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The Wash-off of Reactive Dyes on Cellulosic Fibres. Part 1: Dichlorotriazinyl Dyes on Cotton

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ABSTRACT

Three dichlorotriazinyl reactive dyes were applied, at 2% omf, to woven cotton and the dyeings then washed-off using tap water, sodium bicarbonate and six commercial surfactants, the latter in both the presence and absence of sodium carbonate. The duration and temperature of wash-off, as well as the concentration of sodium bicarbonate used, were varied and the effects of these variables on both the extent of removal of dye from the dyeings and the wash fastness of the dyeings were determined. The finding that the extent of removal of unfixed dye increased with increasing temperature and duration of wash-off can be attributed to the increasing severity that accompanied an increase in time and temperature of wash-off. Each of the six surfactants alone and sodium carbonate alone was more effective in removing dye than tap water alone; the use of each of the surfactants in conjunction with sodium carbonate resulted in enhanced effectiveness of the surfactants. In terms of the effect of wash-off on the wash-fastness of the dyeings, it was found that dyeings which had been washed-off using tap water only or using each of the six surfactants alone, at each of the temperatures and durations of wash-off, displayed lower wash fastness than those dyeings which had been washed-off using sodium carbonate alone or using the six surfactants in the presence of alkali. However, there was little difference between the six surfactants, when used in both the presence and absence of sodium carbonate, in terms of the level of wash-fastness achieved. It was also evident that, in general, there was no difference in wash fastness between dyeings that had been washed-off using each of three concentrations of sodium carbonate and using each of the six surfactants in conjunction with alkali. From the wash-fastness and dye removal results secured, it appears that the use of surfactants in wash-off is unnecessary and that a wash-off using between 2 and 5 g/l sodium carbonate is sufficient to achieve an adequate level of wash fastness. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Characteristically, reactive dyes on cellulosic fibres display excellent fastness to wet treatments, especially washing and laundering. However, in order for reactive dyeings to possess such high levels of wet fastness on these substrates, it is customary to remove all unfixed dye from the dyed material. This is usually achieved by *washing-off* the dyeings; generally, whilst different dye-makers tend to propose different wash-off methods for their reactive dyes, wash-off is typically achieved using one or more treatments with hot water or detergent solutions or hot alkaline solutions, or some combination thereof. Alternatively, an after treatment with selected cationic fixing agents can be performed on the dyeings, especially when the dyed material has not been efficiently washed-off after dyeing.[1]

Despite the fact that reactive dyes have attracted enormous scientific interest since their commercial introduction for the dyeing and printing of cellulosic fibres some 40 years ago, surprisingly little published work has attended their wash-off. As mentioned, a variety of methods can be used for the wash-off of reactive dyeings; the temperature, duration and the nature of the wash-off process depends on several factors including, for example, the depth of shade applied, the type of dye used, the type and construction of the substrate, etc. Since the purpose of washing-off is to remove either all the unfixed dye or at least a sufficient proportion of the unfixed dye such that the washed-off dyeing displays the desired, typically very good, fastness to wet treatments, it is important that wash-off is as effective as possible. Also, owing to the demands for increased productivity and reduced costs of dyeing, the wash-off process should be as efficient as possible, using a minimum of water, chemicals and detergents. This latter consideration is also important from an environmental viewpoint, insofar as the use of water, chemicals and detergents should be at a minimum.

The purpose of this study was to determine the minimum level of wash-off of reactive dyes on cellulosic fibres that was sufficient to enable the dyeings to achieve a satisfactory level of fastness to washing. In this study, a variety of types of reactive dye have been examined on several types of cellulosic fibres. This first part of the study concerns the wash-off of dichlorotriazinyl reactive dyes on cotton.

EXPERIMENTAL

Materials

Fabric

Scoured and bleached woven cotton (139 g/m^2) obtained from Whaleys was used.

Dyes

Three commercial reactive dyes, namely Procion Red MX-5B (CI Reactive Red 2), Procion Yellow MX-G (CI Reactive Orange 86) and Procion Blue MX-G (CI Reactive Blue 163), were used. Each dye was kindly supplied by Zeneca Colours and was not purified prior to use.

Surfactants

Six commercial surfactants, namely Sandozin NIE (alkylene oxide), which was generously supplied by Sandoz (UK), as well as Synperonic 13/15 (polyethoxylated alcohol), Synperonic 13/12 (oxo alcohol ethoxylate), Synperonic A7 (fatty alcohol ethoxylate), Brij 700 with antioxidant (polyethoxylated alcohol with 0.01% BHA and 0.005% citric acid as antioxidant) and Matexil DN-VL 500 (modified fatty alcohol/ethylene oxide condensate), each kindly supplied by ICI Surfactants, were used for the washing-off of the reactive dyeings. The six surfactants were chosen as being typical representatives of different types of surfactant.

Other reagents

All other reagents were laboratory grade reagents obtained either from Aldrich or BDH.

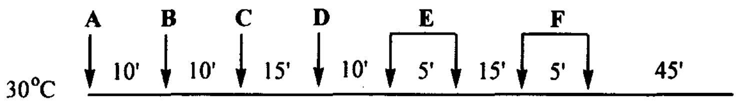
Procedures

Dyeing

All dyeings were carried out in distilled water, using fabric (5 g) which had been wetted out in cold distilled water, in glass dyepots of 300 ml capacity housed in a Zeltex Vistacolor laboratory scale dyeing machine, employing a 40:1 liquor ratio. The dyeing method used was the standard method[2] for the application of Procion MX dyes shown in Fig. 1. After dyeing, the samples were rinsed at 25°C for 10 min, twice, in the same dyeing machine, using tap water and a 30:1 liquor ratio and allowed to dry in the open air.

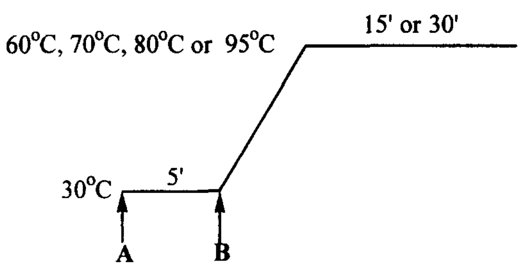
Wash-off

The dyed samples which had been rinsed in tap water were washed-off, at 60, 70, 80 and 95°C for either 15 or 30 min; some samples were also washed-off at 98°C. Wash-off was carried out using either tap water or sodium carbonate solution (1 g/l, 2 g/l or 5 g/l) or using one of the six surfactants (5 g/l) either alone or in combination with sodium carbonate (2 g/l). After wash-off, the samples were rinsed in tap water at 50°C for 10 min. Both wash-off and the final rinsing were carried out using a 30:1 liquor ratio; the method used for wash-off is shown in Fig. 2.



A	Predissolved dye	
	Fabric	
B	NaCl	2.5 g/l
C	NaCl	7.5 g/l
D	NaCl	25 g/l
E	Na_2CO_3	0.5 g/l
	(dissolved and well diluted)	
F	Na_2CO_3	3.5 g/l

Fig. 1. Dyeing method.



A Fabric
B Tap water, surfactant and/or sodium carbonate

Fig. 2. Wash-off method.

