ELSEVIER

Dyes and Pigments, Vol. 27, No. 3, pp. 169–182, 1995

0143-7208/95 $9.50 + 0.00

0143-7208(94)00052-2

A Study of the Dyeing of Cotton with Commercial Dichlorotriazinyl Reactive Dyes

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(Received 6 July 1994; accepted 10 August 1994)

ABSTRACT

The extent of fixation of six dichlorotriazinyl dyes on cotton, achieved using four commercially recommended dyeing methods, was determined. The extent of dye fixation was enhanced by modifying one of the four recommended dyeing methods, this being achieved using either pH 8 or pH 9 buffer, instead of $NaHCO_3$ used in the particular (all-in bicarbonate) recommended dyeing method.

INTRODUCTION

Dichlorotriazinyl reactive dyes, as exemplified by the *Procion MX* (Zeneca) range of dyes used in this work, were introduced for the dyeing of cellulosic fibres in 1956. The dyes are characterized by their high reactivity and bifunctionality, which permits the dyes to be applied to cellulosic substrates at both low (30–50°C) and high (80°C) temperatures. Indeed, in the case of *Procion MX* dyes, four dyeing methods are recommended for their application to cellulosic fibres, two of which are carried out at 30°C, one at 50°C and the remaining one at 30/80°C.[1]

The exhaustion dyeing of cellulosic fibres with all types of reactive dyes suffers from a major disadvantage, namely that during dyeing the dye can react not only with the fibre nucleophile (cellulosate anion) but also with nucleophiles (commonly hydroxyl ions) present in the dyebath; such hydrolysis of the reactive dye reduces the efficiency of dye–fibre

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reaction (fixation) and results in dye wastage, the need to thoroughly wash-off reactive dyeings, and effluent problems.

The purpose of this work was to determine whether the extent of fixation of typical commercial *Procion MX* dyes on cotton could be improved by modifying the recommended application methods.

EXPERIMENTAL

Materials

Fabric

Scoured and bleached, fluorescent brightener-free woven cotton was used.

Dyes and auxiliaries

Commercial samples of Procion Blue MX-G (CI Reactive Blue 163), Procion Blue MX-2G 125 (CI Reactive Blue 109), Procion Red MX-5B (CI Reactive Red 2), Procion Red MX-8B (CI Reactive Red 11), Procion Yellow MX-3R (CI Reactive Orange 4) and Procion Yellow MX-4R (CI Reactive Orange 14), each supplied by Zeneca Specialities, were employed. A sample of Sandozin NIE was supplied by Sandoz (UK).

All other reagents were of AnalaR grade.

Procedures

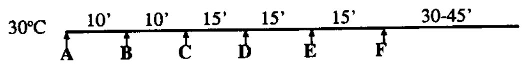
Dyeing

Four dyeing methods, each recommended by Zeneca Specialities,[1] were used, namely a standard method, low alkali method, bicarbonate/soda ash method and an all-in bicarbonate method (Fig. 1); a summary of the conditions employed for each of these four dyeing methods is given in Table 1. In addition, 12 other dyeing methods were employed, each being based on the Zeneca all-in bicarbonate method; the conditions used for each of these additional dyeing methods are displayed in Table 1. Each of the dyes was applied at both 2% and 4% omf.

Measurement of dyebath exhaustion (%E)

At the end of dyeing, the dyed fabric was squeezed to return surplus dye liquor to the dyebath and the dyebath then allowed to cool to room temperature. The absorbance of an appropriately diluted aliquot of the cool, residual dyebath was measured using a Philips PU 8700 spectrophotometer at the λ_{max} of the dye and, by reference to the absorbance of

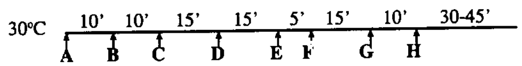
(a) *Standard method*



Having prepared the dyebath and set the pH to below 7:

A	Dye	2 or 4% omf
B	NaCl	2.5 gl^{-1}
C	NaCl	7.5 gl^{-1}
D	NaCl	25 gl^{-1} (35 gl^{-1})
E	Dissolved Na_2CO_3	0.2 gl^{-1} (0.4 gl^{-1})
F	Dissolved Na_2CO_3 slowly	3.8 gl^{-1} (7.6 gl^{-1})

