* dyeing machine, following the procedures recounted in  
346 2.2.1 and one that used sealed, 1000 cm<sup>3</sup> capacity, polypropylene plastic bags housed in a *Miele*  
347 *PT8257* tumble dryer, as described in section 2.2.2. These two particular dyeing methods were the  
348 same as those utilised in previous parts of the paper that described the dyeing of cotton using  
349 commercial grades of direct dyes (5) and reactive dyes (8).

350

351 As observed previously (8), whereas the 300 cm<sup>3</sup> stainless steel dyepot/*Roaches Pyrotec S* dyeing  
352 machine combination enabled consistently level dyeings to be obtained at liquor ratios of 1:50, 1:20,  
353 1:10, 1:6 and 1:3, inconsistently level dyeings were secured using liquor ratios  $\leq 1:2$ . The previously  
354 described (8) alternative 1000 cm<sup>3</sup> PP bag/*Miele PT8257* tumble dryer combination was therefore

355 employed to secure consistently level dyeings at liquor ratios of 1:2 and 1:1.5. It is assumed (8) that  
 356 level dyeings could be achieved at these two low liquor ratios because of enhanced fabric:dye liquor  
 357 interchange provided by the use of the larger capacity container and the random, tumbling action  
 358 afforded by the tumble dryer. However, as observed in the preceding study that used commercial  
 359 grade reactive dyes (8), the uniformity of dyeings obtained using a 1:1 liquor ratio in the case of the  
 360 PP bag/tumble dryer method was not always faultless, especially in the case of dyeings carried out  
 361 in the presence of added NaCl, it was decided that the results of the 1:1 liquor ratio dyeings would  
 362 not be included in this part of the paper.

363

364 The compatibility of the two dyeing methods was assessed by comparing dyeings, carried out using  
 365 a 1:3 liquor ratio, which had been obtained in both the absence and presence of  $50 \text{ g l}^{-1}$  added NaCl,  
 366 employing both dyeing tube/ dyeing machine and PP bag/tumble dryer methods. The 1:3 liquor ratio  
 367 was selected because consistently level dyeings were achieved using this particular liquor ratio for  
 368 both dyeing methods. Figure 4 shows that only small colorimetric differences were observed  
 369 between the dyeings carried out using the two dyeing methods, as demonstrated by the  $L^*$ ,  $a^*$  and  
 370  $b^*$  data; in addition, the  $\Delta E_{\text{CIELAB}}$  values calculated between corresponding dyeings were  $\ll 1.0$  and  
 371 the colour strength data secured for the respective dyeings were very similar.

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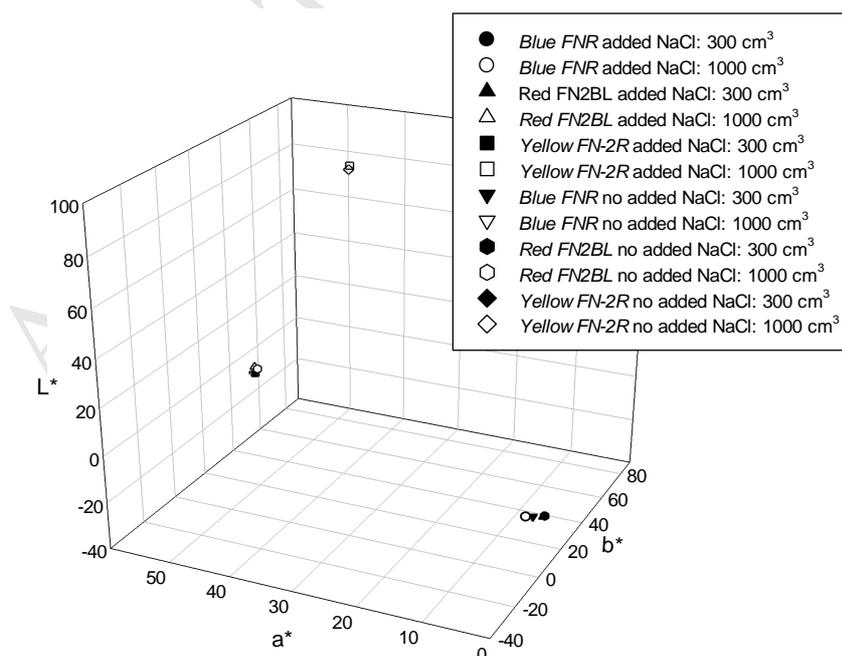
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382 Figure 4 comparison of dyeings achieved using dyeing tube/ dyeing machine and PP bag/tumble dryer dyeing  
 383 methods; absence and presence of  $50 \text{ gl}^{-1}$  NaCl; 1:3 liquor ratio

384

385 It was thus concluded that the two types of dyeing vessel/agitation system were compatible in terms  
 386 of the quality (depth of shade, hue and chroma) of the dyeings produced. These findings were the  
 387 same as those secured in the previous study that used commercial grade reactive dyes (8).

388

389 To summarise, consistently level dyeings were obtained over the range of liquor ratios 1:50 to 1:1.5,  
 390 insofar as dyeings at liquor ratios of 1:50, 1:20, 1:10, 1:6 and 1:3 were obtained using the dyeing  
 391 tubes/dyeing machine dyeing method described in 2.2.1, whilst dyeings at liquor ratios of 1:2 and  
 392 1:1.5 were obtained using the PP bags/tumble dryer dyeing method described in 2.2.2.

393

### 394 3.2 colour strength

395 Figure 5 shows the impact which reducing the liquor ratio from 1:50 to 1:1.5 had upon the colour  
 396 strength ( $f_k$  values) of 2% omf dyeings obtained using the three reactive dyes on woven cotton  
 397 fabric, in both the absence and presence of  $50 \text{ gl}^{-1}$  added NaCl.

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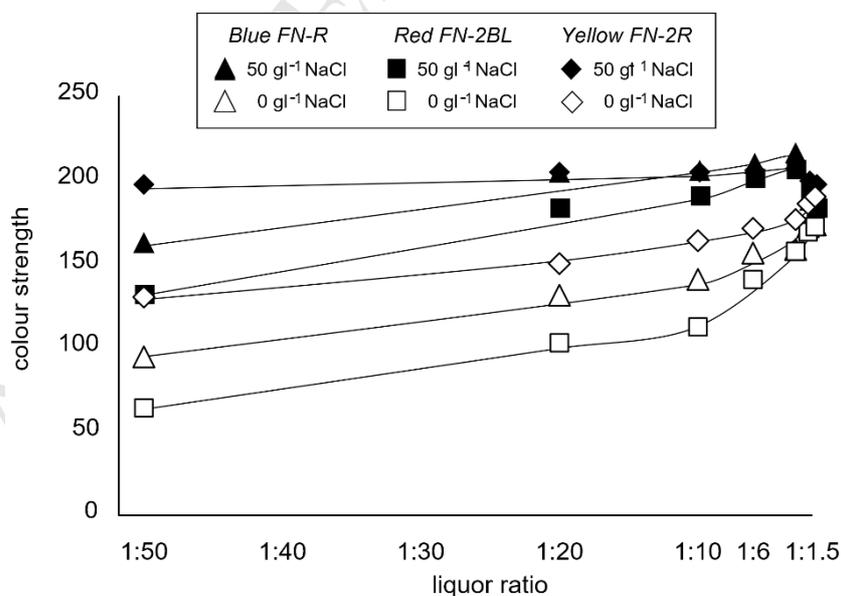
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Figure 5 Effect of liquor ratio on colour strength; absence and presence of  $50 \text{ gl}^{-1}$  NaCl

409

410 The corresponding colorimetric data obtained for the dyeings (Table 1) show that, as expected,  
 411 reducing the liquor ratio from 1:50 to 1:1.5 did not impart changes to the colour of the dyeings and,  
 412 also, that the presence or absence of added sodium chloride did not affect the colour of the dyeings.