TABLE 1
Wash-off at 60°C for 30 min; CI Reactive Red 2

After treatment	*K/S*	*K/S*	*%K/S*	*L**	*a**	*b**	*C*	*h°*
Nil	8.33	—	—	49.42	59.20	0.21	59.20	0.20
Water	7.93	0.40	4.80	49.47	57.58	0.11	57.58	0.11
Sandozin NIE (5 g/l)	7.87	0.46	5.52	49.49	57.34	0.09	57.34	0.09
Na_2CO_3 (2 g/l)	7.52	0.81	9.72	49.84	56.78	0.07	56.78	0.07
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l)	7.54	0.79	9.48	49.80	56.82	0.07	56.82	0.07

TABLE 2
Wash-off at 70°C for 30 min; CI Reactive Red 2

After treatment	*K/S*	*ΔK/S*	*%ΔK/S*	*L**	*a**	*b**	*C*	*h°*
Nil	8.33	—	—	49.42	59.20	0.21	59.20	0.20
Water	7.88	0.45	5.40	49.51	57.38	0.10	57.38	0.10
Sandozin NIE (5 g/l)	7.82	0.51	6.12	49.50	57.21	0.08	57.21	0.08
Na_2CO_3 (2 g/l)	7.36	0.97	11.64	50.11	56.70	−0.16	56.70	359.8
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l)	7.33	1.00	12.00	50.16	56.72	−0.19	56.72	359.8

TABLE 3
Wash-off at 80°C for 15 min; CI Reactive Red 2

After treatment	*K/S*	*ΔK/S*	*%ΔK/S*	*L**	*a**	*b**	*C**	*h°*
Nil	8.33	—	—	49.42	59.20	0.21	59.20	0.20
Water	7.90	0.43	5.16	49.50	57.46	0.10	57.46	0.10
Sandozin NIE (5 g/l)	7.83	0.50	6.00	49.55	57.23	0.08	57.23	0.08
Synperonic 13/15 (5 g/l)	7.80	0.53	6.36	49.58	57.17	0.06	57.17	0.06
Synperonic 13/12 (5 g/l)	7.78	0.55	6.60	49.46	57.13	0.02	57.13	0.02
Brij 700 (5 g/l)	7.75	0.58	6.96	49.53	57.03	0.05	57.03	0.05
Matexil DN-VL, 500 (5 g/l)	7.71	0.62	7.44	49.61	57.06	0.03	57.06	0.03
Synperonic A7 (5 g/l)	7.69	0.64	7.68	49.59	56.93	0.05	56.93	0.05
Na_2CO_3, (1 g/l)	7.52	0.81	9.72	49.84	56.84	−0.04	56.84	359.9
Na_2CO_3 (2 g/l)	7.30	1.03	12.36	50.21	56.80	−0.21	56.80	359.8
Na_2CO_3 (5 g/l)	7.27	1.06	12.73	50.29	56.81	−0.16	56.81	359.8
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l)	7.34	0.99	11.88	50.14	56.83	−0.17	56.83	359.9
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l)	7.27	1.06	12.73	50.26	56.78	−0.24	56.78	359.7
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l)	7.19	1.14	13.69	50.38	56.75	−0.28	56.86	359.7
Na_2CO_3 (2 g/l) + Matexil DN-VL, 500 (5 g/l)	7.12	1.21	14.53	50.46	56.69	−0.31	56.69	359.7
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l)	7.11	1.22	14.65	50.48	56.60	−0.34	56.60	359.7

TABLE 4
Wash-off at 80°C for 30 min; CI Reactive Red 2

After treatment	*K/S*	*ΔK/S*	*%ΔK/S*	*L**	*a**	*b**	*C*	*h°*
Nil	8.33	—	—	49.92	59.20	0.21	59.20	0.20
Water	7.74	0.59	7.08	49.54	57.04	0.06	57.04	0.06
Sandozin NIE (5 g/l)	7.73	0.60	7.20	49.55	57.02	0.01	57.02	0.01
Synperonic 13/15 (5 g/l)	7.75	0.58	6.96	49.49	57.12	0.04	57.12	0.04
Synperonic 13/12 (5 g/l)	7.70	0.63	7.56	49.58	56.95	−0.03	56.95	359.9
Brij 700 (5 g/l)	7.63	0.70	8.40	49.66	56.81	−0.05	56.81	359.5
Matexil DN-VL 500 (5 g/l)	7.67	0.66	7.92	49.61	56.89	−0.06	56.89	359.4
Synperonic A7 (5 g/l)	7.58	0.75	9.00	49.76	56.80	−0.02	56.80	359.8
Na_2CO_3 (1 g/l)	7.32	1.01	12.12	50.18	56.77	−0.19	56.77	359.8
Na_2CO_3 (2 g/l)	6.93	1.40	16.81	50.71	56.52	−0.36	56.52	359.6
Na_2CO_3 (5 g/l)	6.87	1.46	17.53	50.84	56.40	−0.43	56.40	359.5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l)	6.90	1.43	17.17	50.78	56.47	−0.39	56.47	359.6
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l)	7.00	1.33	15.97	50.61	56.58	−0.30	56.58	359.7
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l)	6.83	1.50	18.01	50.80	56.33	−0.49	56.33	359.5
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l)	7.04	1.29	15.49	50.53	56.67	−0.32	56.67	359.6
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l)	6.68	1.65	19.81	50.97	56.17	−0.71	56.17	359.2
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l)	6.63	1.70	20.41	50.90	55.72	−0.80	55.73	359.1

Colour measurement

The reflectance values of the dry, dyed samples were measured using a Colorgen reflectance spectrophotometer interfaced to an IBM PC under illuminant D_{65}, using a 10° Standard Observer, with specular component excluded and UV component included. The corresponding K/S and the L^*, a^*, b^*, C, h°. values of the samples were calculated at the appropriate $\lambda_{max.}$ of each dye. Each fabric sample was folded twice so as to realise a total of four thicknesses of fabric.

Wash fastness testing

The fastness testing of the dyed samples was carried out in accordance with the ISO CO6/C2 method.[3]

RESULTS AND DISCUSSION

It was decided to apply 2% omf dye throughout this study as this was considered to represent a typical, commercial depth of shade. The dyeing

TABLE 5
Wash-off at 95°C for 15 min; CI Reactive Red 2

After treatment	*K/S*	$\Delta K/S$	$\%\Delta K/S$	L^*	a^*	b^*	*C*	$h°$
Nil	8.33	—	—	49.42	59.20	0.21	59.20	0.20
Water	7.74	0.59	7.08	49.54	57.04	0.06	57.04	0.06
Sandozin NIE (5 g/l)	7.69	0.64	7.68	49.59	56.93	0.05	56.93	0.05
Synperonic 13/15 (5 g/l)	7.63	0.70	8.40	49.67	56.85	0.04	56.85	0.04
Synperonic 13/12 (5 g/l)	7.61	0.72	8.64	49.69	56.88	0.02	56.88	0.02
Brij 700 (5 g/l)	7.59	0.74	8.88	49.73	56.83	0.01	56.83	0.01
Matexil DN-VL 500 (5 g/l)	7.54	0.79	9.48	49.81	56.81	-0.03	56.81	359.9
Synperonic A7 (5 g/l)	7.51	0.82	9.84	49.86	56.80	-0.05	56.80	359.9
Na_2CO_3 (1 g/l)	7.23	1.10	13.21	50.33	56.75	-0.27	56.75	359.7
Na_2CO_3 (2 g/l)	6.75	1.58	18.97	50.88	56.19	-0.61	56.19	359.3
Na_2CO_3 (5 g/l)	6.72	1.61	19.33	50.93	56.08	-0.66	56.08	359.3
Na_2CO_1 (2 g/l) + Sandozin NIE (5 g/l)	6.73	1.60	19.21	50.90	56.14	-0.64	56.14	359.3
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l)	6.66	1.67	20.05	50.97	56.02	-0.76	56.03	359.2
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l)	6.56	1.77	21.25	50.95	55.04	-0.92	55.05	359.0
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l)	6.59	1.74	20.89	51.03	55.34	-0.87	55.35	359.1
Na_2CO_3 (2 g/l) + Matexil DN-VL, 500 (5 g/l)	6.44	1.89	22.69	51.10	53.89	-1.15	53.90	359.9
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l)	6.42	1.91	22.93	51.15	53.70	-1.20	53.71	358.7

method used was that recommended by the dye-maker (Fig. 1). As mentioned, the six surfactants used were selected on the basis of them being typical representatives of different types of non-ionic surfactant. It was not the intention of this work to compare the effectiveness of each surfactant and to infer superiority of one product over another. In this context, no attempt was made to 'normalise' the surfactants in terms of the relative concentration of active ingredients and, therefore, each of the surfactants was used at the strength provided by the respective maker.

