ELSEVIER

Dyes and Pigments, Vol. 33, No. 1, pp. 11–31, 1997

PII: S0143-7208(96)00033-2 0143-7208/97 $17.00 + 0.00

The Wash-off of Reactive Dyes on Cellulosic Fibres Part 2. Monochlorotriazinyl Dyes on Cotton

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(Received 8 March 1996; accepted 16 April 1996)

ABSTRACT

One monochlorotriazinyl and two bis-monochlorotriazinyl dyes were applied to cotton fabric at 1, 2 and 4% omf and the dyeings then washed-off using tap water, sodium carbonate and five commercial surfactants, the latter in both the presence and absence of sodium carbonate. The concentration of sodium carbonate was varied and its effects on both the extent of dye removal from the dyeings and the wash fastness of the dyeings were determined. Sodium carbonate, as well as each of the five surfactants used, was more effective in removing dye than tap water alone; the use of each of the surfactants in conjunction with sodium carbonate enhanced the effectiveness of the surfactants in removing unfixed dye. Dyeings which had been washed-off using sodium carbonate alone or using the five surfactants in the presence of alkali, were found to exhibit superior wash fastness to dyeings that had been washed-off using tap water only or each of the surfactants alone. In general, it appears that the use of surfactants in the wash-off of monochlorotriazinyl reactive dyes may be unnecessary and that an adequate level of wash-off can be achieved using 2 g litre^{-1} sodium carbonate alone. The avoidance of surfactants in wash-off and the alternative use of sodium carbonate may result in a process that is not only more cost-effective but also more environmentally friendly.

Keywords: Reactive dyes, cotton, wash-off, alkali, non-detergent.

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INTRODUCTION

This year commemorates the commercial introduction, 40 years ago, of reactive dyes for cellulosic fibres. Over the intervening decades, both the chemistry and application of reactive dyes has evoked enormous scientific interest and has been the subject of myriad publications; furthermore, the past 40 years has witnessed the introduction of numerous commercial ranges of reactive dyes for cellulosic fibres from a variety of manufacturers as well as the demise of many commercial ranges of reactive dyes.

Although reactive dyes on cellulosic fibres exhibit characteristically very good/excellent fastness to wet treatments, the exhaustion application of the dyes to the fibres suffers the notable disadvantage 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. In turn, this hydrolysis of the reactive dyes reduces the efficiency of dye–fibre reaction (fixation) and results in dye wastage, the need to thoroughly wash-off reactive dyeings and substantial effluent problems. These major deficiencies have accompanied reactive dyes since their commercial introduction in 1956 and still burden contemporary ranges of reactive dyes for cellulosic fibres. Indeed, despite the astonishing amount of research that has been expended on the dyes over the last 40 years, it can be argued that relatively little progress has been made in surmounting these particular deficiencies.

This paper concerns the wash-off of reactive dyes on cellulosic fibres. Although the wash-off process varies according to each dye maker's recommendations, it usually consists of one or more treatments with hot detergent solutions or hot water; alternatively, some types of reactive dyes can be aftertreated with selected cationic fixing agents when the dyeing has not been efficiently washed-off.[1] Despite the profusion of publications that have attended reactive dyes since 1956, little published work concerning the wash-off of reactive dyes from cellulosic fibres exists. As mentioned in the first part of this paper,[2] the nature of the wash-off depends on several factors, such as the depth of shade applied, the type of dye used, as well as the type and construction of the substrate. The effectiveness of wash-off is of critical importance since the characteristically very high fastness to wet treatments exhibited by reactive dyes on cellulosic substrates can be achieved only when either all or a major proportion of unfixed dye has been removed from the dyeing using a wash-off process.[3] Moreover, as the need for environmentally friendly chemical processes continues to increase, the wash-off process, apart from being efficient, should also be of low environmental impact.

EXPERIMENTAL

Materials

Fabric
Scoured and bleached woven cotton (130 g/m^2), obtained from Whaleys, was used.

Dyes
Three commercial reactive dyes, namely Procion Red H-EXL (C.I. Reactive Red 58), Procion Yellow H-EXL (C.I. Reactive Yellow 138:1) and Procion Royal H-EXL (no available C.I. number), were used. Each dye was kindly supplied by Zeneca Colours and was not purified prior to use.

Surfactants
Five commercial surfactants were used for the wash-off of the reactive dyeings, namely Sandozin NIE (alkylene oxide), which was generously supplied by Sandoz (UK), Lanapex R (a mixture of modified phosphate esters with polyphosphates), Synperonic 13/12 (oxo alcohol ethoxylate), Synperonic A7 (fatty alcohol ethoxylate) and Matexil DN-VL 500 (modified fatty alcohol/ethylene oxide condensate), each kindly supplied by ICI Surfactants. The five surfactants were chosen as being typical representatives of different types of surfactant.

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

Procedures

Dyeing
All dyeings were carried out in distilled water, using fabric (2 g) which had been wetted out in cold distilled water, in metal dyepots of 300 cm^3 capacity, housed in a Zeltex Polycolor laboratory-scale dyeing machine, employing a 20:1 liquor ratio. The dyeing method used was the eXceL Standard application method[4] shown in Fig. 1. The chemical requirements for dyeing are shown in Table 1.