413

414 Table 1 Colorimetric parameters for 2% omf dyeings; absence and presence of 50 gl<sup>-1</sup> NaCl

liquor ratio	<i>Novacron</i>	NaCl/gl <sup>-1</sup>	L*	a*	b*	C*	h°	$\lambda_{\max}$
1:50	<i>Blue FNR</i>	50	27.8	5.3	-34.3	34.7	278.7	620
		0	35.1	1.2	-33.4	33.4	272.0	
	<i>Red FN2BL</i>	50	37.3	56.5	0.1	56.5	0.1	540
		0	44.1	53.9	-5.9	54.3	353.8	
	<i>Yellow FN-2R</i>	50	65.8	42.2	86.5	96.2	64.0	440
		0	69.7	35.5	85.1	92.3	67.3	
1:20	<i>Blue FNR</i>	50	24.4	6.1	-31.9	32.4	280.8	620
		0	30.6	3.1	-33.3	33.4	275.3	
	<i>Red FN2BL</i>	50	33.7	54.8	4.6	54.9	4.8	540
		0	39.5	55.4	-2.4	55.5	357.6	
	<i>Yellow FN-2R</i>	50	64.4	43.8	84.7	95.4	62.7	440
		0	68.1	38.5	85.2	93.5	65.7	
1:10	<i>Blue FNR</i>	50	24.5	6.6	-32.9	33.5	281.4	620
		0	29.5	3.2	-32.4	32.6	275.6	
	<i>Red FN2BL</i>	50	32.8	52.9	4.3	53.1	4.7	540
		0	37.7	53.0	-1.8	53.0	358.1	
	<i>Yellow FN-2R</i>	50	63.5	43.0	83.1	93.6	62.6	440
		0	66.3	38.8	83.8	92.3	65.2	
1:6	<i>Blue FNR</i>	50	24.0	6.2	-31.7	32.2	281.0	620

		0	28.1	4.0	-32.3	32.6	277.0	
	<i>Red FN2BL</i>	50	32.5	53.2	5.6	53.5	6.0	540
		0	36.0	54.5	0.5	54.5	0.5	
	<i>Yellow FN-2R</i>	50	63.7	43.4	83.6	94.2	62.6	440
		0	65.7	40.8	83.6	93.0	64.0	
	<i>Blue FNR</i>	50	23.6	6.3	-31.3	31.9	281.4	620
		0	28.0	4.3	-32.8	33.1	277.4	
1:3	<i>Red FN2BL</i>	50	32.4	53.5	6.0	53.9	6.4	540
		0	34.9	54.1	1.8	54.1	1.9	
	<i>Yellow FN-2R</i>	50	64.1	43.9	84.4	95.1	62.5	440
		0	65.5	40.9	83.8	93.2	64.0	
	<i>Blue FNR</i>	50	25.7	5.2	-32.2	32.6	279.2	620
		0	26.8	4.5	-32.0	32.3	278.1	
1:2	<i>Red FN2BL</i>	50	32.8	53.3	4.8	53.5	5.2	540
		0	34.4	54.4	2.9	54.5	3.1	
	<i>Yellow FN-2R</i>	50	64.3	43.1	84.1	94.5	62.9	440
		0	64.6	41.9	83.2	93.1	63.2	
	<i>Blue FNR</i>	50	25.9	5.2	-32.2	32.6	279.2	620
		0	26.7	4.4	-31.7	32.0	277.9	
1:1.5	<i>Red FN2BL</i>	50	33.6	54.1	4.0	54.2	4.2	540
		0	34.0	53.8	3.1	53.9	3.3	
	<i>Yellow FN-2R</i>	50	63.9	43.2	83.1	93.6	62.5	440
		0	64.4	42.7	83.3	93.6	62.9	

415

416

417 Figure 5 reveals that the effect of liquor ratio on colour yield differed for dyeings which had been  
 418 carried out in the presence and absence of added NaCl. In the case of the dyeings undertaken in  
 419 the presence of added electrolyte, colour yield increased with decreasing liquor ratio over the range  
 420 1:50 to 1:3, for each of the three dyes used, and, thereafter, the  $f_k$  values gradually decreased with  
 421 further reduction in liquor ratio. In the case of dyeings that were carried out in the absence of added  
 422 NaCl, colour yield increased with decreasing liquor ratio over the complete range of liquor ratios  
 423 examined, for each of the three dyes studied.

424

425 These findings parallel those obtained previously for three commercial grade reactive dyes on  
 426 cotton (8).

427

### 428 3.3 dye exhaustion

429 Figure 6 shows that for dyeings which had been undertaken in the presence of  $50 \text{ gl}^{-1}$  added NaCl,  
 430 dye exhaustion increased with decreasing liquor ratio over the range 1:50 to 1:3 and thereafter  
 431 remained largely unchanged with further reduction in liquor ratio to 1:1.5. Furthermore, when dyeing  
 432 had been carried out in the absence of added NaCl (Figure 6) dye exhaustion increased with  
 433 decreasing liquor ratio over the liquor ratio 1:50 to 1:1.5.

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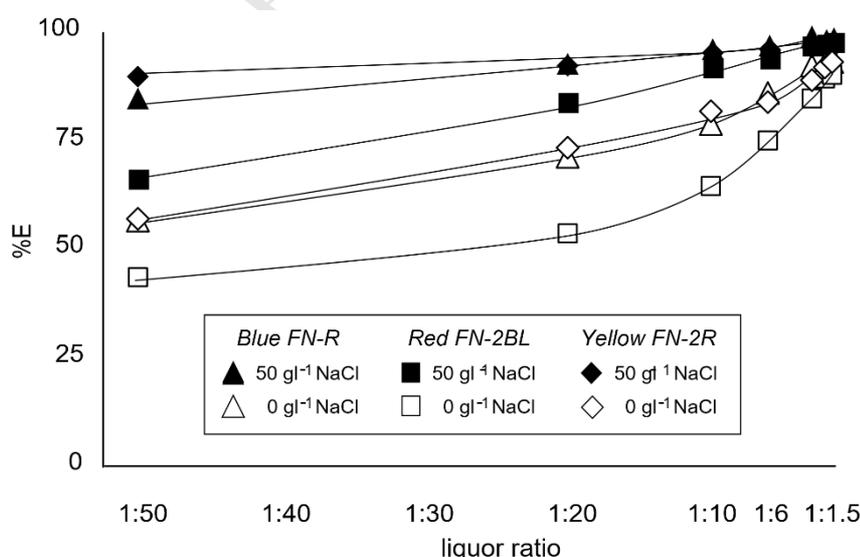


Figure 6 Effect of liquor ratio on dye exhaustion; absence and presence of  $50 \text{ gl}^{-1}$  NaCl

445

446 Thus, the trends in colour yield that accompanied a decrease in liquor ratio for dyeings carried out in  
 447 both the presence and absence of added NaCl (Figure 5) reflect the extents of dye fixation (%F)  
 448 obtained for the dyeings (Figure 6).

449

450 Figure 6 also reveals that the promotional effect of decreasing liquor ratio on the extent of dye  
 451 exhaustion achieved for each of the three dyes used was less pronounced in the case of dyeings  
 452 which had been carried out in the presence of 50  $\text{gl}^{-1}$  added NaCl. As these findings parallel those  
 453 obtained previously for three commercial grade reactive dyes on cotton, they can be explained  
 454 using the arguments proposed earlier (8).

455

456 In terms of the effects of both added inorganic electrolyte and reduced liquor ratio on the adsorption  
 457 of reactive dyes on cellulosic fibres, the previously mentioned theoretical model expressed in the  
 458 forms of Eq 4 and Eq 5 (7) was used to describe the partition of commercial grade reactive dyes (8)  
 459 between the fibre phase and the solution phase, where  $[D]$  is the total amount of dye within the  
 460 immersion dyeing system, which comprises dye that is present in the interstitial dye solution within  
 461 the fibre phase,  $[D_{sol}]_f$  together with that present in the bulk dyebath dye solution in the dyebath  
 462 phase,  $[D_{sol}]_s$ .  $S$  the substantivity coefficient and  $L$  the fractional liquor ratio..

463

$$464 \quad S = \frac{[D_{sol}]_f}{[D_{sol}]_s} = \left( \frac{[D] - [D_{sol}]_s}{[D_{sol}]_s} \right) \quad 4$$

$$465 \quad S = \frac{[D_{sol}]_f}{\frac{[D_{sol}]_s}{L}} = \left( \frac{[D] - \frac{[D_{sol}]_s}{L}}{\frac{[D_{sol}]_s}{L}} \right) \quad 5$$

466

467 According to Eq 4, the partition,  $[D_{sol}]_f/[D_{sol}]_s$ , of the reactive dye between the fibre and dyebath  
 468 phases is determined by the magnitude of the term  $[D_{sol}]_s$ , namely, the concentration of dye within  
 469 the bulk dyebath solution phase. When 50  $\text{gl}^{-1}$  NaCl is added to an aqueous reactive dyebath, the  
 470 dyes aggregate, which reduces the solubility of the dye and, consequently, the amount of dye in

471 solution within the dyebath phase,  $[D_{sol}]_s$ , is reduced. Because  $[D_{sol}]_s$  is reduced by the addition of  
472 inorganic electrolyte, the term  $([D] - [D_{sol}]_s/[D_{sol}]_s)$  will increase correspondingly, so that the  
473 substantivity coefficient of the dye,  $S$ , will increase, which will result in the partition of the reactive  
474 dye between the aqueous phase and the fibre phase shifting towards the fibre phase. Thus,  
475 according to Eq 4, owing the combined effects of increased dye aggregation and reduced dye  
476 solubility on the concentration gradient between the amount of dye in the dyebath and the amount of  
477 dye in the fibre phase, dye uptake should increase in the presence of  $50\text{gl}^{-1}$  added NaCl, at each of  
478 the liquor ratios employed for dyeing, as was indeed observed for each of the three dyes used in  
479 this work (Figures 5 and 6).