Wash-off

The tables that follow show the colour strength (K/S values) and the calorimetric parameters (L^*, a^*, b^*, C and h°) of the dyeings, as well as the difference in colour strength (ΔK/S) between dyeings which had not been washed-off and which had been washed-off as well as the percentage difference in colour strength (%ΔK/S) between unwashed-off and washed-off dyeings; these two latter parameters were calculated using eqns (1) and (2), respectively.

TABLE 6
Wash-off at 95°C for 30 min; CI Reactive Red 2

After treatment	*K/S*	*ΔK/S*	*%ΔK/S*	*L**	*a**	*b**	*C*	*h°*
Nil	8.33	—	—	49.42	59.20	0.21	59.20	0.20
Water	7.66	0.67	8.04	49.63	56.86	0.04	56.86	0.04
Sandozin NIE (5 g/l)	7.60	0.73	8.76	49.71	56.84	0.02	56.84	0.02
Synperonic 13/15 (5 g/l)	7.53	0.80	9.60	49.83	56.80	−0.04	56.80	359.9
Synperonic 13/12 (5 g/l)	7.50	0.83	9.96	49.89	56.76	−0.06	56.76	359.9
Brij 700 (5 g/l)	7.47	0.86	10.32	49.94	56.70	−0.08	56.70	359.9
Matexil DN-VL 500 (5 g/l)	7.41	0.92	11.04	50.03	56.72	−0.12	56.72	359.8
Synperonic A7 (5 g/l)	7.37	0.96	11.52	50.10	56.66	−0.17	56.66	359.8
Na_2CO_3 (1 g/l)	7.17	1.16	13.93	50.40	56.62	−0.29	56.62	359.7
Na_2CO_3 (2 g/l)	6.65	1.68	20.17	50.96	55.91	−0.76	55.92	359.2
Na_2CO_3 (5 g/l)	6.53	1.80	21.61	51.02	54.76	−0.98	54.77	358.9
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l)	6.63	1.70	20.41	51.02	55.72	−0.80	55.73	359.1
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l)	6.56	1.77	21.25	51.10	55.04	−0.92	55.05	359.0
Na_2CO_3 (2 g/l) + Synperonic 13112 (5 g/l)	6.45	1.88	22.57	51.16	53.98	−1.13	53.99	358.8
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l)	6.42	1.91	22.93	51.07	53.70	−1.18	53.71	358.7
Na_2CO_3 (2 g/l) + Matexil DN-VL, 500 (5 g/l)	6.31	2.02	24.25	51.20	52.62	−1.52	52.64	358.3
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l)	6.29	2.04	24.49	51.24	52.54	−1.75	52.57	358.1

$$\Delta K/S = K/S_{\text{before wash-off}} - K/S_{\text{after wash-off}} \tag{1}$$

$$\%K/S = \frac{K/S_{\text{before wash-off}} - K/S_{\text{after wash-off}}}{K/S_{\text{before wash-off}}} \times 100 \tag{2}$$

In this work, a large number of dyed samples were produced; although there were very small differences in the K/S values and the calorimetric parameters of the dyed samples before wash-off, in each of the tables that follow, the average K/S and calorimetric parameters values were employed.

CI Reactive Red 2

The colour strength (K/S values) in Table 1 demonstrate that, when wash-off had been carried out at 60°C for 30 min, the colour strength of each of the four dyeings that had been washed-off was lower than that of the corresponding unwashed-off dyeing. As expected, this finding shows that unfixed reactive dye was present on the samples and that wash-off removed this unfixed dye. It is also evident that the colour strength of the washed-off dyeings decreased in the order:

TABLE 7
Wash-off at 80°C for 15 min; CI Reactive Orange 86

After treatment	*K/S*	*ΔK/S*	*%ΔK/S*	*L**	*a**	*b**	*C*	*h°*
Nil	5.20	—	—	76.91	22.08	67.49	71.01	71.8
Water	4.91	0.29	5.58	77.25	21.54	66.87	70.25	72.1
Sandozin NIE (5 g/l)	4.77	0.43	8.27	77.38	21.19	66.39	69.69	72.3
Synperonic 13/15 (5 g/l)	4.94	0.26	5.00	77.22	21.62	66.98	70.38	72.1
Synperonic 13/12 (5 g/l)	4.81	0.39	7.50	77.34	21.29	66.52	69.84	72.2
Brij 700 (5 g/l)	4.89	0.31	5.96	77.26	21.49	66.80	70.17	72.1
Matexil DN-VL, 500 (5 g/l)	4.84	0.36	6.92	77.31	21.36	66.63	69.97	72.2
Synperonic A7 (5 g/l)	4.86	0.34	6.54	77.29	21.44	66.70	70.06	72.1
Na_2CO_3 (1 g/l)	4.66	0.54	10.38	77.48	21.01	66.03	69.29	72.3
Na_2CO_3 (2 g/l)	4.51	0.69	13.27	77.65	20.93	65.56	68.82	72.2
Na_2CO_3 (5 g/l)	4.37	0.83	15.96	77.74	20.72	64.97	68.19	72.3
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l)	4.39	0.81	15.58	77.73	20.76	65.07	68.30	72.3
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l)	4.61	0.59	11.35	77.54	20.98	65.87	69.13	72.3
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l)	4.52	0.68	13.08	77.63	20.93	65.59	68.85	72.3
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l)	4.54	0.66	12.69	77.61	20.95	65.66	68.92	72.3
Na_2CO_3 (2 g/l) + Matexil DN-VL, 500 (5 g/l)	4.46	0.74	14.23	77.70	20.90	65.41	68.67	72.2
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l)	4.50	0.70	13.46	77.66	20.91	65.53	68.79	72.3

$$\text{water} < \text{Sandozin NIE} < Na_2CO_3(2\,g/l) < Na_2CO_3(2\,g/l) + \text{Sandozin NIE}(5\,g/l)$$

This shows that wash-off using an alkaline solution of Sandozin NIE was the most effective in removing unfixed dye from the dyeings; this finding was clearly confirmed by the ΔK/S and %ΔK/S values shown in Table 1.

When wash-off was carried out at 70°C (Table 2), it was found that the results followed exactly the same pattern as those shown in Table 1 in that treatment with an alkaline solution of Sandozin NIE was the most effective in removing unfixed dye from the dyeings; this finding was again clearly confirmed by the ΔK/S and %ΔK/S values shown in Table 2.

