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Recycling of Exhausted Reactive Dyebaths

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ABSTRACT

The recycling of exhausted dyebaths offers the potential of reduced dyeing costs by lowering the consumption of water, chemicals and energy as well as by reducing waste treatment costs. If the residual dye in the exhausted dyebath is to be reused by reconstitution of the dyebath with fresh dye, the dyeing behaviour of the residual dye should, ideally, be identical to that of the fresh dye. In the case of the reactive dyeing of cotton, the exhausted dyebath was found to contain both hydrolysed and reactive dye; the dyeing behaviour of the residual dye in the exhausted reactive differed from that of the fresh reactive dye.

INTRODUCTION

The considerable rationalisation of dyeing processes that has occurred in recent years has been directed towards increasing productivity and reducing costs. In the latter context, since energy costs are intimately linked to water usage,[1] attention has focussed on reducing the amount of water used in dyeing. Short liquor ratio batchwise exhaust dyeing methods are now widely employed, the low liquor ratios serving to lower costs by reducing the amounts of water and chemicals used as well as reducing the energy consumed in liquor circulation and heating. However, increasing environmental legislation over recent years has led to an increase in dyeing costs; it can be anticipated that such waste management costs will continue to increase as discharge limits become increasingly severe. Recently, it has been estimated[2] that effluent treatment costs incurred for the batchwise

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reactive dyeing of cotton are virtually identical to the cost of the water used in dyeing.

Since, at the end of dyeing, the residual dyebath will contain un-exhausted dye, auxiliaries and electrolytes, it is possible that if the concentration of the various components of the exhausted dyebath could be adjusted to their required strengths, the residual dyebath could be reused. Such recycling of exhausted dyebaths further offers the potential of lowering costs through the reduction of the amounts of water, chemicals and energy consumed; the reductions in water and chemical usage will also serve to reduce effluent treatment costs.

Two approaches can be made concerning the residual dye in exhausted dyebaths. Firstly, the residual dye can be reused in subsequent dyeing; for this, the concentration of dye in the exhausted dyebath must be determined and, during reconstitution of the dyebath prior to subsequent dyeing, the dye concentration increased to the desired level using fresh dye. However, with this approach, if it is intended to reuse the residual dye in subsequent dyeing (i.e. to dye a substrate with the residual dye), it is necessary that the dyeing behaviour and fastness characteristics of the residual dye do not differ from those of fresh dye. Whilst this prerequisite may be satisfied for some dye–fibre systems (e.g. non-metallised acid–nylon and direct–cotton), this is unlikely to be the case for reactive dyes on cotton, owing to the well-known propensity of the dyes to undergo hydrolysis during dyeing. Thus, an alternative approach to reusing dye in dyebath recycling is to remove the dye from the exhausted dyebath prior to subsequent dyeing; various techniques for decolourising dyebaths for reuse in dyeing have been described, including reverse osmosis,[3] ozonolysis[4,5] and charged ultrafiltration.[6]

The purpose of the research project from which this paper is taken is to investigate the feasibility of reusing the exhausted reactive dyebath obtained at the end of dyeing of cotton. This paper concerns the results of a preliminary study of the dyeing behaviour of four residual, commercial, Procion H-E (Zeneca) dyes.

EXPERIMENTAL

Materials

A sample of bleached, unmercerised woven cotton (124 g m^{-2}) was used. Each of the four commercial reactive dyes used, namely Procion Red H-E3B (CI Reactive Red 120), Procion Red H-E7B (CI Reactive Red 141), Procion Red H-EXL (CI Reactive Red 58) and Procion Green H-E4BD (CI Reactive Green 19), were generously supplied by Zeneca Specialties Plc; the structure of only one of the dyes, CI Reactive Red 120 (Fig. 1),