480

481 This model (7) therefore attributes the characteristically low substantivity displayed by the dyes  
482 towards cellulosic fibres, when applied in the absence of added electrolyte to the high aqueous  
483 solubility of the dyes; such high aqueous dye solubility was also considered to account for the  
484 remarkable ability of added inorganic electrolyte to promote reactive dye uptake (7). Accordingly,  
485 the low extent of colour yield (Figure 5) and dye exhaustion (Figure 6) observed when dyeing had  
486 been carried out in the absence of added electrolyte at high liquor ratios (ie 1:50, 1:20, 1:10) can be  
487 attributed to the intrinsically low dye-fibre substantivity created at such high liquor ratios. In contrast,  
488 the high  $f_k$  and %E values secured at low liquor ratios (ie 1:2 and 1:1.5) were the result of the  
489 inherently high dye-fibre substantivity that prevailed at such low liquor ratios.

490

491

492 Based on the above considerations, it follows that because of the marked influence of dye solubility  
493 on reactive dye uptake than the particular liquor ratio that is used for dyeing will exert an equally  
494 marked effect on dye uptake. This situation arises because liquor ratio determines the amount of  
495 dyebath water that is available for the dye to dissolve; additionally (7), since liquor ratio determines  
496 both the amounts of reactive dye and added electrolyte in the dyebath, the extent to which added  
497 electrolyte encourages dye uptake are influenced by liquor ratio, because the magnitude of dye-  
498 inorganic electrolyte interactions are influenced by liquor ratio.

499

500 In this context, this particular interpretation of the promotional effect imparted by added inorganic  
501 electrolyte on commercial grade reactive dyes, as described by Eq 4 (7, 8), also provided an  
502 explanation of the nature by which reactive dye uptake on cotton was promoted by a reduction in  
503 liquor ratio (7, 8) via the related Eq 5. Indeed, it was presumed (7, 8) that both a reduction in the  
504 liquor ratio utilised in dyeing and the addition of inorganic electrolyte to the dyebath impart the same  
505 promotional effect on reactive dye uptake insofar as both measures encourage dye aggregation in  
506 the dyebath, which reduces the solubility of the dye and results in the substantivity of the dye being  
507 increased. Thus, the findings (Figures 5 and 6) that both colour strength and dye exhaustion  
508 generally increased with decreasing liquor ratio over the range of liquor ratios studied (ie 1:50 to  
509 1:1.5), can be attributed to the combined effects of increased dye aggregation and reduced dye  
510 solubility upon the concentration gradient between the amount of dye in the dyebath and the amount  
511 of dye in the fibre phase. This is reflected in the relationship depicted in Eq 5, which predicts that as  
512 liquor ratio is reduced, the amount of water in the dyebath available for dye dissolution decreases,  
513 so that the concentration of dye in the dye solution within the bulk dyebath,  $[D_{sol}]_s$ , will be lowered.  
514 Because  $[D_{sol}]_s$  therefore decreases with decreasing liquor ratio then owing to the term  $([D] -$   
515  $[D_{sol}]_s/[D_{sol}]_s)$  in Eq 5, the substantivity coefficient of the dye,  $S$ , will increase and the partition of dye  
516 between the aqueous phase (dyebath) and the fibre phase will shift towards the fibre. Accordingly,  
517 dye uptake should increase with decreasing liquor ratio, as was indeed observed for each of the  
518 three dyes used in this work.

519

520 Accordingly, liquor ratio, as expressed by  $L$ , has a direct impact on the amount of dye in solution in  
521 the bulk dyebath phase,  $[D_{sol}]_s$ , owing to the term  $([D_{sol}]_s/L)$  in Eq 5. Thus, values of  $[D_{sol}]_s$  will  
522 decrease with decreasing liquor ratio, from which it follows that values of  $[D_{sol}]_f$  will correspondingly  
523 increase, so that dye uptake is promoted.

524

525 Thus the observed low %E and  $f_k$  values (figures 6 and 5 respectively) observed for high liquor ratio  
526 dyeings (ie 1:50, 1:20, 1:10) can be attributed to the inherently low dye-fibre substantivity at such

527 high liquor ratios, whereas the high extent of dye exhaustion obtained at low liquor ratios (ie 1:2 and  
528 1:1.5) results from the intrinsically high dye-fibre substantivity that exists at such high liquor ratios.

529

530 If the promotion of reactive dye uptake imparted by both reduced liquor ratio and added inorganic  
531 electrolyte is each the result of increased dye aggregation and reduced dye solubility on the  
532 magnitude of the substantivity coefficient of the dye (via Eq 4 and 5), then the extent to which dye  
533 uptake is promoted should be lowest when the promotional impact of reduced liquor ratio and added  
534 electrolyte are minimal, as will arise when high liquor ratio dyeings are carried out in the absence of  
535 added electrolyte and should be greatest when the influence of reduced liquor ratio and added  
536 electrolyte are maximal, which will occur when low liquor ratio dyeings are undertaken in the  
537 presence of added inorganic electrolyte. Because reducing liquor ratio and adding electrolyte impart  
538 the same outcome in terms of dye uptake, it follows that the promotional effect of added NaCl  
539 should decrease with decreasing liquor ratio, as was indeed observed (Figures 5 and 6).

540

541 When dyeing had been carried out in the presence of 50  $\text{gl}^{-1}$  NaCl, Figures 5 and 6 show that higher  
542 values of  $f_k$  and %E were obtained than when dyeing had been undertaken in the absence of added  
543 electrolyte, for each of the three dyes used. Thus, in the presence of added NaCl, the prevailing  
544 level of dye-fibre substantivity was higher than that in the absence of added inorganic electrolyte  
545 because of the additional promotional effect exerted by the NaCl on the level of dye-fibre  
546 substantivity that prevailed at each liquor ratio. Hence, when dyeing had been carried out in the  
547 presence of added NaCl, because of the inherently high dye-fibre substantivity provided by the 50  
548  $\text{gl}^{-1}$  added electrolyte, the promotional effect of reduced liquor ratio on dye exhaustion was limited to  
549 lower liquor ratios (ie 1:50 to 1:6); indeed, values of both  $f_k$  and E% were essentially constant over  
550 the range of liquor ratios 1:3 to 1:1.5 (Figures 5 and 6).

551

552 Again, these observations parallel those obtained previously in the case of three commercial grade  
553 reactive dyes applied to cotton (8).

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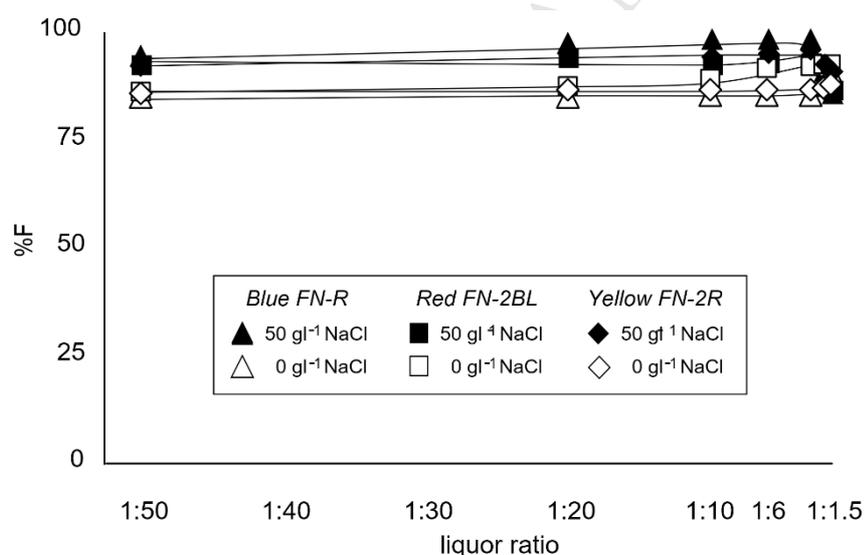
## 555 3.4 dye fixation

556 Figure 7 shows the effect of reducing liquor ratio from 1:50 to 1:1.5 on the extent of dye fixation, %F,  
 557 achieved for 2% omf dyeings of the three, electrolyte-free reactive dyes, in both the absence and  
 558 presence of 50  $\text{gl}^{-1}$  added NaCl. It is apparent that at each liquor ratio used, the level of fixation  
 559 achieved differed only slightly for the three different dyes, which was expected, since the three dyes  
 560 are members of the same commercial range.