Rinsing and wash-off
At the end of dyeing, the sample was rinsed twice in tap water for 10 min at 70°C and washed-off using the following methods:

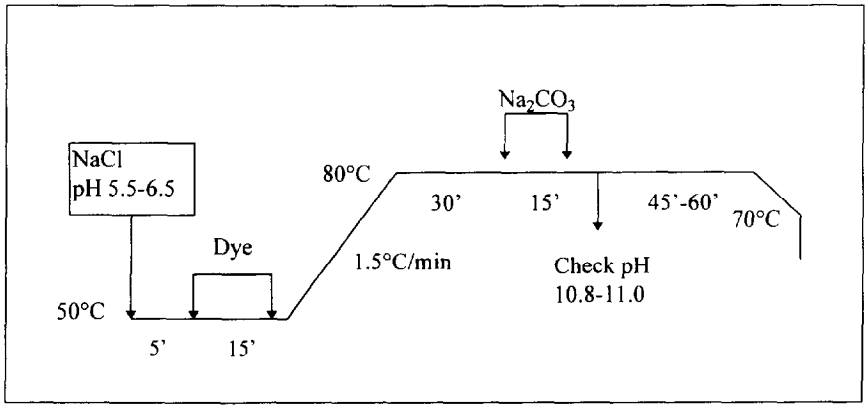

Fig. 1. Dyeing method.

TABLE 1
Chemical Requirements and Fixation Times of the Dyeings[5]

Depth of shade (%)	*Sodium chloride (g litre^{-1})*	*Sodium carbonate (g litre^{-1})*	*Fixation times*
1	45	15	45
2	60	15	45
4	70	20	60

(i) the recommended wash-off process[5] using 1 g litre^{-1} Lanapex R at 98°C for 30 min;
(ii) tap water at 95°C for 30 min;
(iii) an aqueous sodium carbonate (1 g litre^{-1}, 2 g litre^{-1} or 5 g litre^{-1}) solution at 95°C for 30 min;
(iv) an aqueous solution of each of the five surfactants (5 g litre^{-1}) either alone or in conjunction with sodium carbonate (2 g litre^{-1}) at 95°C for 30 min.

Both rinsing and wash-off were carried out using a 30:1 liquor ratio. At the end of wash-off, the sample was rinsed in tap water at 70°C for 10 min and then in cold tap water for a further 10 min. The method used for rinsing and wash-off is shown in Fig. 2.

Colour measurement

The reflectance values of the dry, lightly ironed, dyed samples were measured using a Colorgen reflectance spectrophotometer interfaced to a personal computer under illuminant D_{65}, using a 10° Standard Observer, with specular component excluded and UV component included. The corresponding

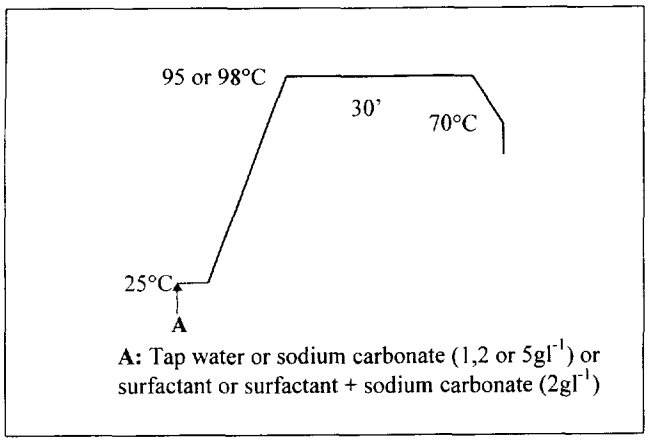

Fig. 2. Wash-off method.

K/S and L*, a*, b*, C* and h° values of the samples were calculated at the appropriate λ_{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 C06/C2 method.[6]

RESULTS AND DISCUSSION

The decision to apply three different depths of shade, namely 1, 2 and 4%, was made in order to investigate the effect of dye concentration on the efficiency of wash-off. The selection of the five commercial surfactants was based on their being representative of different types of non-ionic surfactant; it was not the intention of this work to compare the effectiveness of each surfactant or 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 ingredient and so each of the surfactants was used at the strength provided by the respective maker.

Wash-off

In the tables and figures that follow the colour strength (K/S values) and the colorimetric parameters (L*, a*, b*, C* and h°) of the dyeings are shown, as well as the difference in colour strength (ΔK/S) between dyeings which had not been washed-off and dyeings which had been washed-off. In addition, the

percentage difference in colour strength (%ΔK/S) between unwashed-off and washed-off dyeings are displayed. The latter two parameters were calculated as described previously.[2]

C.I. Reactive Red 58

From Tables 2 to 4 it can be seen that the colour strength (K/S value) of the washed-off dyeings was lower than that of the corresponding unwashed-off dyeings, indicating that unfixed reactive dye was removed during wash-off. The ΔK/S and %ΔK/S values shown in Tables 2–4 reveal that of the various wash-off methods used, that which employed water only was the least effective in removing unfixed dye from the dyeings. It is also evident that an alkaline solution of each of the surfactants was more effective in removing unfixed dye than either surfactant alone or Na_2CO_3 alone. In the case of the five surfactants used, there was little difference in the extent to which they removed dye; this was also manifest when the surfactants were used in conjunction with sodium carbonate, even though the effectiveness of the five surfactants was markedly enhanced when they were used in combination with 2 g litre^{-1} sodium carbonate. In the case of sodium carbonate alone, the colour strength of the washed-off dyeings decreased in the order 1 g litre^{-1} < 2 g litre^{-1} < 5 g litre^{-1}, the difference between the effectiveness of 2 g litre^{-1} and 5 g litre^{-1} being very small.