A comparison of Table 1 and Table 2 shows that the samples which had been washed-off at 70°C for 30 min were of lower colour strength than those washed-off at 60°C for the same time. In the case of wash-off at both temperatures, the corresponding calorimetric parameters of the dyeings reveal that each of the four methods caused a slight blueing of the shade of the dyeing and that, in general, this change in shade increased with increasing extent of dye removal. From Table 1 and Table 2 it is also evident that

TABLE 8
Wash-off at 80°C for 30 min; CI Reactive Orange 86

After treatment	*K/S*	*ΔK/S*	*%ΔK/S*	*L**	*a**	*b**	*C*	*h°*
Nil	5.20	—	—	76.91	22.08	67.49	71.01	71.8
Water	4.88	0.32	6.15	77.27	21.46	66.77	70.13	72.1
Sandozin NIE (5 g/l)	4.69	0.51	9.81	77.45	21.03	66.12	69.38	72.3
Synperonic 13/15 (5 g/l)	4.92	0.28	5.38	77.24	21.56	66.90	70.29	72.1
Synperonic 13/12 (5 g/l)	4.82	0.38	7.31	77.33	21.32	66.56	69.89	72.2
Brij 700 (5 g/l)	4.86	0.34	6.54	77.30	21.42	66.73	70.08	72.2
Matexil DN-VL 500 (5 g/l)	4.78	0.42	8.08	77.36	21.22	66.42	69.73	72.2
Synperonic A7 (5 g/l)	4.83	0.37	7.12	77.32	21.36	66.60	69.94	72.2
Na_2CO_3 (1 g/l)	4.64	0.56	10.77	77.50	21.00	65.96	69.22	72.3
Na_2CO_3 (2 g/l)	4.36	0.84	16.15	77.74	20.70	64.92	68.14	72.3
Na_2CO_3 (5 g/l)	4.23	0.97	18.65	77.80	20.43	64.29	67.46	72.3
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l)	4.29	0.91	17.50	77.77	20.55	64.58	67.77	72.3
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l)	4.48	0.72	13.85	77.68	20.91	65.31	68.58	72.2
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l)	4.38	0.82	15.77	77.73	20.74	65.02	68.25	72.3
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l)	4.41	0.79	15.19	77.72	20.80	65.16	68.40	72.3
Na_2CO_3 (2 g/l) + Matexil DN-VL, 500 (5 g/l)	4.34	0.86	16.54	77.75	20.66	64.82	68.03	72.3
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l)	4.36	0.84	16.15	77.77	20.67	64.80	68.02	72.3

sodium carbonate reduced the colour strength of the dyeings by almost twice that achieved using tap water, at the same temperature and time of wash-off. When Sandozin NIE was used on its own, the surfactant caused a decrease of K/S that was slightly greater than that produced by water alone and, when the surfactant was used in combination with 2 g/l sodium carbonate, no further marked decrease in colour strength was observed.

From Table 3, it is evident that wash-off at 80°C for 15 min using each of the six surfactants resulted in a higher reduction in colour strength than that obtained when only tap water was used. Differences between the surfactants, in terms of the decrease in colour strength achieved, were obtained, although these were small; the ΔK/S and %ΔK/S values shown in Table 3 reveal that Synperonic A7 was the most effective surfactant. However, it is also evident from the results presented in Table 3 that none of the six surfactants alone was as effective as sodium carbonate in removing unfixed dye. Clearly, in the case of wash-off using the three concentrations of alkali used, the colour strength of the dyeings increased in the order 1 g/l < 2 g/l < 5 g/l, although, as the ΔK/S and %ΔK/S values reveal, there was little difference between the extent of dye removal achieved using 2 g/l and 5 g/l alkali. When the six

TABLE 9
Wash-off at 95°C for 15 min; CI Reactive Orange 86

After treatment	*K/S*	*ΔK/S*	*%ΔK/S*	*L**	*a**	*b**	*C*	*h°*
Nil	5.2	—	—	76.91	22.08	67.49	71.01	71.8
Water	4.79	0.41	7.88	77.36	21.24	66.46	69.77	72.2
Sandozin NIE (5 g/l)	4.64	0.56	10.77	77.48	21.03	66.01	69.28	72.3
Synperonic 13/15 (5 g/l)	4.78	0.42	8.08	77.39	21.19	66.38	69.68	72.3
Synperonic 13/12 (5 g/l)	4.73	0.47	9.04	77.41	21.09	66.25	69.53	72.3
Brij 700 (5 g/l)	4.76	0.44	8.46	77.38	21.16	66.35	69.64	72.3
Matexil DN-VL 500 (5 g/l)	4.71	0.49	9.42	77.43	21.04	66.18	69.44	72.3
Synperonic A7 (5 g/l)	4.68	0.52	10.00	77.46	21.02	66.09	69.35	72.3
Na_2CO_3 (1 g/l)	4.5	0.7	13.46	77.64	20.92	65.57	68.83	72.3
Na_2CO_3 (2 g/l)	4.27	0.93	17.88	77.78	20.51	64.48	67.66	72.3
Na_2CO_3 (5 g/l)	4.18	1.02	19.62	77.83	20.33	64.04	67.19	72.3
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l)	4.24	0.96	18.46	77.79	20.45	64.34	67.51	72.3
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l)	4.46	0.74	14.23	77.71	20.87	65.36	68.61	72.2
Na_2CO_3 (2 g/1) + Synperonic 13/12 (5 g/l)	4.4	0.8	15.38	77.72	20.78	65.12	68.36	72.3
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l)	4.44	0.76	14.62	77.71	20.86	65.31	68.56	72.2
Na_2CO_3 (2 g/l) + Matexil DN-VL, 500 (5 g/l)	4.37	0.83	15.96	77.74	20.72	64.97	68.19	72.3
Na_2CO_3 (2 g/l). + Synperonic A7 (5 g/l)	4.29	0.91	17.50	77.77	20.55	64.58	67.77	72.3

surfactants were used in conjunction with 2 g/l sodium carbonate, the effectiveness of the surfactants in removing dye was increased, typically by a factor of two. With the exception of Sandozin NIE, the extent of dye removal achieved using 5 g/l surfactant in conjunction with 2 g/l sodium carbonate was greater than that secured using 2 g/l and 5 g/l alkali alone. The calorimetric parameters of the dyeings reveal that each of the wash-off treatments caused a slight blueing of the shade of the dyeing and that this change in shade generally increased with increasing extent of dye removal. Differences were found between the surfactants, in terms of the decrease in colour strength achieved when used in conjunction with sodium carbonate; the ΔK/S and %ΔK/S values shown in Table 3 reveal that Synperonic A7 was the most effective surfactant.