561

562 The effect of decreasing the liquor ratio used for dyeing on dye fixation differed for dyeings which  
 563 had been carried out in the absence and presence of added NaCl (Figure 7). Values of %F  
 564 increased gradually with decreasing liquor ratio over the range 1:50 to 1:3, for each of the three  
 565 dyes used, and thereafter decreased gradually with decreasing liquor, in the case of dyeings that  
 566 were carried out in the presence of added NaCl.

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576 Figure 7 Effect of liquor ratio on dye fixation; absence and presence of 50  $\text{gl}^{-1}$  NaCl

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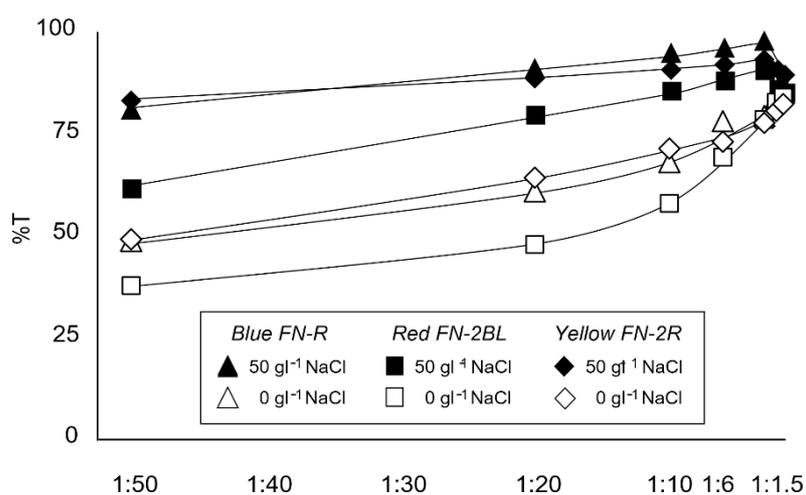
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587 Figure 8 Effect of liquor ratio on total fixation; absence and presence of 50  $\text{gl}^{-1}$  NaCl

588

589 However, Figure 7 also reveals that the extent of dye fixation generally increased gradually with  
590 decreasing liquor ratio over the complete range of liquor ratios examined, for each of the three dyes  
591 studied, when dyeing had been undertaken in the absence of added NaCl.

592

593 Figure 8 shows the effect of liquor ratio variation on the extent of total dye fixation achieved for 2%  
594 omf dyeings, in both the absence and presence of 50  $\text{gl}^{-1}$  added NaCl. Although values of %T  
595 differed for the three different dyes, at each liquor ratio used, this diminished with decreasing liquor  
596 ratio, until, at a 1:1.5 liquor ratio, similar levels of total dye fixation were achieved for each of the  
597 dyes. In the case of dyeings undertaken in the presence of added electrolyte, the extent of total  
598 fixation increased with decreasing liquor ratio over the range 1:50 to 1:3 and, thereafter, decreased  
599 gradually with decreasing liquor to 1:1.5. For dyeings that were carried out in the absence of added  
600 electrolyte, the %T values increased with decreasing liquor ratio over the complete range of liquor  
601 ratios examined (ie 1:50 to 1:1.5), for each of the three dyes studied.

602

603 The observed increase in %T that accompanied a reduction in liquor ratio over the range 1:50 to  
604 1:1.5 in both the absence and presence of added NaCl (Figure 8) can be attributed to a  
605 corresponding increase in dye exhaustion over the same liquor ratio range (Figure 6); indeed, the  
606 similarity between the sets of curves displayed in Figure 6 and Figure 9 is quite apparent.

607

608 Although these observations once again parallel those obtained previously for three commercial  
609 grade reactive dyes on cotton (8), in this previous part of the paper, it was concluded that,  
610 irrespective of whether dyeing had been carried out in the absence or presence of added

611 electrolyte, diluent electrolyte present in the commercial dyes used may have exerted a promotional  
612 effect on dye uptake.

613 However, in the present work, as diluent-free reactive dyes were, diluent electrolyte derived from the  
614 dyes cannot have contributed to these observed findings and, therefore, an alternative explanation  
615 is required.

616

### 617 3.5 effect of initial dye concentration on dyeing

618 In terms of the results presented in Figures 5 to 8, the only dyebath variables that could have  
619 contributed to the observed variation of colour strength, dye exhaustion, dye fixation and total dye  
620 fixation, respectively, as a function of liquor ratio, are the amount of water in the dyebath and the  
621 concentration of the dye. In the latter context, as discussed in the cases of both commercial direct  
622 dyes (5) and commercial grade reactive dyes (8), although a constant amount of each of the three  
623 diluent-free reactive dyes used in this work was applied to the cellulosic substrate (ie 2% on mass of  
624 fibre), irrespective of the liquor ratio used for dyeing, the dye concentration in the dyebath at the  
625 start of dyeing will differ according to the particular liquor ratio employed. Thus, the dye  
626 concentration in the dyebath will have increased by ~33, based on liquor volume, over the liquor  
627 ratio range of 1:50 to 1:1.5 used (ie  $0.4 \text{ g l}^{-1}$  @ 1:50;  $1 \text{ g l}^{-1}$  @ 1:20;  $2 \text{ g l}^{-1}$  @ 1:10;  $3.3 \text{ g l}^{-1}$  @ 1:6;  $6.6$   
628  $\text{g l}^{-1}$  @ 1:3;  $10 \text{ g l}^{-1}$  @ 1:2,  $13.3 \text{ g l}^{-1}$  @ 1:1.5), even though the concentrations of both added NaCl (ie  
629  $50 \text{ g l}^{-1}$ ) and added  $\text{Na}_2\text{CO}_3$  (ie  $15 \text{ g l}^{-1}$ ) will have remained constant, over the same range of liquor  
630 ratio, based on liquor volume.

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#### 632 3.5.1 dyeing in the absence of added electrolyte

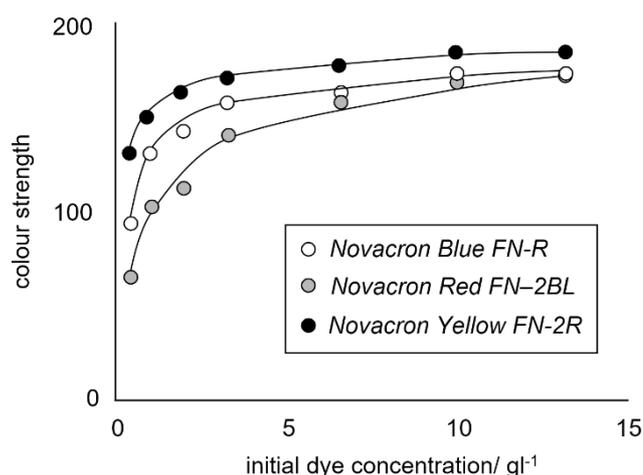
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Figure 9 colour strength as a function of initial dye concentration; absence of NaCl

642

643 Figure 9 shows the colour strength achieved for dyeings carried out in the absence of added NaCl

644 at liquor ratios of 1:50 to 1:1.5, as a function of initial dye concentration. Although an increase in

645 initial dye concentration over the range 0.4 to 3.3  $\text{gl}^{-1}$  (corresponding to liquor ratios of 1:50 to 1:6)

646 resulted in a sharp increase in colour strength, further increase in initial dye concentration over the

647 range 6.6 to 13.3  $\text{gl}^{-1}$  (corresponding to liquor ratios of 1:3 to 1:1.5) resulted in a more gradual

648 increase in colour strength. The results in Figure 9 concur with those displayed in Figure 5, which

649 show that in the absence of added NaCl, colour yield increased with decreasing liquor ratio over the

650 complete range of liquor ratios examined (ie 1:50 to 1:1.5), for each of the three dyes studied.