The colorimetric parameters of the washed-off samples in Table 2–4 show that each of the wash-off treatments caused a slight blueing of the shade and that this change in shade generally increased with increasing extent of dye removal.

Procion Royal H-EXL and C.I. Reactive Yellow 138:1

Tables 5–10 show the results obtained for the wash-off of 1, 2 and 4% omf dyeings of Procion Royal H-EXL and C.I. Reactive Yellow 138:1, respectively. The results followed the same pattern as those obtained for C.I. Reactive Red 58 (Tables 2–4) in that the colour strength of the washed-off dyeings decreased in the order: water < surfactant < Na_2CO_3 < Na_2CO_3 (2 g litre^{-1}) + surfactant (5 g litre^{-1})

The colorimetric parameters of the washed-off samples in Tables 5–10 reveal that each of the washed-off treatments caused a slight blueing of the shade, the extent of which generally increased with increasing extent of dye removal.

Discussion

Sodium carbonate proved to be remarkably efficient in removing unfixed dye from the dyed substrate, especially when used in conjunction with each of the five surfactants. To explain this, the argument previously recounted[2] will be forwarded.

TABLE 2
Wash-off of 1% omf C.I. Reactive Red 58

Wash-off method	*K/S*	$\Delta K/S$	$\%\Delta K/S$	*L**	*a**	*b**	*C**	*h°*
Nil	5.32	—	—	49.64	50.47	−9.56	51.37	349.3
Water	4.37	0.95	17.86	51.88	47.66	−9.80	48.66	348.4
Lanapex R (1 g litre^{-1})	4.24	1.08	20.30	52.26	48.07	−9.81	49.06	348.5
Lanapex R (5 g litre^{-1})	4.04	1.28	24.06	53.74	47.49	−9.54	48.44	348.6
Sandozin NIE (5 g litre^{-1})	4.06	1.26	23.68	52.18	47.70	−9.89	48.71	348.3
Synperonic 13/12 (5 g litre^{-1})	3.99	1.33	25.00	52.21	47.18	−9.83	48.19	348.2
Synperonic A7 (5 g litre^{-1})	4.02	1.30	24.44	52.16	47.32	−9.82	48.33	348.3
Matexil DN-VL 500 (5 g litre ^{1})	4.06	1.26	23.68	51.89	47.16	−9.81	48.17	348.2
Na_2CO_3 (1 g litre^{-1})	3.85	1.47	27.63	53.36	48.27	−9.92	49.28	348.4
Na_2CO_3 (2 g litre^{-1})	3.73	1.59	29.89	52.84	46.54	−9.81	47.56	348.1
Na_2CO_3 (5 g litre^{-1})	3.70	1.62	30.45	53.18	46.89	−10.02	47.95	347.9
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	3.70	1.62	30.45	53.53	47.75	−9.50	48.69	348.7
Na_2CO_3 (2 g litre ^{1}) + Sandozin NIE (5 g litre ^{1})	3.66	1.66	31.20	53.02	46.41	−10.09	47.50	347.7
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre ^{1})	3.68	1.64	30.83	53.15	46.57	−10.12	47.65	347.7
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	3.56	1.76	33.08	53.41	46.70	−10.31	47.34	347.4
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	3.71	1.61	30.26	53.48	47.73	−9.42	48.65	348.8

TABLE 3
Wash-off of 2% omf C.I. Reactive Red 58

Wash-off method	*K/S*	$\Delta K/S$	$\%\Delta K/S$	*L**	*a**	*b**	*C**	h°
Nil	9.55	—	—	43.22	53.53	−6.69	53.95	352.9
Water	8.36	1.19	12.46	44.47	52.36	−7.35	59.87	352.0
Lanapex R (1 g litre $^{-1}$)	8.17	1.38	14.45	43.83	48.07	−9.66	49.03	348.6
Lanapex R (5 g litre^{-1})	7.75	1.80	18.85	46.54	51.60	−7.54	52.15	351.7
Sandozin NIE (5 g litre^{-1})	7.94	1.61	16.86	44.58	51.45	−7.83	52.04	351.3
Synperonic 13/12 (5 g litre^{-1})	7.72	1.83	19.16	44.90	51.33	−7.91	51.94	351.2
Synperonic A7 (5 g litre^{-1})	7.68	1.87	19.58	44.85	51.06	−8.01	51.69	351.1
Matexil DN-VL 500 (5 g litre^{-1})	7.83	1.72	18.01	44.55	51.14	−7.90	51.75	351.2
Na_2CO_3 (1 g litre $^{-1}$)	7.11	2.44	25.55	45.48	50.41	−7.84	51.02	351.2
Na_2CO_3 (2 g litre^{-1})	7.06	2.49	26.07	45.61	50.38	−8.05	51.02	350.9
Na_2CO_3 (5 g litre^{-1})	6.92	2.63	27.54	46.32	51.54	−7.71	52.11	351.5
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	6.78	2.77	29.01	46.63	51.57	−7.62	52.13	351.6
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	7.01	2.54	26.60	45.81	50.71	−8.20	51.37	350.8
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	7.01	2.54	26.60	46.34	51.85	−7.51	52.39	351.8
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	6.72	2.83	29.63	46.17	50.22	−8.45	50.93	350.4
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre $^{-1}$)	6.72	2.83	29.63	46.69	51.46	−7.65	52.03	351.5