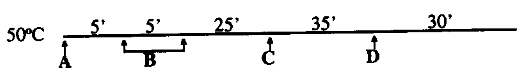
(b) *Low alkali method*



Having prepared the dyebath and set the pH to below 7:

A	Dye	2 or 4% omf
B	NaCl	2.5 gl^{-1}
C	NaCl	7.5 gl^{-1}
D	NaCl	25 gl^{-1} (35 gl^{-1})
E	Dissolved Na_2CO_3	0.125 gl^{-1} (0.175 gl^{-1})
F	Dissolved Na_2CO_3	0.125 gl^{-1} (0.175 gl^{-1})
G	Dissolved NaOH	0.125 gl^{-1} (0.2 gl^{-1})
H	Dissolved NaOH	0.125 gl^{-1} (0.2 gl^{-1})

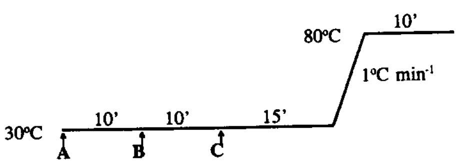
(c) *Bicarbonate/Soda Ash method*



Having prepared the dyebath and set the pH to below 7:

A	Dye	2 or 4% omf
B	NaCl over 5 minutes	40 gl^{-1}
C	Dissolved $NaHCO_3$	2 gl^{-1} (3.5 gl^{-1})
D	Dissolved Na_2CO_3	6 gl^{-1} (10 gl^{-1})

(d) *'All-in' bicarbonate method*



A	Na_2CO_3 dissolved	5 gl^{-1} (5 gl^{-1})
B	dye	
C	NaCl	75 gl^{-1} (90 gl^{-1})

Fig. 1. Dyeing methods (figures in brackets refer to 4% omf dye).

TABLE 1
Application Conditions Used

Dyeing method	*Temperature (°C)*		*Time (min)*		*pH adjustment*
	Initial	*Final*	*Initial temperature*	*Final temperature*	
1[a]	30	80	35	15[e]	$NaHCO_3$
2[b]	30	30	120	—	Na_2CO_3/NaOH
3[c]	50	50	120	—	Na_2CO_3/$NaHCO_3$
4[d]	30	30	120	—	Na_2CO_3
5	40	80	35	15[e]	$NaHCO_3$
6	40	85	35	15[e]	$NaHCO_3$
7	30	80	35	15[e]	pH 8 buffer[f]
8	40	85	35	15[e]	pH 9 buffer[f]
9	30	90	35	15[e]	pH 9 buffer[f]
10	50	85	35	15[e]	pH 8 buffer[f]
11	30	80	35	15[e]	pH 9 buffer[f]
12	40	80	35	15[e]	pH 9 buffer[f]
13	45	85	35	15[e]	pH 8 buffer[f]
14	45	85	35	15[e]	pH 9 buffer[f]
15	45	98	35	15[e]	pH 9 buffer[f]
16	45	130	35	15[e]	pH 9 buffer[f]

[a] All-in bicarbonate method.
[b] Low alkali method.
[c] Bicarbonate/soda ash method.
[d] Standard method.
[e] Dyebath temperature raised to top temperature at 1°C min^{-1}.
[f] Phosphate buffer.

the dyebath prior to dyeing, the percentage exhaustion of the dyebath (%E) was calculated using eqn (1).

$$\%E = \frac{A_1 - A_2}{A_1} \times 100 \qquad (1)$$

where A_1 and A_2 are the absorbances of the dyebath before and after dyeing, respectively.

Determination of dye fixation (%F)
At the end of dyeing, the dyed fabric was cut into two pieces; one piece was allowed to dry in the open air and the other piece was treated in an aqueous solution containing 5 g l^{-1} Sandozin NIE and 2·5 g l^{-1} Na_2CO_3, using a 50 : 1 liquor ratio at 98°C for 30 min and finally rinsed thoroughly in tap water before being allowed to dry in the open air. The colour

strength (K/S) of each of the two dry, dyed samples was measured using the procedure described below and the extent of fixation achieved was calculated using eqn (2).

$$\%F = \frac{K_1/S_1 - K_2/S_2}{K_1/S_1} \times 100 \quad (2)$$

where K_1/S_1 and K_2/S_2 are, respectively, the colour strengths of the unwashed and washed dyed samples.