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659 Figure 10 dye exhaustion as a function of initial dye concentration; absence of NaCl

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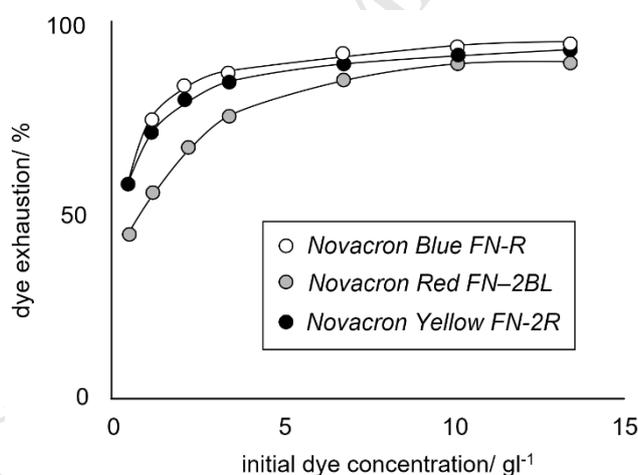
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659 Figure 10 dye exhaustion as a function of initial dye concentration; absence of NaCl

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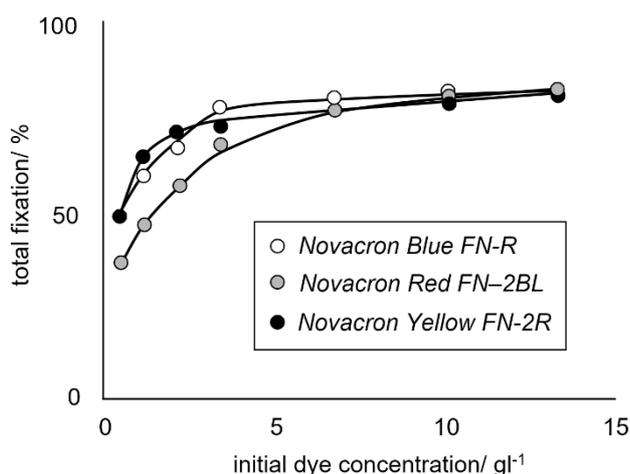
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669 Figure 11 total dye fixation as a function of initial dye concentration; absence of NaCl

670

671 As the observed variation in  $f_k$  values as a function of liquor ratio in the absence of 50  $\text{gl}^{-1}$  added  
672 NaCl (Figure 5) reflected the observed variation in both dye exhaustion (Figure 6) and total dye  
673 fixation (Figure 8) achieved for the dyeings, it follows that a plot of %E (Figure 10) and %T (Figure  
674 11) as a function of initial dye concentration should be similar to that displayed in Figure 9, as  
675 indeed was observed.

676

677 Comparing Figures 9 to 11 reveals that despite the fact that the scale of the vertical axis in Figure 9  
678 differs by a factor of 2 compared to the axes in Figures 10 and 11, the strong resemblance between  
679 the three Figures is evident, insofar as following an initial, sharp increase in colour strength (Figure  
680 9), %E (Figure 10) and %T (Figure 11) over the initial dye concentration range 0.4 to 3.3  $\text{gl}^{-1}$   
681 (corresponding to liquor ratios of 1:50 to 1:6), values of  $f_k$  (Figure 9), %E (Figure 10) and %T (Figure  
682 11) increase gradually with further increase in initial dye concentration over the range 6.6 to 13.3  $\text{gl}^{-1}$   
683 (corresponding to liquor ratios of 1:3 to 1:1.5).

684

685 If the promotional effect of reducing liquor ratio on dye uptake recorded in Figures 9 to 11 was due  
686 to an increase in dye concentration in the dyebath, it follows that irrespective of whether dyeing had  
687 been carried out in the absence or presence of 50  $\text{gl}^{-1}$  added NaCl, colour strength, %E and %T  
688 should increase with increasing initial dye concentration. However, as discussed previously (5),  
689 since liquor ratio is a fraction (eg 1/5, 1/10, etc.) then it can be expressed mathematically by the  
690 fractional liquor ratio,  $L$ , (units = mass/volume, such as  $\text{gl}^{-1}$ ) which decreases with increasing liquor  
691 ratio (eg  $L = 1$  at a 1:1 liquor ratio,  $L = 0.1$  at a 1:10 liquor ratio, etc.). When values of initial dye  
692 concentration are plotted as a function of fractional liquor ratio,  $L$ , the essentially linear relationship

693 shown in Figure 12 is secured (the liquor ratios that correspond to the values of  $L$  are displayed on  
694 the plot).

695

696 As initial dye concentration increases more or less linearly as a function of  $L$  (Figure 12) then if dye  
697 concentration in the dyebath contributed to the observed promotion of colour strength (Figure 11),  
698 %E (Figure 10) and %T (Figure 11) that accompanied a reduction in liquor ratio, the magnitude of  
699 this contribution should be proportional to the concentration of dye in the dyebath. However, the  
700 findings that curvilinear plots were obtained for the variation in colour strength, %F and %T as a  
701 function of initial dye concentration (Figures 9 to 11) do not correlate with the linear relationship  
702 obtained for the variation in the initial concentration of dye in the dyebath as a function of fractional  
703 liquor ratio (Figure 12). Indeed, the marked difference in the rates of increase observed for colour  
704 strength, %F and %T that occurred prior to and after an initial dye concentration of  $3.3 \text{ gl}^{-1}$   
705 (corresponding to a liquor ratio of 1:6) does not fit with the linear relationship displayed in Figure 12.  
706 Similar findings were reported in the case of the uptake of commercial grade direct dyes (5) and  
707 reactive dyes (8) on cotton.

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718 To explain these results, it is useful to reflect that as the liquor ratio employed for dyeing was  
719 reduced, not only did the initial concentration of dye in the dyebath increase (in a linear fashion

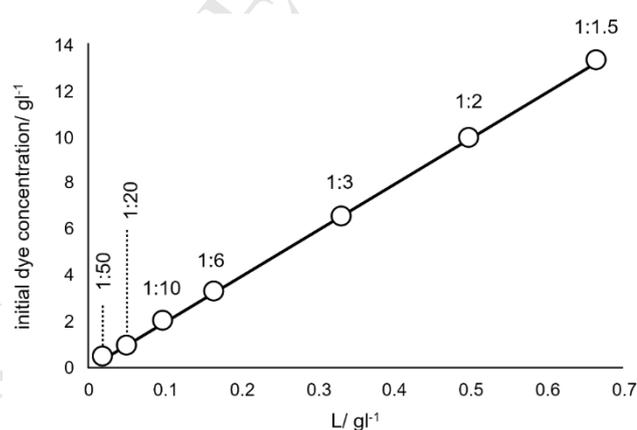


Figure 12 initial dye concentration as a function of fractional liquor ratio (8)

720 according to Figure 12) but also, the amount of water in the dyebath available for dye dissolution  
721 decreased.

722

723 Based on the notion that dye solubility is the principal determinant of reactive dye-fibre substantivity  
724 and the proposal that the solubility of the reactive dye in the dyebath phase governs the partition of  
725 the dye between the fibre and dyebath phases (ie the extent of dye uptake), the effect of both  
726 electrolyte- and reduced liquor ratio-induced aggregation and consequent reduced solubility on  
727 reactive dye uptake can be interpreted using Eqs 4 and 5 (8).

728

729 Because the amount of water available in a dyebath for dye dissolution/dye dispersion to occur  
730 depends on the liquor ratio employed for dyeing, liquor ratio governs both the rate and extent of dye  
731 transfer from the dyebath to the fibre, since it determines the magnitude of the concentration  
732 gradient,  $[D_{sol}]_f/[D_{sol}]_s$ , that exists between the amount of dye that is present in the interstitial dye  
733 solution within the fibre phase,  $[D_{sol}]_f$  together with that present in the bulk dyebath dye solution in  
734 the dyebath phase,  $[D_{sol}]_s$ , which, in turn, determines the substantivity coefficient,  $S$ , of the dye and  
735 the distribution of the reactive dye between the aqueous and fibre phases.

736

737 Thus, according to this theoretical model, as liquor ratio decreases, the amount of water available in  
738 the dyebath also reduces, with the result that the solubility of the dye in solution in the dyebath  
739 phase (ie  $[D_{sol}]_s$ ) will likely decrease and, therefore, because of the term  $([D] - [D_{sol}]_s/[D_{sol}]_s)$  in Eq 4  
740 and 5, so that the substantivity coefficient of the dye,  $S$ , will increase correspondingly, which results  
741 in the partition of the reactive dye between the aqueous phase and the fibre phase shifting towards  
742 the fibre phase; dye uptake is therefore promoted, as indeed was observed (Figures 9 to 11).

743

744 From the foregoing it follows that in the case of dyeings undertaken in the absence of added NaCl,  
745 the marked increase in colour strength, %F and %T as a function of initial dye concentration  
746 (Figures 9 to 11) observed at high liquor ratios (ie between 1:50 and 1:6) and thus low values of  
747 initial dye concentration (ie 0.4 and 3.3  $\text{gl}^{-1}$ ), can be attributed to the promotion of dye uptake

748 imparted by the combined effects of reducing the amount of water in the dyebath and increasing the  
749 initial dye concentration. As such, the intrinsic low level of dye-fibre substantivity that prevailed at  
750 these high liquor ratios (ie between 1:50 to 1:6) in the absence of added NaCl, was augmented by  
751 reducing liquor ratio because the effective concentration of dye in solution in the dyebath available  
752 for dyeing,  $[D_{sol}]_s$ , was reduced, as less water was available within the dyebath phase for dye  
753 dissolution. Also, reducing liquor ratio encouraged the inherent propensity of the reactive dyes to  
754 aggregate in the dyebath, because the amount of water in the dyebath was reduced and the initial  
755 dye concentration in the dyebath had been correspondingly increased. Such enhanced dye  
756 aggregation will, according to the proposed theoretical model (7), result in increased dye uptake.