TABLE 4
Wash-off of 4% omf C.I. Reactive Red 58

Wash-off method	*K/S*	$\Delta K/S$	$\%\Delta K/S$	*L**	*a**	*b**	*C**	*h°*
Nil	14.31	—	—	38.21	53.20	−3.18	53.29	356.6
Water	13.45	0.86	6.01	38.61	52.93	−3.93	53.08	355.8
Lanapex R (1 g litre^{-1})	13.15	1.16	8.11	38.83	51.92	−4.18	52.09	355.4
Lanapex R (5 g litre^{-1})	12.81	1.50	10.48	40.36	52.24	−3.54	52.36	356.1
Sandozin NIE (5 g litre^{-1})	12.79	1.52	10.62	38.89	51.80	−4.74	52.02	354.8
Synperonic 13/12 (5 g litre^{-1})	12.91	1.40	9.78	38.67	51.63	−4.62	51.84	354.9
Synperonic A7 (5 g litre^{-1})	13.01	1.30	9.08	38.54	51.64	−4.71	51.85	354.8
Matexil DN-VL 500 (5 g litre^{-1})	12.91	1.40	9.78	38.84	51.83	−4.76	52.05	354.8
Na_2CO_3 (1 g litre^{-1})	11.74	2.57	17.96	40.25	52.92	−3.87	53.06	355.8
Na_2CO_3 (2 g litre^{-1})	11.58	2.73	19.08	39.44	50.92	−4.66	51.14	354.8
Na_2CO_3 (5 g litre^{-1})	11.43	2.88	20.13	39.88	51.32	−4.86	51.55	354.6
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	11.25	3.06	21.38	40.41	52.56	−3.58	52.68	356.1
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	11.01	3.30	23.06	40.70	52.4	−3.81	52.53	355.8
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	11.07	3.24	22.64	40.20	51.29	−5.17	51.55	354.2
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	10.98	3.33	23.27	40.27	51.05	−5.49	51.35	353.9
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	11.19	3.12	21.80	40.28	52.12	−3.56	52.24	356.1

TABLE 5
Wash-off of 1% omf Procion Royal H-EXL

Wash-off method	*K/S*	$\Delta K/S$	$\%\Delta K/S$	*L**	*a**	*b**	*C**	*h*°
Nil	6.69	—	—	46.40	−2.60	−39.04	39.13	266.2
Water	5.32	1.37	20.48	49.80	−2.76	−37.62	37.72	265.8
Lanapex R (1 g litre^{-1})	5.10	1.59	23.77	50.73	−3.68	−37.53	37.71	264.4
Lanapex R (5 g litre^{-1})	4.84	1.85	27.65	51.39	−4.03	−37.03	37.25	263.8
Sandozin NIE (5 g litre^{-1})	4.82	1.87	27.95	50.10	−3.18	−37.44	37.57	265.1
Synperonic 13/12 (5 g litre^{-1})	4.79	1.90	28.40	50.11	−2.81	−36.86	36.97	265.6
Synperonic A7 (5 g litre^{-1})	4.78	1.91	28.55	50.26	−9.88	−37.16	37.27	265.6
Matexil DN-VL 500 (5 g litre^{-1})	4.87	1.82	27.20	49.74	−2.78	−37.21	37.32	265.7
Na_2CO_3 (1 g litre^{-1})	4.75	1.94	29.00	50.81	−3.75	−37.07	37.26	264.2
Na_2CO_3 (2 g litre^{-1})	4.68	2.01	30.04	50.47	−2.73	−37.40	37.50	265.8
Na_2CO_3 (5 g litre^{-1})	4.50	2.19	32.74	50.83	−2.72	−37.11	37.20	265.8
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	4.64	2.05	30.64	51.26	−3.98	−37.08	37.29	263.9
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	4.46	2.23	33.33	51.27	−3.04	−37.44	37.57	265.4
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	4.61	2.08	31.09	51.04	−3.15	−37.53	37.66	265.2
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	4.47	2.22	33.18	51.28	−3.03	−37.38	37.50	265.4
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	4.53	2.16	32.29	51.10	−3.17	−37.24	37.37	265.1