Table 3 showed the results obtained when wash-off had been carried out at 80°C for 15 min; Table 4 presents the results obtained when the time of wash-off was extended to 30 min at this particular temperature. It is evident from Table 4 that the results followed exactly the same pattern as those shown in Table 3 in that after treatment with each of the six surfactants removed more dye than tap water, that the three concentrations of sodium

TABLE 10
Wash-off at 95°C for 30 min; CI Reactive Orange 86

After treatment	*K/S*	*ΔK/S*	*%ΔK/S*	*L**	*a**	*b**	*C*	*h°*
Nil	5.20	—	—	76.91	22.08	67.49	71.01	71.8
Water	4.81	0.39	7.50	77.34	21.28	66.47	69.79	72.2
Sandozin NIE (5 g/l)	4.66	0.54	10.38	77.46	21.04	66.08	69.35	72.3
Synperonic 13/15 (5 g/l)	4.82	0.38	7.31	97.34	21.30	66.50	69.83	72.2
Synperonic 13/12 (5 g/l)	4.77	0.43	8.27	77.38	21.19	66.39	69.69	72.3
Brij 700 (5 g/l)	4.79	0.41	7.88	77.35	21.26	66.49	69.81	72.2
Matexil DN-VL 500 (5 g/l)	4.69	0.51	9.81	77.45	21.03	66.12	69.38	72.3
Synperonic A7 (5 g/l)	4.65	0.55	10.58	77.49	21.01	66.00	69.26	72.3
Na_2CO_3 (1 g/l)	4.47	0.73	14.04	77.69	20.90	65.44	68.70	72.2
Na_2CO_3 (2 g/l)	4.20	1.00	19.23	77.81	20.37	64.14	67.30	72.4
Na_2CO_3 (5 g/l)	4.06	1.14	21.92	77.86	20.08	63.46	66.56	72.4
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l)	4.11	1.096	20.96	77.84	20.19	63.70	66.82	72.4
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l)	4.40	0.80	15.38	77.70	20.81	65.21	68.45	72.3
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l)	4.31	0.89	17.12	77.76	20.59	63.41	66.67	72.0
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l)	4.38	0.82	15.77	77.72	20.77	65.09	68.32	72.3
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l)	4.28	0.92	17.69	77.78	20.53	64.53	67.72	72.3
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l)	4.33	0.87	16.73	77.80	20.41	64.24	67.40	72.3

carbonate removed more dye than each of the surfactants alone and, also, that alkaline solutions of the six surfactants were the most effective in removing unfixed dye from the dyeings. These findings are clearly shown by the ΔK/S and %ΔK/S values presented in Table 4. In addition, wash-off imparted a slight blueing to the shade of the dyeing to an extent that generally increased with increasing extent of dye removal. A comparison of the results displayed in Table 3 and Table 4 shows that an increase in the duration of wash-off, from 15 to 30 min, at 80°C, resulted in an increase in the extent of dye removal.

Table 5 and Table 6 show the results obtained when wash-off had been carried out at 95°C for 15 and 30 min, respectively. The results followed exactly the same pattern as those discussed previously for wash-off at 80°C (Table 3 and Table 4) in that after treatment with each of the six surfactants removed more dye than tap water, that the three concentrations of sodium carbonate removed more dye than each of the surfactants alone and, also, that alkaline solutions of the six surfactants were the most effective in removing unfixed dye from the dyeings; in addition the shade of the dyeings became bluer as the amount of dye removed increased. Furthermore, a

TABLE 11
Wash-off at 80°C for 15 min; CI Reactive Blue 163

After treatment	*K/S*	*ΔK/S*	*%ΔK/S*	*L**	*a**	*b**	*C*	*h°*
Nil	7.26	—	—	48.98	−13.92	−30.06	33.13	245.1
Water	6.62	0.64	8.82	49.91	−13.20	−29.98	32.76	246.2
Brij 700 (5 g/l)	6.60	0.66	9.09	49.95	−13.23	−29.94	32.73	246.1
Sandozin NIE (5 g/l)	6.57	0.69	9.50	50.00	−13.25	−29.91	32.71	246.1
Matexil DN-VL 500 (5 g/l)	6.56	0.70	9.64	50.02	−13.29	−29.93	32.75	246.0
Synperonic 13/15 (5 g/l)	6.52	0.74	10.19	50.10	−13.27	−29.90	32.71	246.0
Synperonic A7 (5 g/l)	6.49	0.77	10.61	50.16	−13.31	−29.88	32.71	245.9
Synperonic 13/12 (5 g/l)	6.45	0.81	11.16	50.24	−13.34	−29.86	32.70	245.9
Na_2CO_3 (1 g/l)	6.36	0.90	12.40	50.41	−13.36	−29.80	32.66	245.8
Na_2CO_3 (2 g/l)	5.99	1.27	17.49	51.04	−13.38	−29.19	32.11	245.3
Na_2CO_3 (5 g/l)	5.97	1.29	17.77	51.08	−13.39	−29.17	32.10	245.3
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l)	6.02	1.24	17.08	51.00	−13.36	−29.26	32.17	245.4
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l)	5.96	1.30	17.91	51.10	−13.41	−29.12	32.06	245.2
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l)	5.90	1.36	18.73	51.21	−13.33	−28.97	31.89	245.1
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l)	5.95	1.31	18.04	15.12	−13.48	−29.09	32.06	245.1
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l)	5.93	1.33	18.32	51.16	−13.45	−29.04	32.00	245.2
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l)	5.86	1.40	19.28	51.29	−13.50	−28.87	31.87	245.2

comparison of the results displayed in Table 5 and Table 6 shows that an increase in the duration of wash-off, from 15 to 30 min, at 95°C, resulted in an increase in the extent of dye removal. When the results presented in Table 5 and Table 6 are compared to those displayed in Table 3 and Table 4, it is apparent that an increase in the temperature of wash-off, from 80 to 95°C, resulted in an increase in the extent of dye removal.

CI Reactive Orange 86 and CI Reactive Blue 163

The results obtained for the wash-off of 2% omf dyeings at 80°C and 95°C, for 15 and 30 min using tap water, aqueous (1, 2 and 5 g/l) sodium carbonate as well as each of the six surfactants in both the absence and presence of 2 g/l sodium carbonate are presented in Tables 7–10 in the case of CI Reactive Orange 86 and in Tables 11–14 in the case of CI Reactive Blue 163. The results followed exactly the same pattern as those discussed previously for CI Reactive Red 2 (Tables 3–6) in that wash-off using each of the six surfactants removed more dye than tap water, the three concentrations of sodium carbonate removed more dye than each of the surfactants alone and alkaline solutions of the six surfactants were the most effective in removing unfixed

TABLE 12
Wash-off at 80°C for 30 min; CI Reactive Blue 163

After treatment	*K/S*	$\Delta K/S$	$\%\Delta K/S$	L^*	a^*	b^*	*C*	$h°$
Nil	7.26	—	—	48.98	−13.92	−30.06	33.13	245.1
Water	6.54	0.72	9.92	50.06	−13.30	−29.91	32.73	246.0
Brij 700 (5 g/l)	6.51	0.75	10.33	50.12	−13.34	−29.89	32.73	245.9
Sandozin NIE (5 g/l)	6.49	0.77	10.61	50.17	−13.33	−29.90	32.74	245.9
Matexil DN-VL 500 (5 g/l)	6.44	0.82	11.29	50.26	−13.35	−29.83	32.68	245.8
Synperonic 13/15 (5 g/l)	6.46	0.80	11.02	50.22	−13.36	−29.86	32.71	245.8
Synperonic A7 (5 g/l)	6.42	0.84	11.57	50.30	−13.39	−29.84	32.71	245.8
Synperonic 13/12 (5 g/l)	6.38	0.88	12.12	50.37	−13.32	−29.78	32.62	245.9
Na_2CO_3 (1 g/l)	6.20	1.06	14.60	50.70	−13.37	−29.65	32.53	245.7
Na_2CO_3 (2 g/l)	5.84	1.42	19.56	51.33	−13.42	−28.82	31.79	245.0
Na_2CO_3 (5 g/l)	5.76	1.50	20.66	51.48	−13.46	−28.61	31.62	244.8
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l)	5.88	1.38	19.01	51.25	−13.45	−28.92	31.89	245.0
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l)	5.83	1.43	19.70	51.35	−13.40	−28.80	31.76	245.0
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l)	5.74	1.52	20.94	51.52	−13.44	−28.57	31.57	244.8
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l)	5.80	1.46	20.11	51.41	−13.41	−28.72	31.70	244.9
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l)	5.77	1.49	20.52	51.46	−13.44	−28.64	31.64	244.8
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l)	5.71	1.55	21.35	51.58	−13.49	−28.49	31.52	244.6

dye from the dyeings. In the case of CI Reactive Orange 86, wash-off was observed to have very little effect on the shade of the dyeings and, in the case of CI Reactive Blue 163, the shade of the dyeings became very slightly yellower as the amount of dye removed increased.