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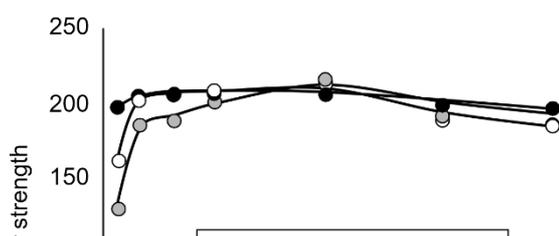
758 When lower liquor ratios were used for dyeing (ie 1:3 to 1:1.5), the observed far more gradual  
759 increase in colour strength that accompanied an increase in initial dye concentration (ie 6.6 to 13.3  
760  $\text{gl}^{-1}$ ) (Figures 9 to 11), implies that the combination of reduced dyebath volume and increased initial  
761 dye concentration resulted in increasing levels of dye aggregation and, thus, increasing reductions  
762 in dye solubility, within the dyebath. However, the observed far more gradual increase in dye uptake  
763 as a function of decreasing liquor ratio can be attributed to the combined promotional effects of  
764 reduced liquor ratio and increasing initial dye concentration having exerted a comparatively lower  
765 boost to the intrinsically high levels of dye-fibre substantivity that prevailed at such lower liquor  
766 ratios (ie 1:3 to 1:1.5). Furthermore, with decreasing liquor ratio, so the magnitude of the combined  
767 promotional effects of increased dye aggregation and reduced dye solubility will have increased, in  
768 a linear manner perhaps (Figure 12), with the result that the influence on dye uptake exerted by the  
769 combined promotional effects declined, relatively, with increasing liquor ratio, owing to excessive  
770 dye aggregation and reduced dye solubility. Such a situation was proposed to explain the findings  
771 obtained using commercial grade reactive dyes on cotton (8).

772

### 773 3.5.2 dyeing in the presence of added electrolyte

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782 Figure 13 colour strength as a function of initial dye concentration; presence of  $50 \text{ gl}^{-1}$  NaCl

783

784 The plot of colour strength as a function of initial dye concentration for dyeings obtained in the  
 785 presence of  $50 \text{ gl}^{-1}$  NaCl (Figure 13) differ in shape to those obtained in the absence of added  
 786 electrolyte (Figure 11) in that, an initial sharp increase in colour strength over the initial dye  
 787 concentration of  $0.4$  to  $3.3 \text{ gl}^{-1}$  (corresponding to liquor ratios of 1:50 to 1:6), is followed by a gradual  
 788 decrease in  $f_k$  values with further increase in initial dye concentration over the range  $6.6$  to  $13.3 \text{ gl}^{-1}$   
 789 (corresponding to liquor ratios of 1:3 to 1:1.5).

790

791 The results in Figure 13 concur with those displayed in Figure 5 which show that in the presence of  
 792  $50 \text{ gl}^{-1}$  added NaCl, colour yield, increased with decreasing liquor ratio over the range 1:50 to 1:6,  
 793 for each of the three dyes used, before decreasing with further reduction in liquor ratio to 1:1.5.

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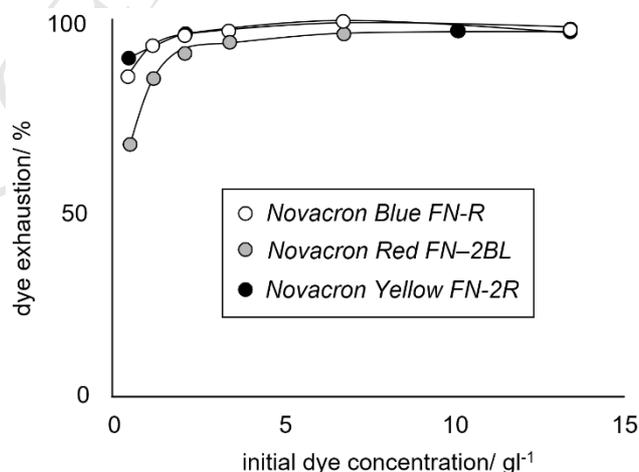
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802 Figure 15 total dye fixation as a function of initial dye concentration; presence of  $50 \text{ gl}^{-1}$  NaCl

803



804 As the variation in colour strength as a function of liquor ratio in the presence of  $50 \text{ gl}^{-1}$  added NaCl  
 805 (Figure 5) reflected the observed variation in both dye exhaustion (Figure 6) and total dye fixation  
 806 (Figure 8) achieved for the dyeings, it follows that a plot of %E (Figure 14) and %T (Figure 15) as a  
 807 function of initial dye concentration should be similar to that displayed in Figure 13, as indeed was  
 808 observed. Although the plots in Figure 13 are condensed vertically compared with those in Figures  
 809 14 and 15, owing to the use of different vertical axes scales, the three graphs bear strong parallels:  
 810 the initial, sharp increase in colour strength (Figure 13), %E (Figure 14) and %T (Figure 15) over the  
 811 initial dye concentration range of  $0.4$  to  $3.3 \text{ gl}^{-1}$  (corresponding to liquor ratios of 1:50 to 1:6), was  
 812 followed by a gradual decrease in either  $f_k$  value (Figure 13), %F (Figure 14) and %T (Figure 15)  
 813 with further increase in initial dye concentration from  $6.6$  to  $13.3 \text{ gl}^{-1}$  (corresponding to liquor ratios of  
 814 1:3 to 1:1.5).

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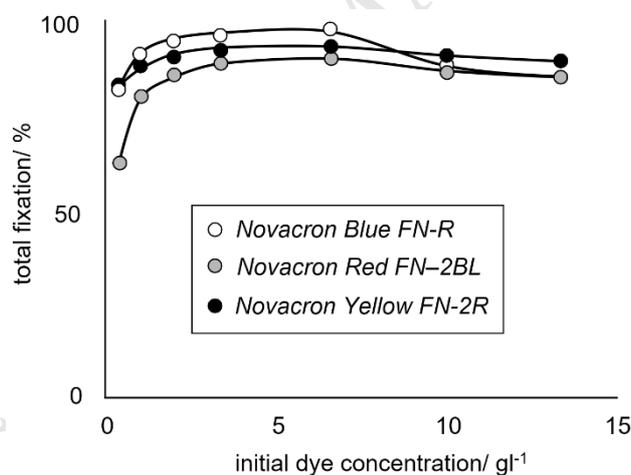
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825 Figure 15 total dye fixation as a function of initial dye concentration; presence of  $50 \text{ gl}^{-1}$  NaCl

826

827 These findings parallel those obtained previously for three commercial grade reactive dyes on  
 828 cotton (8).

829

830 From the foregoing discussions of the possible effect of increased initial dye concentration on colour  
 831 strength (Figure 9), %E (Figure 10) and %T (Figure 11) in the absence of added NaCl, the sharp

832 increases observed for colour strength, dye fixation and total dye fixation over the initial dye  
833 concentration range 0.4 to 3.3  $\text{gl}^{-1}$  when dyeing had been undertaken in the presence of added  
834 electrolyte (Figures 13 to 15) can be attributed to the promotional effect on dye uptake imparted by  
835 the combined effects of reducing the amount of water in the dyebath and increasing the initial dye  
836 concentration in the dyebath. The inherently lower levels of dye-fibre substantivity that existed at  
837 high liquor ratios (ie between 1:6 and 1:50) even in the presence of added NaCl, would have been  
838 enhanced when liquor ratio was reduced because the effective concentration of dye in solution in  
839 the dyebath phase available for dyeing,  $[D_{so}]_s$ , was reduced, as less water was available within the  
840 dyebath for dye dissolution. In addition, reducing liquor ratio will have encouraged dye aggregation  
841 in the dyebath because of the combined effects of reduced dyebath volume and increased initial dye  
842 concentration.