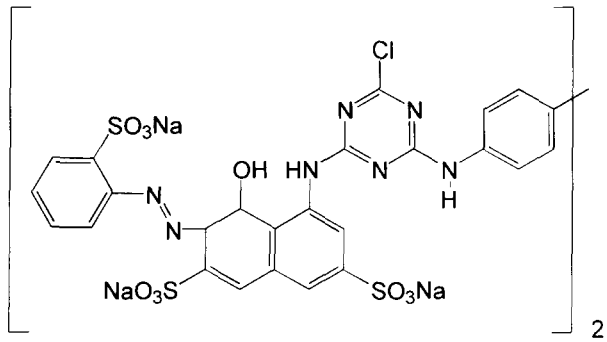


Fig. 1. Structure of CI Reactive Red 120.

is disclosed in the Colour Index.[7] All other chemicals used were of laboratory grade.

Procedures

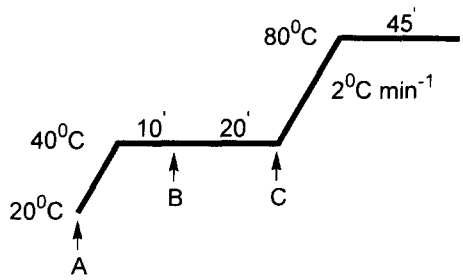
Dyeing

Three sets of dyeings were carried out for each dye, namely a *standard* dyeing, a *residual* dyeing using the residual dyebath obtained from the standard dyeing, and also a *facsimile* dyeing using fresh dye at the same concentration as that employed in the residual dyeing. All dyeing were carried out in sealed, stainless steel dyeing tubes of 250 cm^3 capacity housed in a Roaches fluidised bed laboratory-scale dyeing machine using a liquor ratio of 20:1.

(i) Standard dyeing. In order to minimise errors which would arise during dilution of the concentrated residual dyebaths, dyeings were carried out at 0·1 and 0·2% omf in the cases of CI Reactive Red 120, CI Reactive Red 141 and CI Reactive Red 58, and at 0·3, 0·4 and 0·5% omf in the case of CI Reactive Green 19, using the method shown in Fig. 2.

(ii) Residual dyeing. The residual dyebath obtained from the standard dyeing was allowed to cool to ambient temperature and neutralised by the addition of concentrated sulphuric acid. The volume of the neutralised dyebath was made up to 200 cm^3 using 50 g l^{-1} aqueous sodium sulphate, transferred to a dyeing tube, and dyeing was carried out without the addition of further dye using the method shown in Fig. 3.

(iii) Facsimile dyeing. The dyebath comprised fresh dye at a concentration equal to that of the corresponding residual dyeing; dyeing was carried out using the method shown in Fig. 2. At the end of each dyeing, the dyed sample was removed from the dyebath and excess dye liquor squeezed from the sample into the dyebath; the dyed sample was then dried in a circulating hot-air oven at 40°C.



A Fabric (10g)
Dye

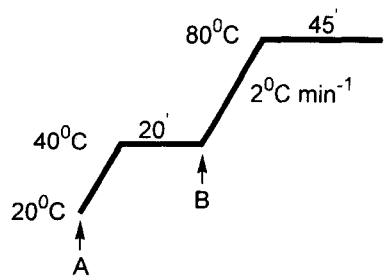
B Na_2SO_4 (10g)

C Na_2CO_3 (4g)

Fig. 2. Standard and facsimile dyeing methods.

Determination of dyebath exhaustion

At the end of each dyeing, the dyebath was allowed to cool to ambient temperature and neutralised by the addition of concentrated sulphuric acid. The neutralised dyebath was then transferred to a 200 cm^3 graduated flask and the volume made up using 50 g l^{-1} aqueous sodium sulphate. A 10 cm^3 aliquot was taken and centrifuged for 10 min at 3500 rpm in a Gallenkamp laboratory centrifuge to remove any particles from the solution that might interfere with subsequent absorbance measurements. The absorbance of the solution at the λ_{max} appropriate to each dye



A Fabric (10g)

B Na_2CO_3 (4g to pH 10)

Fig. 3. Residual dyeing method.