TABLE 6
Wash-off of 2% omf Procion Royal H-EXL

Wash-off method	*K/S*	$\Delta K/S$	$\%\Delta K/S$	*L**	*a**	*b**	*C**	h°
Nil	11.71	—	—	38.15	1.86	−41.60	41.64	272.6
Water	9.87	1.84	15.71	41.00	0.72	−40.81	40.82	271.0
Lanapex R (1 g litre^{-1})	9.75	1.96	16.74	40.90	0.77	−40.64	40.64	271.1
Lanapex R (5 g litre^{-1})	9.38	2.33	19.90	42.53	−0.84	−39.57	39.57	268.8
Sandozin NIE (5 g litre^{-1})	9.36	2.35	20.07	40.92	0.11	−40.40	40.40	270.2
Synperonic 13/12 (5 g litre^{-1})	9.29	2.42	20.67	41.40	0.52	−40.16	40.16	270.7
Synperonic A7 (5 g litre^{-1})	9.57	2.14	18.27	41.22	0.52	−40.51	40.51	270.7
Matexil DN-VL 500 (5 g litre^{-1})	9.40	2.31	19.73	41.08	0.74	−40.33	40.33	271.1
Na_2CO_3 (1 g litre^{-1})	8.81	2.90	24.77	41.70	0.48	−40.12	40.12	270.7
Na_2CO_3 (2 g litre^{-1})	8.64	3.07	26.22	42.09	0.78	−40.52	40.53	271.1
Na_2CO_3 (5 g litre^{-1})	8.37	3.34	28.52	42.12	0.95	−39.97	39.98	271.4
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	8.48	3.23	27.58	42.48	−0.88	−39.13	39.14	268.7
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	8.12	3.59	30.66	43.13	0.13	−40.39	40.39	270.2
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	8.46	3.25	27.75	42.56	−0.87	−39.28	39.29	268.7
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	8.51	3.20	27.33	42.44	0.54	−40.51	40.51	270.8
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	8.60	3.11	26.56	42.40	−0.85	−39.42	39.43	268.8

TABLE 7
Wash-off of 4% omf Procion Royal H-EXL

Wash-off method	*K/S*	$\Delta K/S$	$\%\Delta K/S$	*L**	*a**	*b**	*C**	h°
Nil	17.74	—	—	31.49	5.88	−41.35	41.77	278.1
Water	16.22	1.52	8.57	33.78	4.78	−41.83	42.10	276.5
Lanapex R (1 g litre $^{-1}$)	15.92	1.82	10.26	33.97	4.70	−41.61	41.87	276.4
Lanapex R (5 g litre^{-1})	15.37	2.37	13.36	35.61	3.61	−41.12	41.28	275.0
Sandozin NIE (5 g litre^{-1})	15.35	2.39	13.47	33.44	4.96	−41.41	41.70	276.8
Synperonic 13/12 (5 g litre^{-1})	15.30	2.44	13.75	33.95	4.85	−41.34	41.63	276.7
Synperonic A7 (5 g litre $^{-1}$)	15.41	2.33	13.13	34.12	4.66	−41.57	41.83	276.4
Matexil DN-VL 500 (5 g litre^{-1})	15.30	2.44	13.75	33.88	4.77	−41.37	41.65	276.6
Na_2CO_3 (1 g litre^{-1})	14.31	3.43	19.33	34.81	4.32	−41.34	41.56	276.0
Na_2CO_3 (2 g litre^{-1})	13.39	4.35	24.52	35.12	4.82	−41.30	41.58	276.7
Na_2CO_3 (5 g litre^{-1})	13.18	4.56	25.70	35.42	3.83	−40.87	41.04	275.4
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	13.30	4.44	25.03	35.69	3.47	−40.97	41.11	274.8
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	13.18	4.56	25.70	35.64	3.57	−40.89	41.05	275.0
Na_2CO_3 (2 g litre $^{-1}$) + Synperonic 13/12 (5 g litre $^{-1}$)	13.26	4.48	25.25	35.55	4.45	−41.43	41.67	276.1
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	13.10	4.64	26.16	35.71	3.50	−40.83	40.98	274.9
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	13.22	4.52	25.48	35.63	3.61	−40.95	41.11	275.0

TABLE 8
Wash-off of 1% omf C.I. Reactive Yellow 138:1

Wash-off method	*K/S*	$\Delta K/S$	$\%\Delta K/S$	*L**	*a**	*b**	*C**	h°
Nil	4.89	—	—	71.15	31.74	59.42	67.37	61.9
Water	4.52	0.37	7.57	71.98	30.89	58.56	66.21	62.2
Lanapex R (1 g litre^{-1})	4.38	0.51	10.43	72.53	29.91	57.74	65.03	62.6
Lanapex R (5 g litre^{-1})	4.22	0.67	13.70	73.05	29.62	57.24	64.46	62.6
Sandozin NIE (5 g litre^{-1})	4.23	0.66	13.50	72.17	30.79	57.98	49.13	62.0
Synperonic 13/12 (5 g litre ^{1})	4.25	0.64	13.09	72.30	30.97	58.63	66.31	62.2
Synperonic A7 (5 g litre^{-1})	4.20	0.69	14.11	72.33	30.65	57.91	49.15	62.1
Matexil DN-VL 500 (5 g litre^{-1})	4.24	0.65	13.29	72.14	31.15	58.60	49.64	62.0
Na_2CO_3 (1 g litre^{-1})	4.09	0.80	16.36	72.58	30.31	57.61	65.10	62.3
Na_2CO_3 (2 g litre^{-1})	3.96	0.93	19.02	72.64	30.00	56.91	64.34	62.2
Na_2CO_3 (5 g litre^{-1})	3.81	1.08	22.09	73.16	28.93	56.61	63.57	62.9
Na_2CO_3 (2 g litre ^{1}) + Lanapex R (5 g litre^{-1})	3.90	0.99	20.25	73.05	29.58	57.16	64.36	62.6
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	3.86	1.03	21.06	73.02	30.18	56.91	48.26	62.1
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	3.70	1.19	24.34	73.33	29.99	56.42	47.80	62.0
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre ^{1})	3.86	1.03	21.06	73.06	30.27	56.97	48.28	62.0
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	3.95	0.94	19.22	72.95	29.82	57.43	64.71	62.6