843

844 The observed gradual decrease in both colour strength (Figure 13), %E (Figure 14) and %T (Figure  
845 15) at the lower liquor ratios of 1:3 to 1:1.5 (ie at higher initial dye concentrations of 6.6 to 13.3  $\text{gl}^{-1}$ )  
846 suggest that in the presence of added NaCl, the combined effects of reduced dyebath volume and  
847 increased initial dye concentration imparted very high levels of dye aggregation and, thus, large  
848 extents of reduced dye solubility within the dyebath. The level of dye-fibre substantivity secured at  
849 these low liquor ratios (ie between 1:3 and 1:1.5) in the presence of added 50  $\text{gl}^{-1}$  NaCl can be  
850 expected to have been already very high, because of the promotional effects exerted by the added  
851 electrolyte and low liquor ratios. Thus, it appears that these inherently high levels of dye-fibre  
852 substantivity that prevailed at such lower liquor ratios (ie 1:3 to 1:1.5) may have been overly  
853 amplified by the combined promotional effects of reduced liquor ratio and increasing initial dye  
854 concentration. This can be assumed to have resulted in excessive dye aggregation and marked  
855 reduced dye solubility, which would have caused the observed decrease in colour strength (Figure  
856 13), dye exhaustion (Figure 14) and total dye fixation (Figure 15) at the higher initial dye  
857 concentrations (6.6 to 13.3  $\text{gl}^{-1}$ ) provided at the lower liquor ratios of 1:3 to 1:1.5). Thus, colour  
858 strength, dye exhaustion (Figure 14) and total dye fixation (Figure 15) decreased with increase in  
859 initial dye concentration over the range 6.6 to 13.3  $\text{gl}^{-1}$  (corresponding to liquor ratios of 1:3 to 1:1.5).

860

861 When the plots displayed in Figures 9 to 11 and 13 to 15 are compared, it is apparent that similar  
 862 behaviour was obtained in both the absence and presence of added NaCl, insofar as values of  $f_k$ ,  
 863 %E and %T increased with increasing initial dye concentration over the range 0.4 to 3.3  $\text{gl}^{-1}$  (liquor  
 864 ratios 1:50 to 1:1.6) at a rate that was similar for each of the dyes. Furthermore, the rates of change  
 865 in colour strength, %E and %T achieved for initial dye concentrations upto 3.3  $\text{gl}^{-1}$  were greater than  
 866 those observed at initial dye concentrations  $>3.3 \text{ gl}^{-1}$  (ie over the range 6.6 to 13.3  $\text{gl}^{-1}$ ,  
 867 corresponding to liquor ratios of 1:3 to 1:1.5).

868

869 In this context of the conclusions that diluent electrolyte present in both commercial direct dyes (5)  
 870 and commercial grade reactive dyes (8) may have exerted a promotional effect on dye uptake, the  
 871 findings discussed above clearly show that this is unlikely to have been the case and that the  
 872 variations in dye uptake as a function of liquor ratio can be attributed to the combined effects which  
 873 reduced dyebath volume and increased initial dye concentration have on the extent of dye  
 874 aggregation and increasing reduction in dye solubility, within the dyebath.

875

### 876 3.6 promotional effect of added NaCl on dye uptake

877 The effect of added inorganic electrolyte on the uptake of commercial grade reactive dyes on cotton  
 878 as a function of liquor ratio was described by the *promotional effect*, via Eq 6, which expresses the  
 879 ratio of the colour strength of dyeings achieved in the presence and absence of added electrolyte at  
 880 a given liquor ratio (8).

881

$$882 \text{ \% promotional effect} = \frac{\text{\%E in presence of added NaCl} - \text{\%E in absence of added NaCl}}{\text{\%E in presence of added NaCl}} \times 100$$

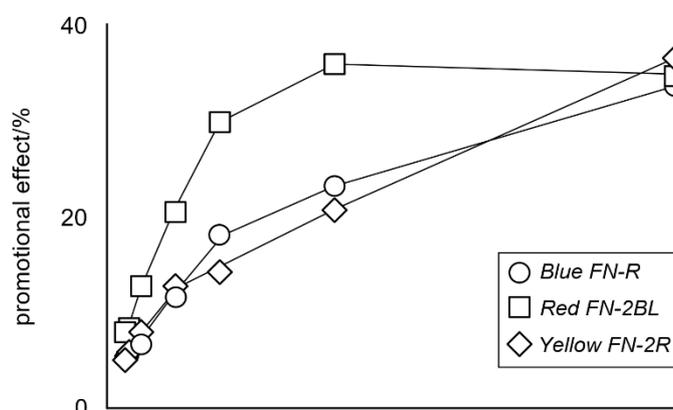
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892 Figure 16 Promotional effect imparted by added electrolyte as a function of liquor ratio

893

894 Using Eq 6, it was found (Figure 16) that the ability of the added  $50 \text{ g l}^{-1}$  NaCl to promote colour  
895 strength reduced with decreasing liquor ratio, as previously observed in the case of commercial  
896 grade reactive dyes on cotton (8). This finding suggests that the added electrolyte was more  
897 effective in promoting colour strength, and thus dye uptake, at longer liquor ratios (ie 1:50) than at  
898 shorter liquor ratios (ie 1:15), even though a constant concentration (ie  $50 \text{ g l}^{-1}$ ) of added NaCl had  
899 been employed at each of the seven liquor ratios examined.

900

901 As mentioned, if it is presumed that the promotion of reactive dye uptake imparted by both added  
902 electrolyte and lowered liquor ratio is each the result of increased dye aggregation and reduced dye  
903 solubility on the effective concentration gradient present within the dyebath, the extent to which dye  
904 uptake is promoted should be greatest when the influence of reduced liquor ratio and added  
905 electrolyte are maximised (ie when low liquor ratio dyeings are undertaken in the presence of added  
906 NaCl) and will be lowest when the promotional impact of reduced liquor ratio and added electrolyte  
907 are minimal (ie when high liquor ratio dyeings are carried out in the absence of added electrolyte).

908

909 As adding electrolyte and reducing liquor ratio promote dye uptake than the promotional effect  
910 imparted by the added inorganic electrolyte should decrease with decreasing liquor ratio, as was  
911 indeed observed (Figure 16). The similarity of the plots obtained for the three pure dyes (Figure 16)  
912 indicate that the added  $50 \text{ g l}^{-1}$  NaCl exerted similar levels of enhanced uptake and, therefore, the  
913 nature of the promotional effect imparted by the inorganic electrolyte was not dye-specific.

914

**915 3.7 fastness**

916 In the case of commercial grade reactive dyes on cotton (8), it was demonstrated that identical  
917 levels of wash fastness were displayed by 2% omf dyeings on cotton carried out in the absence or  
918 presence of 50 g<sup>l</sup><sup>-1</sup> added NaCl.

919

920 The results presented in Figure 17 show that this was also found to be the case for the 2% omf  
921 dyeings obtained using the three diluent-free reactive dyes employed in this work. Thus, dyeing  
922 cotton with pure, diluent-free, reactive dyes in the complete (ie100%) absence of added inorganic  
923 electrolyte has no effect on the characteristic excellent wash fastness displayed by reactive dyes on  
924 cotton.

925

926 The findings displayed in Figure 17 are interesting because, as mentioned above, the depth of  
927 shade of the 2% omf dyeings that were obtained in this study (as expressed by colour strength), can  
928 be expected to be greater than that obtained by applying 2% omf of a commercial grade sample of  
929 the same dyes. This has implications in terms of the wash fastness of the ensuing dyeings, since it  
930 is generally accepted that the level of wash fastness displayed by dyed materials generally  
931 decreases with increasing depth of shade. Hence, the generally very good wash fastness secured  
932 for the three diluent-free reactive dyes employed in this work when they had been applied in the  
933 complete absence of added NaCl is encouraging.

934

**935 4 conclusions**

936 It is possible to dye cotton using pure (diluent-free) reactive dyes in the complete (ie 100%) absence  
937 of added inorganic electrolyte. The ensuing dyeings were of realistic depths of shade and displayed  
938 excellent levels of wash fastness that were characteristic of those exhibited by commercial grade  
939 reactive dyes on cotton and other cellulosic fibres.

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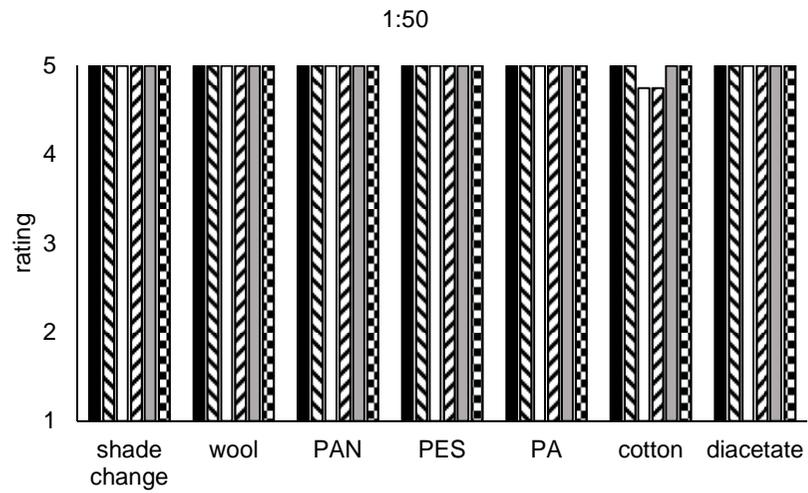
941 The findings reveal that the addition of inorganic electrolyte such as NaCl or Na<sub>2</sub>SO<sub>4</sub> to a reactive  
942 dye dyebath and reducing the liquor ratio employed for immersion dyeing have the same result,

943 namely that of encouraging dye aggregation in the dyebath, which reduces the solubility of the direct  
944 dye in the dyebath, which, in turn, increases the effective concentration gradient between the  
945 amount of dye in the dyebath and fibre phases, resulting in increased dye uptake.