DISCUSSION

From the foregoing, it is clear that the extent of removal of dye from 2% omf dyeings of each of the three reactive dyes on cotton increased with increasing temperature (over the range 60–95°C) and with increasing duration of wash-off (15–30 min). It is also evident that whilst, at a given temperature and duration of wash-off, each of the six surfactants, when used alone, was more effective than tap water in removing unfixed dye, the effectiveness of each surfactant was enhanced when the surfactant used in conjunction with sodium carbonate. These findings warrant discussion.

The observed increase in the removal of unfixed dye that accompanied an increase in temperature of wash-off can be attributed to three factors:

TABLE 13
Wash-off at 95°C for 15 min; CI Reactive Blue 163

After treatment	*K/S*	*ΔK/S*	*%ΔK/S*	*L**	*a**	*b**	*C*	*h°*
Nil	7.26	—	—	48.98	−13.92	−30.06	33.13	245.1
Water	6.47	0.79	10.88	50.20	−13.32	−29.87	32.71	245.9
Brij 700 (5 g/l)	6.42	0.84	11.57	50.32	−13.34	−29.83	32.68	245.9
Sandozin NIE (5 g/l)	6.45	0.81	11.16	50.25	−13.35	−29.84	32.69	245.9
Matexil DN-VL 500 (5 g/l)	6.41	0.85	11.71	50.31	−13.32	−29.82	32.66	245.9
Synperonic 13/15 (5 g/l)	6.37	0.89	12.26	50.39	−13.36	−29.81	32.67	245.8
Synperonic A7 (5 g/l)	6.34	0.92	12.67	50.45	−13.38	−29.79	32.66	245.8
Synperonic 13/12 (5 g/l)	6.30	0.96	13.22	50.52	−13.33	−29.74	32.59	245.9
Na_2CO_3 (1 g/l)	6.05	1.21	16.67	50.95	−13.39	−29.32	32.23	245.5
Na_2CO_3 (2 g/l)	5.82	1.44	19.83	51.37	−13.41	−28.77	31.74	245.1
Na_2CO_3 (5 g/l)	5.64	1.62	22.31	51.68	−13.56	−28.26	31.34	244.3
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l)	5.75	1.51	20.80	51.50	−13.44	−28.60	31.60	244.8
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l)	5.77	1.49	20.52	51.48	−13.43	−28.64	31.63	244.8
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l)	5.71	1.55	21.35	51.61	−13.46	−28.45	31.47	244.4
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l)	5.57	1.69	23.28	51.77	−13.50	−28.05	31.13	244.3
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l)	5.62	1.64	22.59	51.71	−13.51	−28.21	31.28	244.6
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l)	5.65	1.61	22.18	51.67	−13.52	−28.31	31.37	244.4

the solubility of the dye in the aqueous wash-off liquor increased with increasing temperature;

the desorption equilibrium between the dye in the fibre and that in the aqueous wash-off liquor moved in favour of the aqueous phase as temperature increased;[4]

the rate of diffusion of the dye out of the fibre into the aqueous phase increased with increasing temperature.

In the context of the marked ability of sodium carbonate to remove unfixed dye, especially when used in conjunction with each of the six surfactants, it is well known that aqueous, alkaline solutions of detergent are used in both the scouring and the domestic laundering of textiles, in which processes, the alkali solubilises hydrophobes (fats, oils and waxes) that are present on the substrate, thereby expediting their removal by means of their increased water-solubility. In the case of domestic washing formulations, alkali is often used as a builder to assist the wetting and detergent functions of surfactants; in essence, the builder softens the water used for washing. Thus, in the context of this work, it is possible that sodium carbonate

TABLE 14
Wash-off at 95°C for 30 min; CI Reactive Blue 163

After treatment	*K/S*	*ΔK/S*	*%ΔK/S*	*L**	*a**	*b**	*C*	*h°*
Nil	7.26	—	-	48.98	−13.92	−30.06	33.13	245.1
Water	6.36	0.90	12.40	50.44	−13.35	−29.78	32.64	245.8
Brij 700 (5 g/l)	6.28	0.98	13.50	50.56	−13.37	−29.76	32.63	245.8
Sandozin NIE (5 g/l)	6.22	1.04	14.33	50.67	−13.30	−29.70	32.54	245.8
Matexil DN-VL 500 (5 g/l)	6.19	1.07	14.74	50.72	−13.28	−29.62	32.46	245.8
Synperonic 13/15 (5 g/l)	6.14	1.12	15.43	50.80	−13.36	−29.52	32.40	245.6
Synperonic A7 (5 g/l)	6.09	1.17	16.12	50.88	−13.32	−29.41	32.29	245.6
Synperonic 13/12 (5 g/l)	6.06	1.20	16.53	50.93	−13.38	−29.33	32.24	245.4
Na_2CO_3 (1 g/l)	5.85	1.41	19.41	1.31	−13.41	−28.84	31.81	245.0
Na_2CO_3 (2 g/l)	5.55	1.71	23.55	51.80	−13.48	−27.99	31.07	244.2
Na_2CO_3 (5 g/l)	5.39	1.87	25.76	52.03	−13.65	−28.34	31.46	244.2
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l)	5.52	1.74	23.97	51.84	−13.49	−27.89	30.98	244.1
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l)	5.50	1.76	24.24	51.87	−13.52	−27.83	30.94	244.0
Na_2CO_3 (2 g/l) + Matexil DN−VL 500 (5 g/l)	5.43	1.83	25.21	51.96	−13.59	−27.60	30.76	243.9
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l)	5.46	1.80	24.79	51.92	−13.46	−27.70	30.80	244.0
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l)	5.49	1.77	24.38	1.88	−13.57	−27.78	30.92	243.7
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l)	5.34	1.92	26.45	52.08	−13.30	−27.31	30.38	244.0

TABLE 15
Wash Fastness Ratings of Samples Dyed with CI Reactive Red 2

After treatment	*Ch.*	*Cot.*	*Visc.*
Water 60°C 30 min	4	4	4/5
Sandozin NIE (5 g/l) 60°C 30 min	4	4	4/5
Na_2CO_3 (2 g/l) 60°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l) 60°C 30 min	4/5	4/5	5
Water 70°C 30 min	4	4	4/5
Sandozin NIE (5 g/l) 70°C 30 min	4	4	4/5
Na_2CO_3 (2 g/l) 70°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l) 70°C 30 min	4/5	4/5	5

functioned as discussed above, namely that it increased the aqueous solubility of the unfixed dye and, therefore, increased the propensity of the dye to move from the fibre phase to the aqueous phase; furthermore, it can be considered that it assisted the detergency action of the surfactants during wash-off.