(CI Reactive Red 120, 520 nm; CI Reactive Red 141, 520 nm; CI Reactive Red 58, 546 nm; CI Reactive Green 19, 630 nm) was then measured using 1 cm path length quartz cells housed in a Uvikon 860 UV/Visible spectrophotometer. The concentration of dye that corresponded to the measured absorbance value was calculated by reference to the extinction coefficient of the dye obtained from a calibration plot of the dye in water. The percentage dyebath exhaustion (%E) was calculated using eqn (1) where A_1 and A_2 are the absorbances of the dyebath before and after dyeing, respectively.

$$\%E = [1 - (A_2/A_1)] \times 100 \quad (1)$$

Determination of dye fixation

This was carried out by stripping unfixed dye from each of the dry dyeings using a 20% aqueous pyridine solution at 100°C and a liquor ratio of 50 : 1. This stripping treatment was carried out repeatedly until no further dye was removed. The reflectance of the dry, dyed samples over the range 400–700 nm, both before and after pyridine extraction, was measured using a Macbeth 2020+ spectrophotometer interfaced to a Digital Rainbow PC under illuminant D_{65}, with UV component excluded, specular component excluded using a 10° standard observer. Each sample was folded twice so as to present a total of 4 layers of fabric; a total of four measurements was made of each sample and the average reflectance of these measurements taken. The K/S values were calculated from the reflectance values obtained, from which the depth of shade of each dyeing was calculated as the average of the sum of the K/S values over the range 400–700 nm. The percentage fixation (%F) of the dye adsorbed was calculated using eqn (2) where K_1/S_1 and K_2/S_2 are the K/S values of the dyed sample before and after stripping, respectively.

$$\%F = [(K_2/S_2)/(K_1/S_1)] \times 100 \quad (2)$$

RESULTS AND DISCUSSION

In order to reconstitute an exhausted dyebath, knowledge of the concentration of residual dye, auxiliaries and electrolytes is necessary. In this work, the concentration of residual dye in the exhausted standard dyebath was determined spectrophotometrically; no attempt was made to determine the ionic strength of the exhausted standard dyebath. Prior to reuse in the residual dyeings, the exhausted standard dyebath was neutralised using sulphuric acid so that the subsequent residual dyeing commenced at pH 7. The volume of water lost by fibre retention and evaporation

TABLE 1
Dye Exhaustion (%*E*) and Fixation (%*F*) Obtained for the Three Dyeing Methods

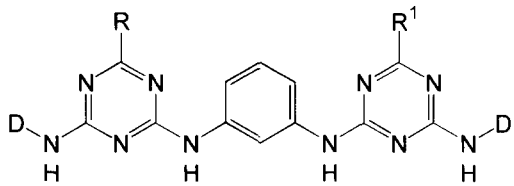
	% *omf*	*Standard dyeing*		*Facsimile dyeing*		*Residual dyeing*	
		%*E*	%*F*	%*E*	%*F*	%*E*	%*F*
CI Reactive Red 120	0·1	88·0	46·1	94·1	58·0	48·5	69·2
	0·2	86·6	52·8	93·3	54·4	48·9	61·4
CI Reactive Red 141	0·1	89·0	57·0	89·9	74·1	46·3	79·6
	0·2	91·4	47·5	91·3	74·2	42·9	79·2
CI Reactive Red 58	0·1	90·0	54·3	89·0	47·6	85·0	32·2
	0·2	89·0	50·6	94·0	43·3	87·0	22·1
CI Reactive Green 19	0·3	94·6	49·2	94·8	62·9	85·8	38·1
	0·4	94·9	48·8	91·3	47·5	87·1	22·7
	0·5	95·6	51·6	94·6	44·4	84·9	21·3

during the standard dyeing was replenished using an appropriate volume of 50 g l^{-1} aqueous sodium sulphate.