Determination of the total dye fixation (%T)
This was calculated using eqn (3):

$$\%T = \frac{\%E}{100} \times \frac{\%F}{100} \times \%\ \text{omf dye applied} \quad (3)$$

Colour measurement
The reflectance value of each dry, dyed sample was measured using a Macbeth 2020 spectrophotometer interfaced to a Digital PC under illuminant D_{65}, with specular component excluded, UV component included and using a 10° standard observer. The fabric sample was folded such that a total of four layers of material were realized; four different measurements were made on the same side of each sample and these four measurements then averaged. The colour strength (K/S) and CIE L^*, a^*, b^*, c^* and $H°$ values were calculated from the reflectance data.

RESULTS AND DISCUSSION

Commonly, the extent of fixation of reactive dyes on cellulosic fibres is determined by 'stripping' unfixed dye from the dyed substrate using, for example, aqueous pyridine.[2] However, in this work, it was decided to treat the dyed fabrics for 30 min in a boiling, aqueous Na_2CO_3/non-ionic detergent solution to remove surplus dye from the dyed fabric. This particular technique, the conditions of which are more severe than those commonly employed in industry, was used rather than an aqueous pyridine 'stripping', as washing-off rather than 'stripping' is employed by commercial dyers. Thus, although the values of dye fixation displayed in this paper may be slightly higher than those obtained had an aqueous pyridine 'stripping' technique been used, the values are not unrealistic in commercial terms.

An initial study was made using 4% omf CI Reactive Blue 163 and the four recommended dyeing methods (labelled 1, 2, 3 and 4 in Table 1), to determine the relative effectiveness of each method in terms of the extent

TABLE 2
Data for CI Reactive Blue 163

Dyeing method	*4% omf*			*2% omf*		
	%F	*c**	*H°*	*%F*	*c**	*H°*
1	50·80	30·5	59·9	42·16	30·7	58·1
5	56·06	30·4	61·3	—	—	—
6	58·02	29·9	63·7	—	—	—
2	59·29	31·6	63·8	50·36	30·3	59·2
3	62·11	31·2	63·3	53·06	30·6	58·6
7	65·77	32·1	68·1	—	—	—
8	66·16	32·4	68·3	—	—	—
9	67·14	32·1	67·7	—	—	—
4	68·69	30·7	64·7	50·99	30·9	60·6
10	69·95	32·1	66·2	—	—	—
11	71·17	32·3	68·4	—	—	—
12	75·44	31·2	68·9	—	—	—
14	63·89	32·0	67·9	63·90	32·2	64·7
16	75·89	30·9	74·7	70·37	30·3	53·9
13	76·55	30·7	60·3	—	—	—
15	86·05	30·9	71·3	81·05	31·9	64·1

of dye fixation (%F) achieved after wash-off; in this part of the study, dyebath exhaustion was not determined. It is evident from the results shown in Table 2 that of the four recommended dyeing methods used, the highest extent of dye fixation was secured using the standard method (4) whilst lowest fixation was achieved using the all-in bicarbonate method (1). As previously mentioned, CI Reactive Blue 163 is bifunctional and therefore capable of reacting with the substrate at both low (30–50°C) and high (80–85°C) temperatures. Thus, in the cases of the low-alkali and standard dyeing methods, in which the dye is applied at 30°C, as well as the bicarbonate/soda ash method which utilizes an application temperature of 50°C, it can be assumed that the dye will react monofunctionally with the fibre; in the case of the all-in bicarbonate method, however, the dye will react bifunctionally as in this particular method, the dye is applied first at low (30°C) and then at high (80°C) temperature. Since, theoretically at least, bifunctional reaction should result in higher dye–fibre fixation, the finding that the all-in bicarbonate method yielded lowest fixation of CI Reactive Blue 163 (Table 2) was surprising. Thus, it was decided to investigate whether the effectiveness of this particular dyeing method could be enhanced; for this, a series of dyeing methods were employed that were based on the all-in bicarbonate method but in which the temperature and pH of application were varied.