TABLE 9
Wash-off of 2% omf C.I. Reactive Yellow 138:1

Wash-off method	*K/S*	*ΔK/S*	*%ΔK/S*	*L**	*a**	*b**	*C**	*h°*
Nil	8.41	—	—	67.07	37.44	65.56	75.50	60.3
Water	7.78	0.63	7.49	67.50	36.81	64.48	74.25	60.3
Lanapex R (1 g litre^{-1})	7.67	0.74	8.80	67.53	36.73	64.16	73.93	60.2
Lanapex R (5 g litre^{-1})	7.48	0.93	11.06	68.60	35.63	63.33	72.66	60.6
Sandozin NIE (5 g litre^{-1})	7.46	0.95	11.30	67.46	36.91	63.84	52.10	60.0
Synperonic 13/12 (5 g litre^{-1})	7.52	0.89	10.58	67.61	36.98	64.10	74.00	60.0
Synperonic A7 (5 g litre^{-1})	7.58	0.83	9.87	67.51	37.10	64.16	52.36	60.0
Matexil DN-VL 500 (5 g litre^{-1})	7.58	0.83	9.87	67.51	37.18	64.19	52.33	59.9
Na_2CO_3 (1 g litre^{-1})	6.99	1.42	16.88	67.90	36.67	63.01	72.91	59.8
Na_2CO_3 (2 g litre^{-1})	6.91	1.50	17.84	68.12	36.28	62.97	72.67	60.1
Na_2CO_3 (5 g litre^{-1})	6.75	1.66	19.74	68.33	35.85	62.84	72.34	60.3
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	6.80	1.61	19.14	68.27	35.94	63.01	72.54	60.3
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	6.55	1.86	22.12	68.33	36.43	62.48	50.78	59.8
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	6.69	1.72	20.45	68.33	36.44	62.88	51.25	59.9
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	6.51	1.90	22.59	68.50	36.28	62.50	50.90	59.9
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	6.89	1.52	18.07	67.97	36.82	62.88	72.87	59.6

TABLE 10
Wash-off of 4% omf C.I. Reactive Yellow 138:1

Wash-off method	*K/S*	$\Delta K/S$	$\%\Delta K/S$	*L**	*a**	*b**	*C**	*h°*
Nil	12.83	—	—	61.71	42.62	65.81	78.41	57.1
Water	11.94	0.89	6.94	62.85	42.10	67.37	79.45	58.0
Lanapex R (1 g litre^{-1})	11.86	0.97	7.56	62.98	41.64	66.27	78.26	57.9
Lanapex R (5 g litre^{-1})	11.29	1.54	12.00	64.04	40.75	65.64	77.26	58.2
Sandozin NIE (5 g litre^{-1})	11.28	1.55	12.08	62.72	41.74	65.86	50.96	57.6
Synperonic 13/12 (5 g litre^{-1})	11.32	1.51	11.77	63.09	41.79	66.33	78.40	57.8
Synperonic A7 (5 g litre^{-1})	11.10	1.73	13.48	63.08	41.80	65.91	50.96	57.6
Matexil DN-VL 500 (5 g litre^{-1})	11.30	1.53	11.93	62.81	42.07	65.77	50.56	57.4
Na_2CO_3 (1 g litre^{-1})	10.90	1.93	15.04	63.21	41.77	65.60	77.77	57.5
Na_2CO_3 (2 g litre ^{1})	10.54	2.29	17.85	63.72	41.21	65.73	77.58	57.9
Na_2CO_3 (5 g litre^{-1})	10.39	2.44	19.02	63.56	41.44	64.94	77.03	57.5
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre ^{1})	10.41	2.42	18.86	63.96	40.82	65.77	77.40	58.2
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	9.53	3.30	25.72	64.01	41.17	64.18	49.25	57.3
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	10.11	2.72	21.20	63.92	41.39	65.13	50.30	57.6
Na_2CO_3 (2 g litre ^{1}) + Synperonic A7 (5 g litre^{-1})	10.21	2.62	20.42	63.66	41.55	64.97	49.96	57.4
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre ^{1})	10.21	2.62	20.42	64.06	40.73	65.63	77.24	58.2

It is well known that aqueous, alkaline solutions of detergents are used in both the scouring and domestic laundering of textiles; in these processes, the alkali solubilises hydrophobes (fats, oils and waxes) present on the substrate, thus expediting their removal. Alkali is also often used in domestic washing formulations as a builder, in order to assist the wetting and detergent functions of surfactants. Thus, in the context of the present study, it is possible that sodium carbonate functioned in a manner described above, namely by increasing both the aqueous solubility of the unfixed dye and its propensity to move from the fibre phase to the aqueous phase as well as assisting the detergency action of the surfactants during wash-off.