Table 1 shows, for each of the four dyes under consideration, the percentage exhaustion and percentage fixation achieved. In the case of the standard dyeings, a high level of dyebath exhaustion was obtained, ranging from 86·6–95·6%, and dye fixation varied from 46·1% to 57%; these values are typical for such bis(monochlorotriazinyl) dyes on cotton.

Before discussing the results obtained for the dyeings carried out from the residual dyebaths, the data obtained from the facsimile dyeings will be considered. As previously stated, the facsimile dyeings were carried out using fresh reactive dye at a concentration that was identical to that of the residual dye present in the exhausted standard dyebaths. Thus, since the same dye and dyeing methods were used for both the facsimile and standard dyeings, the only difference between the two dyeings was the concentration of fresh dye used. Consequently, it can be proposed that relatively small differences should have occurred between the extents of dye exhaustion and fixation achieved for the standard and facsimile dyeings. This was indeed found (Table 1) with respect to dyebath exhaustion, although the extents of dye fixation secured for the facsimile dyeings were, for CI Reactive Reds 120 and 141, slightly greater than those obtained for the respective standard dyeings. Nevertheless, the results in Table 1 clearly indicate that for each of the four dyes used, the level of dyebath exhaustion and fixation obtained for the facsimile dyeings were comparable to those secured for the standard dyeings.

In the case of the residual dyeings, three species of dye could be present



*bis*chloro: R,R^1=Cl
*bis*hydroxy: R,R^1=OH
*mono*chloro, *mono*hydroxy: R=Cl, R^1=OH

Fig. 4. Species of dye present in residual dyebath.

within the residual dyebath, namely bischloro, bishydroxy and monochloro, monohydroxy (Fig. 4). Furthermore, each of these three species can be considered to be substantive towards cotton, and therefore, when dyeing was carried out using the dye in the residual dyebath, each of these three dye species could be adsorbed onto the substrate. However, in view of the well known meritorious effect of dye–fibre reaction on substantivity, the three species of dye can be expected to possess different substantivity towards the substrate. If only unreactive, hydrolysed (i.e. bishydroxy) dye was present in the residual dyebath, then although this species would exhaust onto the substrate (recent work has confirmed the substantivity of this dye towards cotton), none would become fixed; in contrast, if reactive (i.e. bischloro and/or monochloro, monohydroxy) dye was also present in the residual dyebath, fixation would occur during subsequent dyeing. The fixation values obtained for the residual dyeings (Table 1) clearly demonstrate that reactive dye was present in each of the exhausted dyebaths.

If it is tacitly assumed that the fresh, original dye comprised only bischloro dye, and if only bischloro dye were present in the residual dyebath, the extents of dye exhaustion and fixation achieved for the residual dyeings should have compared well with those obtained for the facsimile dyeings which were carried out using fresh and thus only bischloro dye. However, Table 1 shows that for each of the four dyes under consideration, the extents of dyebath exhaustion obtained for the residual dyeings were lower than those achieved for the corresponding facsimile dyeings, and that for CI Reactive Reds 120 and 141 this difference in exhaustion between the residual and facsimile dyeings was of the order of 50%. Table 1 also shows that whilst the extents of fixation of CI Reactive Red 58 and CI Reactive Green 19 achieved for the residual dyeings were about 50% lower than the corresponding facsimile dyeings, the fixation of the two remaining dyes was slightly higher in the case of the residual

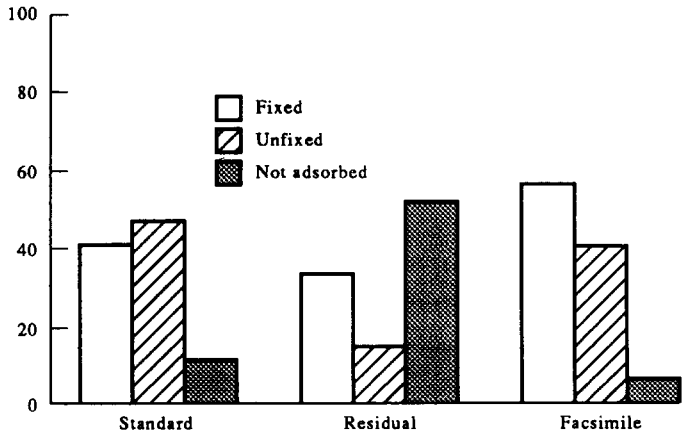


Fig. 5. Percentage of total CI Reactive Red 120 applied (0·1% omf standard dyeing).