In this context, the results obtained for methods 5 and 6 in Table 2 show that an increase in both the initial and the final application temperatures increased the extent of fixation of 4% omf CI Reactive Blue 163. The results secured using method 7, in which the recommended temperatures of 30°C and 80°C were employed but pH 8 buffer was used instead of the recommended sodium bicarbonate, resulted in a further increase in dye fixation; in method 11, when pH 9 buffer was substituted for the pH 8 buffer used in method 7, the extent of dye fixation was further enhanced. Based on these findings, variations in the initial temperature (method 12), final temperature (method 9) and in both initial and final temperatures (methods 8, 14, 15 and 16) were carried out at pH 9 as well as variations in both initial and final temperatures (methods 10 and 13) at pH 8. From the results of these various dyeing methods (Table 2), it is apparent that the highest extent of fixation of 4% omf CI Reactive Blue 163 was secured using method 15, namely an initial temperature of 45°C and a final temperature of 98°C at pH 9. A further set of dyeings were carried out with 2% omf CI Reactive Blue 163 using each of the four commercially recommended dyeing methods as well as methods 14, 15 and 16 (Table 2) from which it is evident that, as had been found in the case of the 4% omf dyeings, the highest extent of fixation of 2% omf CI Reactive Blue 163 was secured using method 16, namely an initial temperature of 45°C and a final temperature of 98°C at pH 9.

The findings displayed in Table 2 clearly show that each of the four recommended dyeing methods varied in terms of the extent of dye–fibre fixation achieved for both 2% and 4% omf dye applied and, that of these methods, the all-in bicarbonate method yielded lowest fixation. Furthermore, it is clearly evident that the all-in bicarbonate dyeing method could be modified so as to enhance the extent of dye fixation secured; in this context, the use of an initial temperature of 45°C and a final temperature of 98°C at pH 9 enabled dye fixation to be increased from 42·2 to 81·1% in the case of the 2% omf dyeing and from 50·8 to 86·05% in the case of the 4% omf dyeing.

In view of the encouraging findings obtained using the modified dyeing methods with CI Reactive Blue 163, the study was extended to five other dyes; for this part of the work, the extents of both dyebath exhaustion (%E) and dye fixation (%F) were determined for each dyeing from which the total amount of the applied dye that was fixed (%T) was calculated. As shown by eqn (3), the %T values displayed in Tables 3–7 represent the amount of dye (expressed as % omf) applied to the fibre that was fixed; from this it follows that the higher the %T value the higher the efficiency of the dye–fibre reaction (fixation). In Tables 3–7, at each of the two concentrations of dye used, the dyeing methods have been arranged

TABLE 3
Data for CI Reactive Blue 109

Dyeing method	*2% omf*					*Dyeing method*	*4% omf*				
	%E	*%F*	*%T*	*c**	*H°*		*%E*	*%F*	*%T*	*c**	*H°*
3	55·18	63·25	0·69	21·9	65·7	10	66·96	72·49	1·94	19·9	69·9
4	66·51	67·59	0·89	21·4	64·3	1	75·10	65·91	1·98	21·2	65·9
2	68·00	72·36	0·98	21·8	65·1	14	60·78	83·17	2·02	19·1	71·9
10	74·00	66·99	0·99	21·9	65·9	4	69·87	74·32	2·08	21·4	69·9
1	73·59	67·58	0·99	21·2	62·4	2	70·84	74·86	2·12	21·4	70·7
13	75·88	72·47	1·09	21·1	66·3	16	64·81	87·21	2·26	20·6	74·8
7	80·08	73·68	1·18	20·7	66·5	15	64·29	91·76	2·36	21·3	72·7
15	69·00	82·65	1·14	22·4	68·5	3	84·00	70·92	2·38	21·0	71·8
12	80·42	76·88	1·24	21·2	67·8	7	85·44	78·38	2·68	18·8	71·8
14	83·80	83·92	1·41	21·4	65·3	13	87·05	81·42	2·84	18·2	74·1
16	76·39	95·65	1·46	22·7	68·8	12	83·30	91·25	3·06	18·8	73·2

in ascending order of %T from which it is apparent that the efficacy of each dyeing method varied not only for each dye used but also for each of the two dye concentrations (2% and 4% omf) employed. In order to obtain a clearer view of the data, the 11 dyeing methods used were ranked on a scale of 1 to 11, with 1 representing that method which gave the dyeing of highest %T and 11 representing that dyeing method which imparted the lowest extent of total dye fixation. Thus, according to this ranking technique, as five dyes were involved, the highest ranking score