TABLE 16
Wash Fastness Ratings of Samples Dyed with CI Reactive Red 2

After treatment	*Ch.*	*Cot.*	*Visc*
Water 80°C 15 min	4	4	4/5
Sandozin NIE 80°C 15 min	4	4	4/5
Synperonic 13/15 80°C 15 min	4	4	5
Synperonic 13/12 80°C 15 min	4	4	5
Brij 700 80°C 15 min	4	4	5
Matexil DN-VL 500 80°C 15 min	4	4	5
Synperonic A7 80°C 15 min	4	4	5
Na_2CO_3 (1 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_2 (2 g/l) + Synperonic 13/15 (5 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_2 (2 g/l) + Synperonic A7 (5 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (5 g/l) 80°C 15 min	4/5	4/5	5
Water 80°C 30 min	4	4	4/5
Sandozin NIE (5 g/l) 80°C 30 min	4	4	5
Synperonic 13/15 (5 g/l) 80°C 30 min	4	4	5
Synperonic 13/12 (5 g/l) 80°C 30 min	4	4	5
Brij 700 (5 g/l) 80°C 30 min	4	4	5
Matexil DN-VL 500 (5 g/l) 80°C 30 min	4	4	5
Synperonic A7 (5 g/l) 80°C 30 min	4	4	5
Na_2CO_3 (1 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Sandozin (5 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l) 80°C 30 min	4/5	5	B
Na_2CO_3 (2 g/l) + and Brij 700 (5 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (5 g/l) 80°C 30 min	4/5	4/5	5

However, it is not entirely clear as to why aqueous sodium carbonate alone was so effective in removing unfixed dye. If it is assumed that the dyes contained sulphonate groups which can be considered to be fully dissociated even at relatively low (acidic) pH values, it is not apparent how this dissociation (solubilisation) could have been enhanced under the alkaline conditions prevalent in the aqueous sodium carbonate wash-off liquor. It can be proposed that ionisation of the hydroxy and carboxylic acid groups in the cotton was increased under alkaline wash-off conditions, in which case, the ensuing increase in ion–ion repulsion operating between the anionic dye and anionic groups in the substrate would result in increased dye desorption. However, whilst such a mechanism may apply to the hydroxy groups in

TABLE 17
Wash Fastness Ratings of Samples Dyed with CI Reactive Red 2

After treatment	*Ch.*	*Cot.*	*Visc*
Water 95°C 15 min	4	4	4/5
Sandozin NIE (5 g/l) 95°C 15 min	4	4	4/5
Synperonic 13/15 (5 g/l) 95°C 15 min	4	4	5
Synperonic 13/12 (5 g/l) 95°C 15 min	4	4	5
Brij 700 (5 g/l) 95°C 15 min	4	4	5
Matexil DN-VL 500 (5 g/l) 95°C 15 min	4/5	4/5	5
Synperonic A7 (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (1 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (5 g/l) 95°C 15 min	4/5	4/5	5
Water 95°C 30 min	4	4	4/5
Sandozin NIE (5 g/l) 95°C 30 min	4	4	4/5
Synperonic 13/15 (5 g/l) 95°C 30 min	4/5	4/5	5
Synperonic 13/12 (5 g/l) 95°C 30 min	4/5	4/5	5
Brij 700 (5 g/l) 95°C 30 min	4/5	4/5	5
Matexil DN-VL 500 (5 g/l) 95°C 30 min	4/5	4/5	5
Synperonic A7 (5 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (1 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (5 g/l) 95°C 30 min	4/5	4/5	5

cotton, it may not apply to the carboxylic acid groups since, owing to the low pH, of such groups, they can be considered as being completely ionised even under low (acidic) pH conditions. Although cotton swells readily in sodium hydroxide solutions, this being the basis of the mercerization process which imparts improved lustre and absorbency to the fibre, it does not swell appreciably in sodium carbonate solution. Thus the effectiveness of sodium carbonate in removing unfixed dye cannot be attributed to fibre swelling which would enhance movement of the dye out of the dyed material.

The observed increase in the removal of unfixed dye that accompanied an increase in the length of time of wash-off can simply be attributed to the duration of each of the above effects having been increased.

TABLE 18
Wash Fastness Ratings of Samples Dyed with CI Reactive Orange 86

After treatment	*Ch.*	*Cot.*	*Visc.*
Water 80°C 15 min	4/5	4	4/5
Sandozin NIE (5 g/l) 80°C 15 min	4/5	4	4/5
Synperonic 13/15 (5 g/l) 80°C 15 min	4/5	4	4/5
Synperonic 13/12 (5 g/l) 80°C 15 min	4/5	4	4/5
Brij 700 (5 g/l) 80°C 15 min	4/5	4	4/5
Matexil DN-VL 500 (5 g/l) 80°C 15 min	4/5	4	4/5
Synperonic A7 (5 g/l) 80°C 15 min	4/5	4	4/5
Na_2CO_3 (1 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l) 80°C 15 min	4/5	4/5	5
Na_2CO_3 (5 g/l) 80°C 15 min	4/5	4/5	5
Water 80°C 30 min	4/5	4	4/5
Sandozin NIE (5 g/l) 80°C 30 min	4/5	4/5	5
Synperonic 13/15 (5 g/l) 80°C 30 min	4/5	4	4/5
Synperonic 13/12 (5 g/l) 80°C 30 min	4/5	4	4/5
Brij 700 (5 g/l) 80°C 30 min	4/5	4	4/5
Matexil DN-VL 500 (5 g/l) 80°C 30 min	4/5	4	4/5
Synperonic A7 (5 g/l) 80°C 30 min	4/5	4	4/5
Na_2CO_3 (1 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (5 g/l) 80°C 30 min	4/5	4/5	5

Wash-fastness

Tables 15–21 show the effect of wash-off on the wash fastness of samples which had been dyed using 2% omf CI Reactive Red 2, CI Reactive Orange 86 and CI Reactive Blue 163. It is evident that, in general, dyeings which had been washed-off using tap water only or using each of the six surfactants alone, at each of the temperatures and durations of wash-off, displayed lower wash fastness than those dyeings which had been washed-off using sodium carbonate alone or the six surfactants in the presence of alkali. Also, it is apparent that there was little difference between the six surfactants, when used in conjunction with sodium carbonate, in terms of the level of wash

TABLE 19
Wash Fastness Ratings of Samples Dyed with CI Reactive Orange 86

After treatment	*Ch.*	*Cot.*	*Visc.*
Water 95°C 15 min	4/5	4	4/5
Sandozin NIE (5 g/l) 95°C 15 min	4/5	4/5	5
Synperonic 13/15 (5 g/l) 95°C 15 min	4/5	4	4/5
Synperonic 13/12 (5 g/l) 95°C 15 min	4/5	4/5	5
Brij 700 (5 g/l) 95°C 15 min	4/5	4	5
Matexil DN-VL 500 (5 g/l) 95°C 15 min	4/5	4/5	5
Synperonic A7 (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (1 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l) 95°C 5 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (5 g/l) 95°C 15 min	4/5	4/5	5
Water 95 °C 30 min	4/5	4	4/5
Sandozin NIE (5 g/l) 95°C 30 min	4/5	4/5	5
Synperonic 13/15 (5 g/l) 95°C 30 min	4/5	4	4/5
Synperonic 13/12 (5 g/l) 95°C 30 min	4/5	4	5
Brij 700 (5 g/l) 95°C 30 min	4/5	4	4/5
Matexil DN-VL 500 (5 g/l) 95°C 30 min	4/5	4/5	5
Synperonic A7 (5 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (1 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l) 95°C 30 min	4/5	4/5	5
Na_2CO_3 (5 g/l) 95°C 30 min	4/5	5	5

fastness achieved. This finding implies that there is little, if any, correlation between the type of surfactant used and wash fastness achieved.