Wash fastness

Tables 11–19 show the effect of wash-off on the wash fastness of samples that had been dyed using 1, 2 and 4% omf C.I. Reactive Red 58, Procion Royal H-EXL and C.I. Reactive Yellow 138:1. It is evident that, in general, dyeings which had been washed-off using tap water only displayed lower wash fastness than those samples which had been washed-off using sodium carbonate or each of the surfactants as well as each of the alkaline surfactant solutions. Dyeings that had been washed-off using each of the five surfactants alone generally exhibited slightly lower wash fastness than dyeings which had been washed-off using either sodium carbonate alone or each of the surfactants in conjunction with alkali. Generally, the level of wash fastness imparted by wash-off with sodium carbonate was identical to that imparted by wash-off with each of the five surfactants in the presence of sodium carbonate.

However, not all of the dyeings exhibited excellent wash fastness (i.e. ratings of 5 for shade change, staining of adjacent cotton and viscose fabrics), this being particularly evident for the 2% omf and, especially, the 4% omf dyeings. This shows that not all of the unfixed reactive dye had been washed-off, which, in turn, indicates that none of the wash-off methods used was fully effective in removing all unfixed dye from the dyeings.

CONCLUSIONS

From the dye removal and wash fastness results obtained, it is apparent that the use of surfactants in the wash-off of monochlorotriazinyl dyes from dyed cotton may be unnecessary and that an adequate level of wash-off can be achieved using 2 g litre^{-1} sodium carbonate alone. The avoidance of surfactants in wash-off and the alternative use of sodium carbonate would result in a process that was not only more cost-effective but also more environmentally friendly.

TABLE 11
Wash Fastness Ratings of Samples Dyed with 1% omf C.I. Reactive Red 58

Wash-off method	*Shade change*	*Staining of adjacent cotton*	*Staining of adjacent viscose*
Nil	3–4	3–4	4
Water	4–5	4–5	5
Lanapex R (1 g litre^{-1})	4–5	5	5
Lanapex R (5 g litre^{-1})	4–5	5	5
Sandozin NIE (5 g litre^{-1})	4–5	5	5
Synperonic 13/12 (5 g litre^{-1})	4–5	5	5
Synperonic A7 (5 g litre^{-1})	4–5	5	5
Matexil DN-VL 500 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (1 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1})	5	5	5
Na_2CO_3 (5 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	5	5	5

TABLE 12
Wash Fastness Ratings of Samples Dyed with 2% omf C.I. Reactive Red 58

Wash-off method	*Shade change*	*Staining of adjacent cotton*	*Staining of adjacent viscose*
Nil	3–4	3–4	3–4
Water	4	4–5	5
Lanapex R (1 g litre^{-1})	4–5	5	5
Lanapex R (5 g litre^{-1})	4–5	5	5
Sandozin NIE (5 g litre^{-1})	4–5	5	5
Synperonic 13/12 (5 g litre^{-1})	4–5	5	5
Synperonic A7 (5 g litre^{-1})	4–5	5	5
Matexil DN-VL 500 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (1 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1})	4–5	5	5
Na_2CO_3 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	4–5	5	5

TABLE 13
Wash Fastness Ratings of Samples Dyed with 4% omf C.I. Reactive Red 58

Wash-off method	*Shade change*	*Staining of adjacent cotton*	*Staining of adjacent viscose*
Nil	3–4	3	3
Water	4	4–5	5
Lanapex R (1 g litre^{-1})	4–5	4–5	5
Lanapex R (5 g litre^{-1})	4–5	4–5	5
Sandozin NIE (5 g litre^{-1})	4–5	5	5
Synperonic 13/12 (5 g litre^{-1})	4	4–5	5
Synperonic A7 (5 g litre^{-1})	4–5	4–5	5
Matexil DN-VL 500 (5 g litre^{-1})	4–5	4–5	5
Na_2CO_3 (1 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1})	4–5	5	5
Na_2CO_3 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	4–5	5	5

TABLE 14
Wash Fastness Ratings of Samples Dyed with 1% omf Procion Royal H-EXL

Wash-off method	*Shade change*	*Staining of adjacent cotton*	*Staining of adjacent viscose*
Nil	4	4	4–5
Water	4–5	5	5
Lanapex R (1 g litre^{-1})	4–5	5	5
Lanapex R (5 g litre^{-1})	4–5	5	5
Sandozin NIE (5 g litre^{-1})	4–5	4–5	5
Synperonic 13/12 (5 g litre^{-1})	4–5	5	5
Synperonic A7 (5 g litre^{-1})	4–5	5	5
Matexil DN-VL 500 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (1 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1})	5	5	5
Na_2CO_3 (5 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	5	5	5