TABLE 4
Data for CI Reactive Orange 14

Dyeing method	*2% omf*					*Dyeing method*	*4% omf*				
	%E	*%F*	*%T*	*c**	*H°*		*%E*	*%F*	*%T*	*c**	*H°*
12	50·86	64·61	0·65	68·7	66·6	14	52·69	60·91	1·28	75·6	63·7
1	60·69	53·84	0·65	68·7	66·3	10	55·93	58·72	1·31	74·4	62·8
4	62·00	55·62	0·68	66·6	67·5	16	60·16	64·98	1·56	75·6	64·8
14	52·94	67·11	0·71	71·3	66·9	1	73·59	55·53	1·63	71·5	65·9
15	50·60	70·92	0·71	72·1	66·7	15	65·17	65·07	1·69	82·8	65·4
10	60·11	59·67	0·71	77·5	68·1	13	74·79	57·02	1·70	76·3	62·7
3	60·30	61·16	0·73	73·2	66·6	7	73·11	59·17	1·73	73·8	64·8
7	57·48	63·59	0·73	70·3	66·2	3	83·60	56·87	1·90	75·9	64·4
13	61·99	61·33	0·76	70·6	67·9	12	74·79	64·51	1·92	75·7	61·4
16	60·16	64·98	0·78	75·9	67·1	4	77·51	62·64	1·94	78·5	63·4
2	69·53	77·28	1·07	71·4	67·5	2	67·82	77·03	2·08	78·1	62·2

TABLE 5
Data for CI Reactive Orange 4

Dyeing method	*2% omf*					*Dyeing method*	*4% omf*				
	%E	*%F*	*%T*	*c**	*H°*		*%E*	*%F*	*%T*	*c**	*H°*
1	59·43	62·26	0·74	68·2	87·6	3	81·54	56·63	1·87	80·4	84·1
3	79·38	52·67	0·84	65·2	87·1	4	81·50	57·36	1·87	77·1	84·2
4	83·66	54·03	0·90	56·6	87·2	10	77·31	63·55	1·96	70·4	85·1
13	77·53	62·49	0·96	69·7	87·1	1	84·78	60·95	2·07	61·6	85·8
16	77·52	66·08	1·02	71·9	87·1	15	73·92	71·03	2·10	80·8	85·7
15	85·87	59·86	1·02	68·2	87·0	14	74·82	71·75	2·14	78·9	83·6
2	87·97	59·36	1·04	59·6	87·4	16	71·46	74·78	2·14	77·8	83·8
14	83·22	63·58	1·05	68·2	86·8	7	90·92	64·86	2·35	66·8	85·6
7	87·50	61·82	1·08	70·1	86·9	2	89·15	67·71	2·41	81·8	83·6
12	88·70	62·70	1·11	73·1	84·4	12	81·54	76·53	2·49	65·9	84·8
10	99·39	61·63	1·23	55·4	86·4	13	90·97	71·28	2·58	69·8	84·2

would be 55 and the lowest 5; obviously, the lower the ranking score the more efficient the dyeing method (i.e. the higher the %T values).

The graphical representations of this ranking are given in Figs 2 and 3 from which it is clear that for the 2% omf dyeings (Fig. 2), method 16 yielded the highest %T values for the five dyes used and, therefore, was the most efficient of the 11 dyeing methods evaluated in terms of the amount of dye applied that was fixed. Figure 2 also shows that the seven dyeing methods in which buffer was used to control dyebath pH, namely