dyeings. Clearly, these differences in exhaustion and fixation observed for the residual and facsimile dyeings demonstrate that the composition of the residual dye differs from that of the original fresh dye, and therefore if the fresh dye comprised only bischloro dye, the residual dyebath, as expected, contained species other than bischloro dye.

Figures 5–13 show the percentage of the total amount of each dye applied during the standard, residual and facsimile dyeings that was fixed, unfixed and not adsorbed onto cotton. It is apparent that for the standard dyeings of all four dyes used, the proportion of unadsorbed dye was low (about 10%) and the amount of fixed dye was roughly equal to the amount of unfixed dye. However, although for the facsimile dyeings of each of the four dyes the proportion of unadsorbed dye was low and

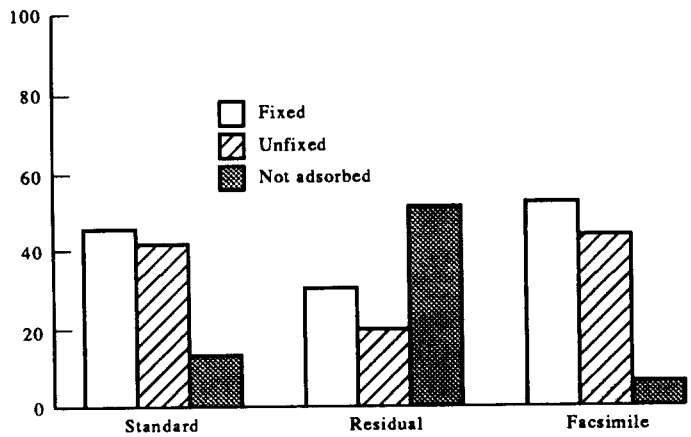


Fig. 6. Percentage of total CI Reactive Red 120 applied (0·2% omf standard dyeing).

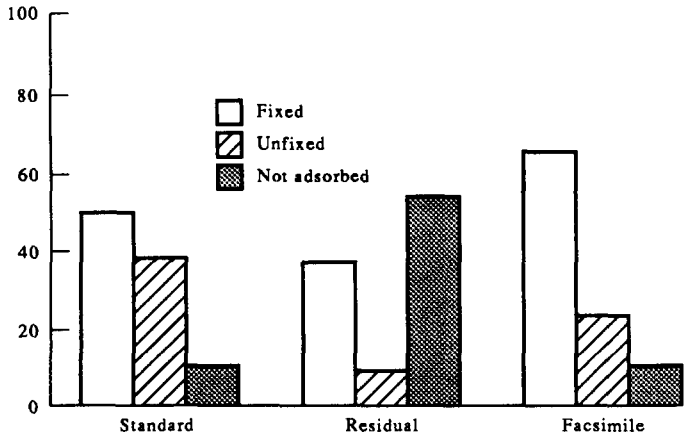


Fig. 7. Percentage of total CI Reactive Red 141 applied (0·1% omf standard dyeing).

thus these dyeings were similar in this context to the standard dyeings, the amount of fixed dye was markedly greater than the amount of unfixed dye in the cases of CI Reactive Reds 120 and 141, as well as for the 0·3% omf dyeing of CI Reactive Green 19; in contrast, the amount of unfixed dye was greater than fixed dye for CI Reactive Red 58 and the other two concentrations of the green reactive dye.