It is also clear from Tables 15–21 that, in general, there was no difference in wash fastness between dyeings that had been washed-off using each of the three concentrations of sodium carbonate and using each of the six surfactants in conjunction with alkali. Thus, although the results in Tables 3–14 showed that sodium carbonate alone generally removed less unfixed dye from the dyeings than was achieved using the surfactants in conjunction with alkali, the wash fastness results presented in Tables 15–21 suggest that the additional dye removal achieved by the co-use of surfactant and alkali had no meritorious effect on wash fastness. Consequently, it can be proposed

TABLE 20
Wash Fastness Ratings of Samples Dyed with CI Reactive Blue 163

After treatment	*Ch.*	*Cot.*	*Visc.*
Water 80°C 15 min	3/4	4	4/5
Brij 700 (5 g/l) 80°C 15 min	3/4	4	4/5
Sandozin NIE (5 g/l) 80°C 15 min	3/4	4	4/5
Matexil DN-VL 500 (5 g/l) 80°C 15 min	3/4	4	4/5
Synperonic 13/15 (5 g/l) 80°C 15 min	3/4	4	5
Synperonic A7 (5 g/l) 80°C 15 min	3/4	4	5
Synperonic 13/12 (5 g/l) 80°C 15 min	3/4	4	5
Na_2CO_3 (1 g/l) 80°C 15 min	4	4/5	5
Na_2CO_3 (2 g/l) 80°C 15 min	4	4/5	5
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l) 80°C 15 min	4	4/5	5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l) 80°C 15 min	4	4/5	5
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l) 80°C 15 min	4	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l) 80°C 15 min	4	4/5	5
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l) 80°C 15 min	4	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l) 80°C 15 min	4	4/5	5
Na_2CO_3 (5 g/l) 80°C 15 min	4	4/5	5
Water 80°C 30 min	3/4	4	4/5
Brij 700 (5 g/l) 80°C 15 min	3/4	4	4/5
Sandozin NIE (5 g/l) 80°C 3O min	3/4	4	5
Matexil DN-VL 500 (5 g/l) 80°C 30 min	3/4	4	5
Synperonic 13/15 (5 g/l) 80°C 30 min	3/4	4	5
Synperonic A7 (5 g/l) 80°C 30 min	3/4	4/5	5
Synperonic 13/12 (5 g/l) 80°C 30 min	4	4/5	5
Na_2CO_3 (1g/l) 80°C 30 min	4	5	5
Na_2CO_3 (2 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l) 80°C 30 min	4	5	5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l) 80°C 30 min	4/5	5	5
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l) 80°C 30 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l) 80°C 30 min	4/5	5	5
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l) 80°C 30 min	4/5	5	5
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l) 80°C 30 min	4/5	5	5
Na_2CO_3 (5 g/l) 80°C 30 min	4/5	5	5

that sodium carbonate alone, is sufficient to achieve an adequate level of wash fastness.

In the case of CI Reactive Red 2 and CI Reactive Orange 86, there was no difference between the three concentrations of alkali used in terms of the level of wash fastness achieved whereas for CI Reactive Blue 163, a concentration of 1 g/l alkali was less effective than 2 g/l and 5 g/l sodium carbonate.

Tables 15–21 also reveal that the temperature and duration of wash-off had little effect on wash fastness, even though Tables 3–14 showed that the extent of dye removal increased with increasing temperature and duration of wash-off. This implies that the additional dye removal achieved by using the

TABLE 21
Wash Fastness Ratings of Samples Dyed with CI Reactive Blue 163

After treatment	*Ch.*	*Cot.*	*Visc.*
Water 95°C 15 min	3/4	4	5
Brij 700 (5 g/l) 95°C 15 min	3/4	4	5
Sandozin NIE (5 g/l) 95°C 15 min	3/4	4	5
Matexil DN-VL 500 (5 g/l) 95°C 15 min	3/4	4	5
Synperonic 13/15 (5 g/l) 95°C 15 min	4	4/5	5
Synperonic A7 (5 g/l) 95°C 15 min	4	4/5	5
Synperonic 13/12 (5 g/l) 95°C 15 min	4	4/5	5
Na_2CO_3 (1 g/l) 95°C 15 min	4	4/5	5
Na_2CO_3 (2 g/l) 95°C 15 min	4/5	5	5
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l) 95°C 15 min	4/5	5	5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l) 95°C 15 min	4/5	5	5
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l) 95°C 15 min	4/5	4/5	5
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l) 95°C 15 min	4/5	5	5
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l) 95°C 15 min	4/5	5	5
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l) 95°C 15 min	4/5	5	5
Na_2CO_3 (5 g/l) 95°C 15 min	4/5	5	5
Water 95°C 30 min	4	4/5	5
Brij 700 (5 g/l) 95°C 30 min	4	4/5	5
Sandozin NIE (5 g/l) 95°C 30 min	4	4/5	5
Matexil DN-VL 500 (5 g/l) 95°C 30 min	4	4/5	5
Synperonic 13/15 (5 g/l) 95°C 30 min	4	4/5	5
Synperonic A7 (5 g/l) 95°C 30 min	4	4/5	5
Synperonic 13/12 (5 g/l) 95°C 30 min	4	4/5	5
Na_2CO_3 (1 g/l) 95°C 30 min	4	4/5	5
Na_2CO_3 (2 g/l) 95°C 30 min	4/5	5	5
Na_2CO_3 (2 g/l) + Brij 700 (5 g/l) 95°C 30 min	4/5	5	5
Na_2CO_3 (2 g/l) + Sandozin NIE (5 g/l) 95°C 30 min	4/5	5	5
Na_2CO_3 (2 g/l) + Matexil DN-VL 500 (5 g/l) 95°C	4/5	5	5
Na_2CO_3 (2 g/l) + Synperonic 13/15 (5 g/l) 95°C	4/5	5	5
Na_2CO_3 (2 g/l) + Synperonic A7 (5 g/l) 95°C 15 min	4/5	5	5
Na_2CO_3 (2 g/l) + Synperonic 13/12 (5 g/l) 95°C 30 min	4/5	5	5
Na_2CO_3 (5 g/l) 95°C 30 min	4/5	5	5

longest (30 min) and highest temperature (95°C) of wash-off had no meritorious effect on wash fastness and, therefore, that wash-off for 15 min at 80°C is sufficient to achieve an adequate level of wash fastness.

Whilst the results displayed in Tables 15–21 confirm the very good wash fastness of such reactive dyes on cotton, it is apparent that none of the dyeings exhibited excellent wash fastness (i.e. ratings of 5 for shade change, staining of cotton adjacent and staining of viscose adjacent). This latter finding obviously demonstrates that all unfixed reactive dye had not been washed-off, which, in turn, implies that none of the wash-off methods used was fully effective in removing all unfixed dye from the dyeings. Consequently, it appears that more stringent wash-off is required to achieve complete unfixed dye removal and, thus, excellent wash fastness ratings; work is in hand to address this matter.

CONCLUSIONS

Although the extent of removal of unfixed reactive dye from the 2% omf dyeings of the three reactive dyes from cotton increased with increasing duration and temperature of wash-off, the level of wash fastness achieved was generally unaffected by these two variables. From the wash fastness and dye removal results secured, it appears that the use of surfactants in wash-off is unnecessary and that a wash-off using between 2 and 5 g/l sodium carbonate is sufficient to achieve an adequate level of wash fastness.

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