TABLE 6
Data for CI Reactive Red 2

Dyeing method	*2% omf*					*Dyeing method*	*4% omf*				
	%E	*%F*	*%T*	*c**	*H°*		*%E*	*%F*	*%T*	*c**	*H°*
13	72·11	62·63	0·86	57·4	−1·2	4	81·28	69·54	1·13	53·6	5·5
3	73·21	63·02	0·92	49·9	3·3	1	75·50	62·11	1·87	53·8	2·1
12	90·95	54·12	0·98	58·1	−0·8	3	72·78	66·50	1·93	52·8	6·2
4	79·28	63·96	1·01	53·3	−0·3	10	74·09	68·69	2·04	56·8	1·7
14	79·68	66·11	1·05	56·1	−2·8	15	83·57	67·37	2·25	57·3	4·7
1	81·77	64·97	1·06	54·1	0·9	13	90·89	66·72	2·43	56·7	2·6
7	83·39	66·00	1·10	56·4	−2·5	16	81·71	77·16	2·52	58·8	0·6
15	82·36	68·72	1·13	57·8	0·4	7	91·70	69·64	2·56	55·6	2·5
16	82·39	74·54	1·21	56·5	−2·2	12	84·40	76·35	2·57	56·1	4·4
2	80·12	75·28	1·23	53·1	−0·6	2	86·75	79·24	2·74	54·5	4·0
10	74·09	96·78	1·43	56·3	−2·9	14	92·15	96·96	3·57	55·5	4·8

TABLE 7
Data for CI Reactive Red 11

Dyeing method	*2% omf*					*Dyeing method*	*4% omf*				
	%E	*%F*	*%T*	*c**	*H°*		*%E*	*%F*	*%T*	*c**	*H°*
3	79·35	67·20	1·06	51·1	−13·2	1	83·00	76·20	2·52	54·8	−7·7
1	76·00	79·14	1·20	53·3	−10·0	3	80·32	79·38	2·55	53·8	−4·1
2	82·34	77·25	1·27	51·7	−12·1	16	67·07	95·75	2·57	54·2	−4·1
10	79·90	80·42	1·28	53·0	−10·8	15	71·75	93·80	2·68	53·0	0·2
16	76·91	85·99	1·32	53·7	−6·4	2	85·79	83·33	2·85	51·5	−7·0
4	86·05	80·13	1·37	50·6	−11·3	10	80·72	88·81	2·86	53·4	−5·7
13	82·46	84·28	1·39	54·5	−9·5	7	85·47	86·82	2·96	52·5	−4·3
14	79·24	89·96	1·42	57·5	−8·1	4	87·95	87·66	3·07	49·8	−5·9
7	81·19	88·44	1·43	53·5	−8·7	14	82·96	95·24	3·16	52·7	−2·9
12	88·21	86·67	1·52	53·9	−7·0	13	86·54	91·68	3·17	51·9	−1·4
15	86·53	92·40	1·59	54·7	−11·1	12	87·36	97·30	3·40	51·4	−3·8

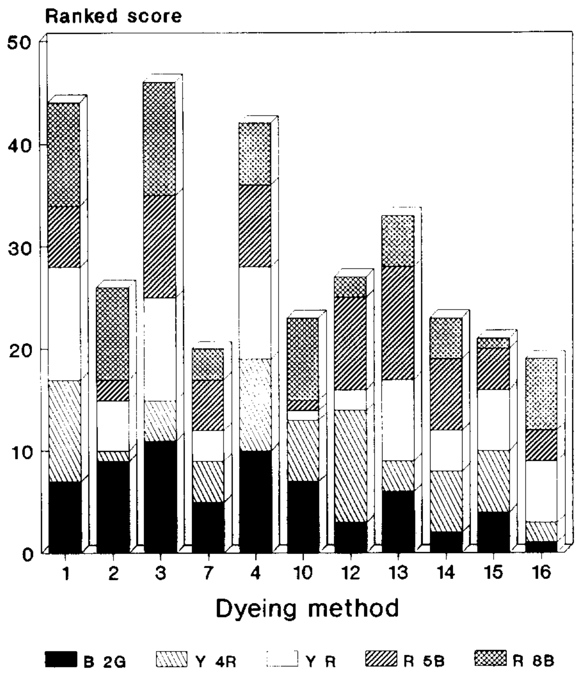


Fig. 2. Ranking of dyeing methods (2% omf dyeings).

methods 7, 10, 12, 13, 14, 15 and 16, were more efficient than the standard, bicarbonate/soda ash and all-in bicarbonate recommended dyeing methods (1, 3 and 4), but the low alkali method (2) was more efficient than two of the buffered dyeing methods (12 and 13).