For each of the four dyes under consideration, at each of the various dye concentrations employed for the standard dyeings, the amount of dye that was adsorbed from the residual dyebaths and fixed to the substrate was lower than that achieved for the respective standard and facsimile dyeings (Figs 5–13). This can be attributed to a lower concentration of reactive dye in the residual dyebaths, resulting from hydrolysis or some

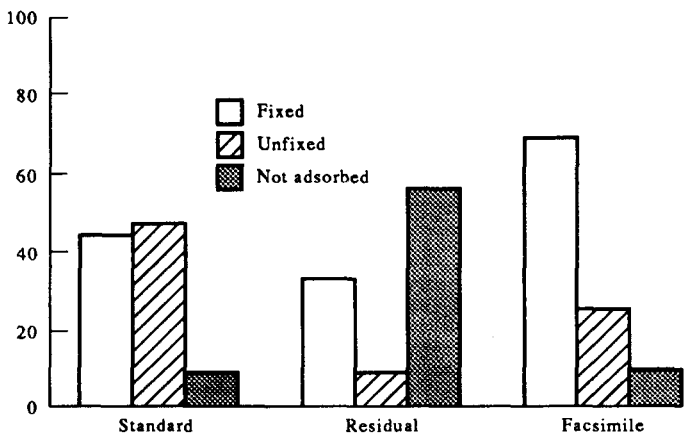


Fig. 8. Percentage of total CI Reactive Red 141 applied (0·2% omf standard dyeing).

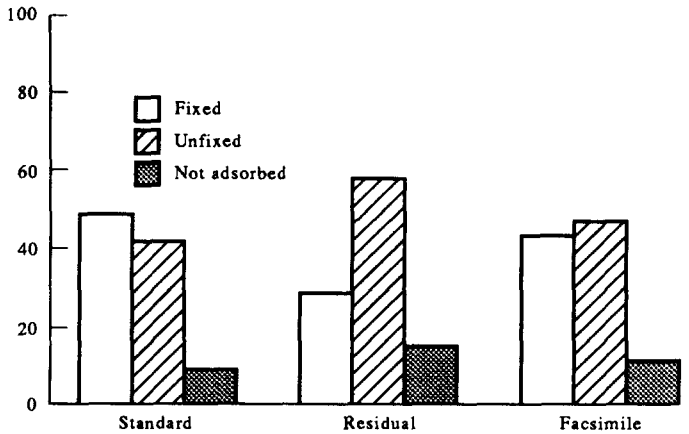


Fig. 9. Percentage of total CI Reactive Red 58 applied (0·1% omf standard dyeing).

other inactivation of the reactive dye having occurred during the previous standard dyeing. In the cases of the residual dyeings obtained for CI Reactive Red 58 and CI Reactive Green 19, the very high proportion of unfixed dye, together with the very low extent of dye fixation achieved (Figs 9–13), implies that the residual dyebaths of these two particular dyes contained a high proportion of non-reactive dye, which, in turn, suggests that during the previous standard dyeing, these two dyes underwent a high degree of hydrolysis. In contrast, the lower amount of unfixed dye achieved for CI Reactive Reds 120 and 141 suggests that the residual dyebaths of these two dyes contained a lower proportion of non-reactive dye and, therefore, that the two dyes possibly underwent a lesser degree of hydrolysis during the standard dyeing.

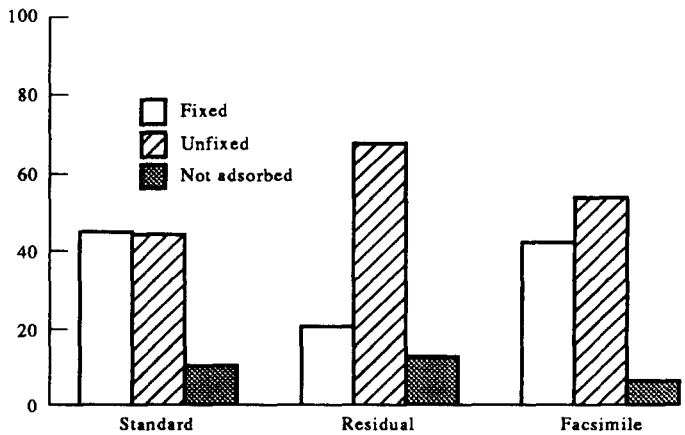


Fig. 10. Percentage of total CI Reactive Red 58 applied (0·2% omf standard dyeing).