TABLE 15
Wash Fastness Ratings of Samples Dyed with 2% omf Procion Royal H-EXL

Wash-off method	*Shade change*	*Staining of adjacent cotton*	*Staining of adjacent viscose*
Nil	4	3–4	4–5
Water	4–5	4–5	5
Lanapex R (1 g litre^{-1})	4–5	5	5
Lanapex R (5 g litre^{-1})	4–5	5	5
Sandozin NIE (5 g litre^{-1})	4–5	4–5	5
Synperonic 13/12 (5 g litre^{-1})	4–5	5	5
Synperonic A7 (5 g litre^{-1})	4–5	4–5	5
Matexil DN-VL 500 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (1 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1})	4–5	5	5
Na_2CO_3 (5 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	4-5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	4–5	5	5

TABLE 16
Wash Fastness Ratings of Samples Dyed with 4% omf Procion Royal H-EXL

Wash-off method	*Shade change*	*Staining of adjacent cotton*	*Staining of adjacent viscose*
Nil	3–4	3	4
Water	4	4–5	4–5
Lanapex R (1 g litre^{-1})	4–5	4–5	5
Lanapex R (5 g litre^{-1})	4–5	5	5
Sandozin NIE (5 g litre^{-1})	4	4	4–5
Synperonic 13/12 (5 g litre^{-1})	4–5	4–5	5
Synperonic A7 (5 g litre^{-1})	4–5	4–5	5
Matexil DN-VL 500 (5 g litre^{-1})	4–5	4–5	5
Na_2CO_3 (1 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1})	4–5	4–5	5
Na_2CO_3 (5 g litre^{-1})	4–5	4–5	5
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	4–5	4–5	5
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	4–5	4–5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	4–5	4–5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	4–5	4–5	5
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	4-5	4–5	5

TABLE 17
Wash Fastness Ratings of Samples Dyed with 1% omf C.I. Reactive Yellow 138:1

Wash-off method	*Shade change*	*Staining of adjacent cotton*	*Staining of adjacent viscose*
Nil	4	4	4–5
Water	4–5	5	5
Lanapex R (1 g litre^{-1})	4–5	5	5
Lanapex R (5 g litre^{-1})	4–5	5	5
Sandozin NIE (5 g litre^{-1})	4–5	5	5
Synperonic 13/12 (5 g litre^{-1})	4–5	5	5
Synperonic A7 (5 g litre^{-1})	4–5	5	5
Matexil DN-VL 500 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (1 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1})	5	5	5
Na_2CO_3 (5 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	5	5	5
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	5	5	5

TABLE 18
Wash Fastness Ratings of Samples Dyed with 2% omf C.I. Reactive Yellow 138:1

Wash-off method	*Shade change*	*Staining of adjacent cotton*	*Staining of adjacent viscose*
Nil	3–4	3–4	4
Water	4–5	5	5
Lanapex R (1 g litre^{-1})	4–5	5	5
Lanapex R (5 g litre^{-1})	4–5	5	5
Sandozin NIE (5 g litre^{-1})	4–5	4–5	5
Synperonic 13/12 (5 g litre^{-1})	4–5	5	5
Synperonic A7 (5 g litre^{-1})	4–5	4–5	5
Matexil DN-VL 500 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (1 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1})	4–5	5	5
Na_2CO_3 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	4–5	5	5

TABLE 19
Wash Fastness Ratings of Samples Dyed with 4% omf C.I. Reactive Yellow 138:1

Wash-off method	*Shade change*	*Staining of adjacent cotton*	*Staining of adjacent viscose*
Nil	3–4	3	4
Water	4	4–5	5
Lanapex R (1 g litre^{-1})	4–5	4–5	5
Lanapex R (5 g litre^{-1})	4–5	5	5
Sandozin NIE (5 g litre^{-1})	4–5	4–5	5
Synperonic 13/12 (5 g litre^{-1})	4–5	5	5
Synperonic A7 (5 g litre^{-1})	4–5	4–5	5
Matexil DN-VL 500 (5 g litre^{-1})	4–5	4–5	5
Na_2CO_3 (1 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1})	4–5	5	5
Na_2CO_3 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Lanapex R (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Sandozin NIE (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic 13/12 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Synperonic A7 (5 g litre^{-1})	4–5	5	5
Na_2CO_3 (2 g litre^{-1}) + Matexil DN-VL 500 (5 g litre^{-1})	4–5	5	5

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to the State Scholarships Foundation of Greece for the provision of funds for D. Katsarelias's studies.

REFERENCES

1. Burkinshaw, S. M. & Katsarelias, D., *Dyes and Pigments*, **29** (1995) 139.
2. Burkinshaw, S. M. & Anthoulias, A., *Dyes and Pigments*, **31** (1996) 171.
3. Burkinshaw, S. M., In *The Chemistry and Application of Dyes*, eds D. R. Waring & G. Hallas. Plenum Press, New York, 1990.
4. Collishaw, P. S., Phillips, D. A. S. & Bradbury, M. J., *J. Soc. Dyers Colour.*, **109** (1993) 284.
5. ICI Technical Information Pamphlet PL 284, Manchester 1988.
6. *Standard Methods for the Determination of the Colour Fastness of Textiles and Leather*, 5th edn. Society of Dyers and Colourists, Bradford, UK, 1990.