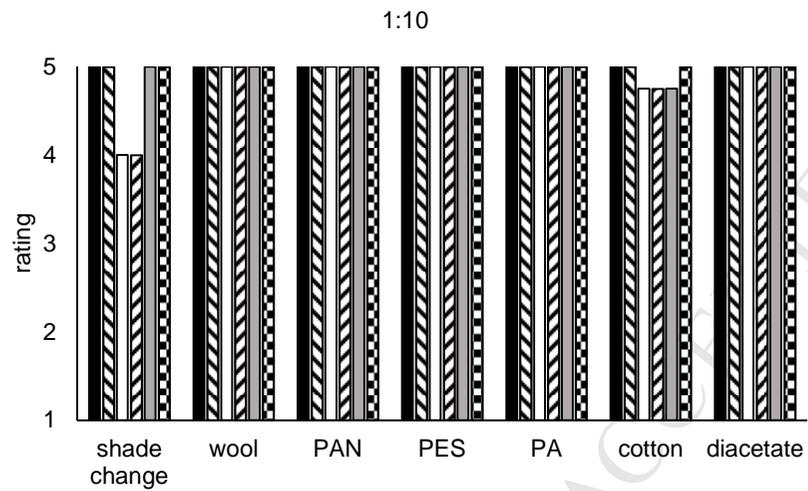
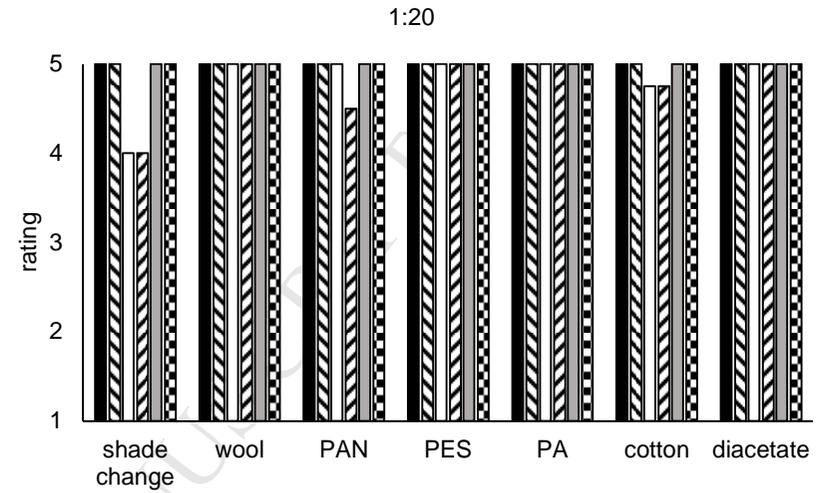
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947 As such, these findings concur with the theoretical models (7) that were proposed to explain the  
948 roles of added NaCl or Na<sub>2</sub>SO<sub>4</sub> as well as reduced liquor ratio, on the adsorption of commercial  
949 grade reactive dyes on cotton.

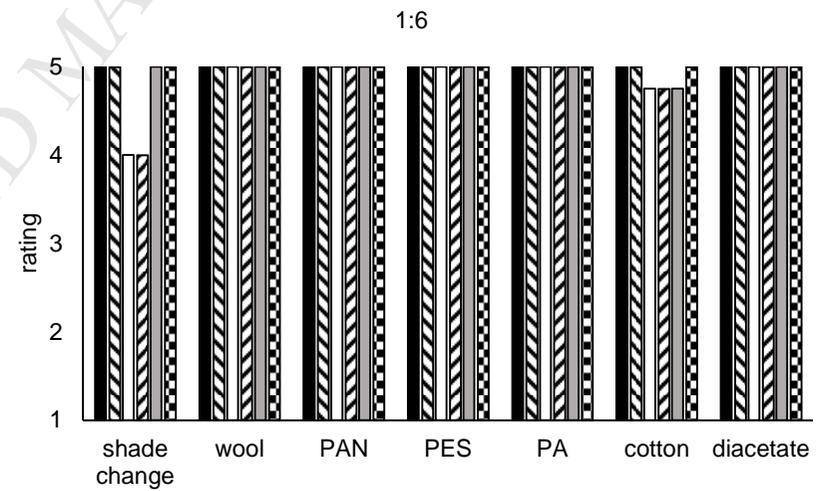
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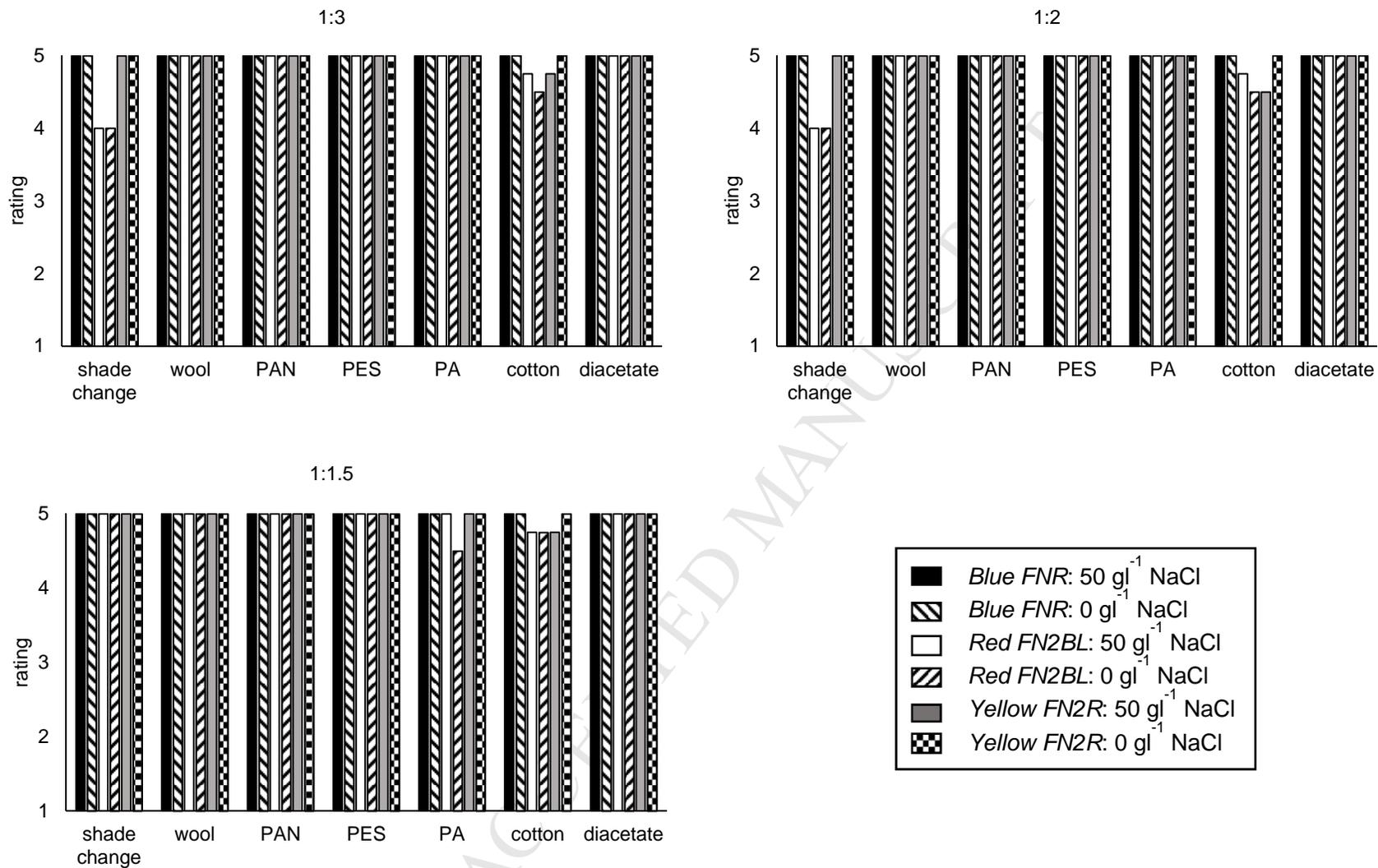


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Figure 17 fastness of dyeings to ISO 105:C06/C2S (60°C)

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