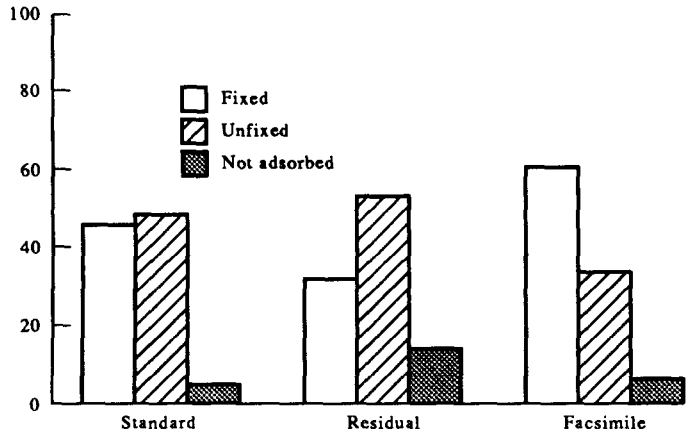


Fig. 11. Percentage of total CI Reactive Green 19 applied (0·3% omf standard dyeing).

These findings, together with those displayed in Table 1, clearly show that for each of the four dyes used, the respective residual dyebaths contained dye that is both substantive towards cotton and also reactive. However, it is apparent from Figs 5–13 that for each of the four dyes used, and at each of the dye concentrations employed for the standard dyeings, the amount of dye that was not adsorbed from the residual dyebaths onto the substrate was higher than that achieved for the respective standard and facsimile dyeings, this effect being especially marked in the cases of CI Reactive Reds 120 and 141. The reasons for this low extent of dye exhaustion observed for the residual dyeings, which in the cases of CI Reactive Reds 120 and 141 amounted to less than 50%, are as yet unclear. As previously mentioned, the residual dyebath can be expected

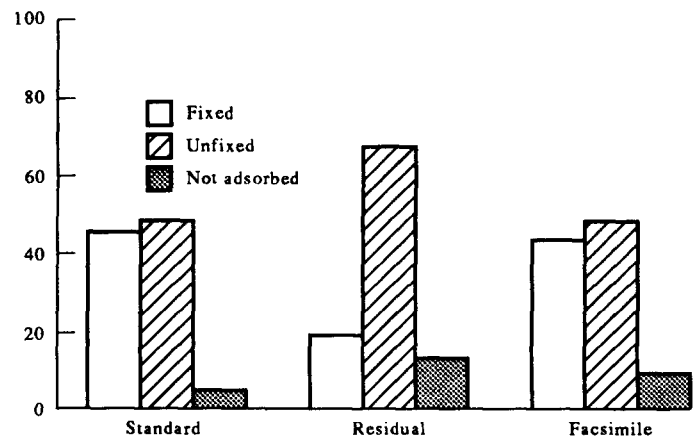


Fig. 12. Percentage of total CI Reactive Green 19 applied (0·4% omf standard dyeing).

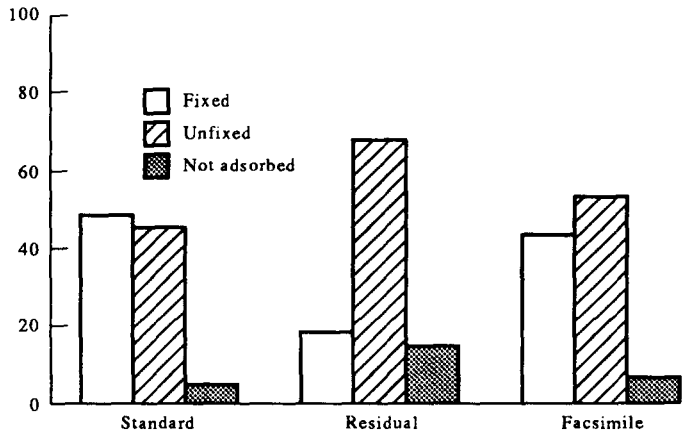


Fig. 13. Percentage of total CI Reactive Green 19 applied (0·5% omf standard dyeing).