In the case of the 4% omf dyeings, Fig. 3 reveals that method 12 was by far the most efficient of the 11 dyeing methods used. It is also apparent that with the exception of method 10, those dyeing methods in which buffer was used to control dyebath pH, namely methods 7, 12, 13, 14, 15 and 16, were more efficient than the standard, bicarbonate/soda ash and all-in bicarbonate recommended dyeing methods (1, 3 and 4); however, the low alkali method (2) was more efficient than five of the buffered dyeing methods (7, 10, 14, 15 and 16).

In view of the fact, as Tables 3–7 and Figs 2 and 3 reveal, that the efficacy of the 11 dyeing methods used varied for each dye used and for each of the two dye concentrations employed, the ranking scores obtained for each dye at each dye concentration were combined so as to provide Fig. 4, which shows the overall ranking of each dye method for both 2% and 4% omf dye. Clearly, method 12 yielded the highest %T values for the five dyes used at both dye concentrations and, therefore, was the most efficient of the 11 dyeing methods evaluated in terms of the amount

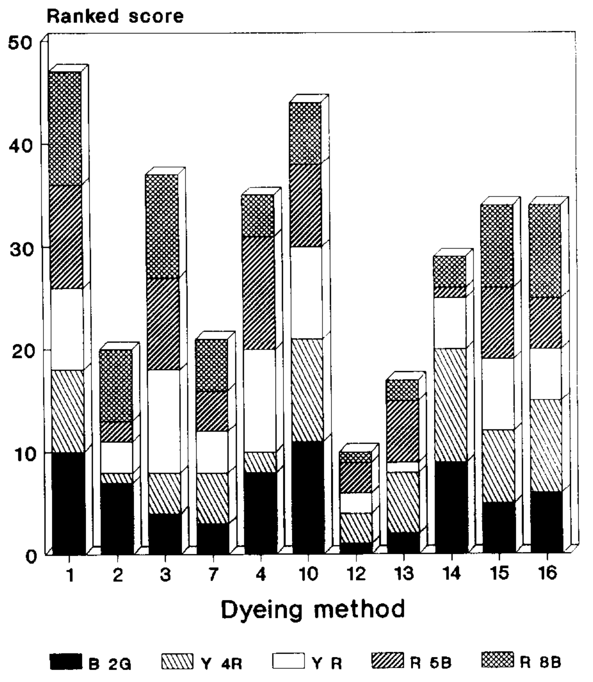


Fig. 3. Ranking of dyeing methods (4% omf dyeings).

of dye applied that was fixed. Although those dyeing methods in which buffer was used to control dyebath pH, namely methods 7, 10 and 12–16, were more efficient than the standard, bicarbonate/soda ash and all-in bicarbonate recommended dyeing methods (1, 3 and 4), only method 7 was more efficient than the low alkali method (2).

As previously explained, methods 7, 10 and 12–16 were each based on the all-in bicarbonate dyeing method (1), as this had been found to yield the lowest extent of fixation of the four recommended dyeing methods; clearly, an explanation of the finding that each of these seven modified dyeing methods was more efficient than method 1 is required. Essentially, the extent of fixation of a reactive dye on cotton depends on the substantivity of the dye as well as the rate and extent of dye hydrolysis that occurs during dyeing. Although the amount of NaCl used in each of the seven modified dyeing methods was the same as that employed in the all-in bicarbonate method, it does not necessarily follow that the substantivity of the dyes towards the substrate was the same for the all-in bicarbonate method and methods 7, 10, and 12–16, as different pH values and temperatures were used for dyeing. The extent of dissociation of the cellulosic substrate is both temperature and pH dependent; at a given (alkaline) pH the degree of dissociation will increase with increasing

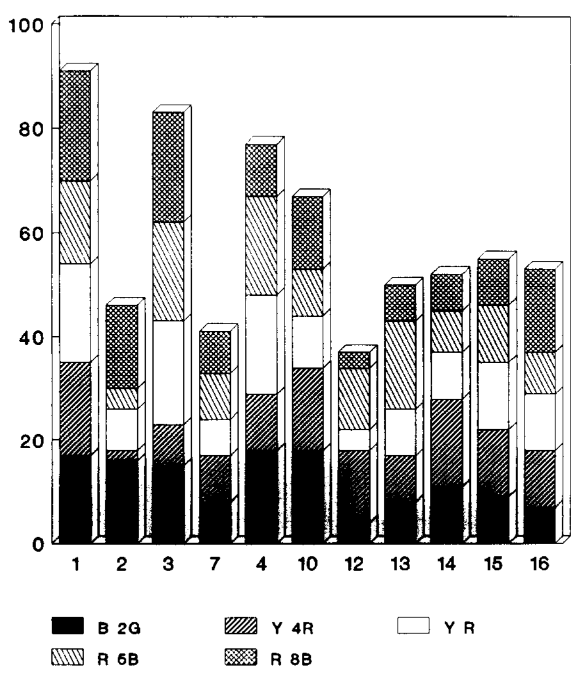


Fig. 4. Ranking of dyeing methods (2% and 4% omf dyeings).

temperature and, at a given temperature dissociation will increase with increasing pH. Thus, as dissociation of the fibre under alkaline conditions will generate cellulosate anions, and as the presence of such anionic groups in the fibre will reduce the substantivity of the anionic dyes towards the substrate, it follows that for the same electrolyte concentration in the dyebath, at a given (alkaline) pH, dye–fibre substantivity will decrease with increasing temperature and, at a given temperature, substantivity will decrease with increasing pH. Furthermore, the rate of dye hydrolysis that occurs during dyeing is also both temperature and pH dependent, insofar as at a given temperature hydrolysis will increase with increasing pH and, at a given (alkaline) pH, the rate of hydrolysis will increase with increasing temperature. From this it follows that in the case of methods 1, 7, 10 and 12–16, the %T values obtained (Fig. 4 and Tables 3–7) should be highest (i.e. dye fixation should be highest) for those methods in which a lower temperature and/or a lower pH was used. This was indeed found, in that the following descending order of efficiency was observed for the 2% and 4% omf dyeings (Fig. 4 and Tables 3–7):

(1) method 12 which involved an initial application temperature of 40°C, a final temperature of 80°C and a pH of 9;
(2) method 7 in which an initial application temperature of 40°C, a final temperature of 85°C and a pH of 8 was used;
(3) method 13 which involved an initial application temperature of 45°C, a final temperature of 85°C and a pH of 8;
(4) methods 14, 15 and 16 in which an initial application temperature of 45°C, a pH of 9 and final temperatures of 85°C, 98°C and 130°C, respectively, were employed;
(5) method 10 which involved an initial application temperature of 50°C, a final temperature of 85°C and a pH of 8;
(6) method 1 in which an initial application temperature of 40°C, a final temperature of 80°C and a pH of 10 was used.

These findings infer that, as expected from the above discussion of substantivity and dye hydrolysis, the lower the pH and the lower the initial and final temperatures of application, the greater the extent of dye fixation, which, in turn, implies a lower extent of dye hydrolysis. These findings also indicate that the use of pH 8 buffer in method 12 rather than the pH 9 buffer that was used may result in improved fixation efficiency; this is being examined in a subsequent study.

In the context of the three remaining recommended dyeing methods (2, 3 and 4), the observation that although the same application temperature (30°C) was used for methods 2 and 4, the highest overall fixation was achieved using method 2 (Fig. 4) can be attributed to the lower pH employed in the latter dyeing method; the observation (Fig. 4) that method 3 was less efficient than either methods 2 or 4 can be attributed to the higher temperature (50°C) used in dyeing method 3. From the foregoing discussion of the temperature and pH dependency of both dye–fibre substantivity and dye–fibre fixation, the high efficiency observed for the low-alkali dyeing method (2) is not unexpected and can be attributed, primarily, to the low temperature (30°C) used.

The c^* and H° values displayed in Tables 2–7 show that in the cases of both the 2% and 4% omf dyeings of the six dyes that were obtained using the various dyeing methods, the colours of the dyeings were very similar, the observed changes in hue angle (H°) of the dyeings that accompanied an increase in dye fixation (depth of shade) being as expected.

CONCLUSION

The results demonstrate that the extent of fixation achieved for each of the six dichlorotriazinyl reactive dyes used can be enhanced by modifying the all-in bicarbonate dyeing method. This enhanced dye fixation can be attributed to a reduction in dye hydrolysis that occurs during dyeing as a result of the use of either pH 8 or pH 9 buffer instead of the $NaHCO_3$ employed in the all-in bicarbonate method. Further work is to be carried out to investigate the use of pH 7 buffer at various application temperatures.

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