to contain three species of dye, each of which can be expected to be substantive towards cotton. The low extent of dye fixation secured for the residual dyeings of the four dyes under consideration can, as discussed above, be attributed to the residual dyebaths containing a reduced proportion of reactive dye as a result of hydrolysis having occurred during prior standard dyeing; this reasoning would also explain the observed high proportion of unfixed dye obtained for the residual dyeings of CI Reactive Green 19 and CI Reactive Red 58. However, the presence in the residual dyebath of a high proportion of hydrolysed reactive dye does not explain the very high amount of dye that was not adsorbed onto the substrate, and therefore an alternative explanation is sought.

Studies using HPLC, CZE and mass spectroscopy are currently being carried out to determine both the nature and proportion of the various coloured species present within the residual dyebaths, in an attempt to explain the results obtained for the residual dyeings. However, it is considered worthwhile to record observations which were made during the work described and which are currently being investigated, that may be of interest in this matter.

As recounted above, prior to spectroscopic analysis the exhausted dyebaths obtained from the standard dyeings were centrifuged to remove particles that would interfere with the absorbance measurements. Indeed, it was found that at the end of the standard dyeing the exhausted dyebath was slightly turbid and the presence of particulate matter was clearly evident. Filtration of the exhausted dyebaths resulted in a small proportion of a coloured residue. Scanning electron and optical microscopic investigation of this residue showed the presence of coloured and uncoloured

fibres and 'fibrils' as well as particles. It is well known that during the dyeing of e.g. wool and polyester, oligomers can diffuse out of the fibre. Whilst the crystalline oligomers obtained from polyester are not dyed with disperse dyes, the low relative molecular mass (M_r) fractions that diffuse out of wool are reactive dyeable.[8] Consequently, it may be possible that during reactive dyeing, in addition to the small fibres and 'fibrils' that are released from the cotton and which may be dyed, low M_r cellulosic fractions are also released into the dyebath and dyed. Such low M_r fractions may not be visible and were not removed by the centrifuging employed in this work. It is possible that if such dyed, low M_r fractions were present within residual dyebaths, they may have exhibited reduced substantivity towards cotton, or low diffusional characteristics within the substrate, which might thus explain the high extent of unadsorbed dye and low dye fixation observed for the residual dyeing. The nature of the coloured and uncoloured particles within the exhausted dyebaths may be due to size being removed from the cotton during dyeing. This particular aspect of the work, together with the possible release of low M_r fractions during the reactive dyeing of cotton in the context of the results presented above, requires much further examination; however, the nature and extent of the products released from cotton during dyeing with reactive dyes is of potential significance in terms of the reuse of reactive dyebaths.

CONCLUSIONS

The residual dyebaths contain both hydrolysed and reactive dye. For each of the four dyes under consideration, the exhaustion and fixation behaviour of the dye in the residual dyebaths bears little similarity to that secured for either the standard or facsimile dyeings; the results demonstrate that differences exist between the four dyes used in terms of the exhaustion and fixation behaviour of the coloured species present in their residual dyebaths. Thus, the reuse of reactive dyebaths is, as expected, not straightforward; whilst the presence of reactive and unreactive dye in the exhausted dyebath may not, initially, appear especially problematic, the differences in dyeing behaviour observed between the dye in the residual dyebath and fresh reactive dye may be of significance in the context of the reuse of reactive dyebaths. Current work that concerns the identification of the various coloured species present in exhausted reactive dyebaths as well as the substantivity and fixation characteristics of these species will provide much needed information relating to the feasibility of recycling of exhausted reactive dyebaths.

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