Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 76 (2008) 799–809
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

The reduction clearing of dyed polyester. Part 1: Colour strength

S.M. Burkinshaw*, N. Kumar

The University of Leeds, School of Design, Leeds LS2 9JT, UK

Received 30 August 2006; received in revised form 24 January 2007; accepted 31 January 2007
Available online 20 February 2007

Abstract

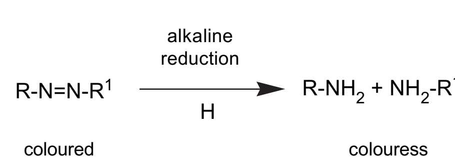
An alternative after treatment has been devised for polyester which has been dyed with disperse dyes. A comparison of colorimetric data obtained for dyeings which had been treated using a traditional, sodium dithionite-based reduction clearing process with those secured for dyeings which had been washed-off for 15 min at 98 °C with detergent-based process showed that the colour strength of the washed-off samples was slightly lower than that of the reduction cleared samples but there was no difference between the λ_{max} of the washed-off and reduction cleared dyeings; in addition, there was little difference between the hue and chroma of the reduction cleared and washed-off dyeings. The washed-off dyeings displayed higher fastness to washing at 60 °C than their reduction cleared counterparts. Thus, in terms of fastness and colorimetric characteristics, the traditional reduction clearing treatment can be replaced by a single, non-dithionite-based wash-off at 98 °C for 15 min. This enabled a major reduction to be achieved in terms of the BOD, COD and TOC that are typically generated as a result of the traditional reduction clearing of disperse dyes on polyester; it also offers the potential of avoiding the environmentally unacceptable generation of aromatic amines.

Keywords: Polyester; Disperse dyes; Reduction clear; After treatment

1. Introduction

All dyeing processes include a 'wash-off' treatment at the end of dyeing to remove surplus dye and dyeing auxiliaries so as to secure optimum fastness and the correct shade. In the case of disperse dyes on polyester, a *reduction clear* treatment is commonly used which typically comprises [1] submitting the rinsed, dyed material to treatment for 20–30 min at 50–70 °C in an aqueous bath containing NaOH, $Na_2S_2O_4$ and surfactant, followed by rinsing and, if necessary, neutralisation with aqueous acetic acid. The reduction clear process is designed to remove surplus dye and dyeing auxiliaries (e.g. migration inhibitors, carrier residues and surfactants) without altering the shade of the dyeing. The process relies on the marked hydrophobicity of polyester which prevents aqueous agencies from penetrating the substrate at temperatures below the commercial boil so that removal of surface-deposited dye, carrier, etc. can be achieved without damage to dye that is adsorbed within the fibre. It is believed that in the case of azo disperse dyes, treatment with the aqueous alkaline solution of the reducing agent destroys the chromophore resulting in colourless amino compounds (Scheme 1) while anthraquininoid disperse dyes are reduced to the corresponding, virtually colourless, low substantivity, water-soluble leuco form of the dye.

When the reduction clearing process was devised in the mid1950s [2], polyester was commonly dyed using carriers at 98 °C and the disperse dyes in use at the time had a propensity to aggregate and deposit on the fibre surface. Although nowadays, carriers are little used, high temperature (130 °C) dyeing of polyester predominates and disperse dyes display excellent dispersion character, reduction clearing continues



Scheme 1.

* Corresponding author. Tel.: +44 113 233 3722; fax: +44 113 233 3740.
E-mail address: s.m.burkinshaw@leeds.ac.uk (S.M. Burkinshaw).

0143-7208/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2007.02.002

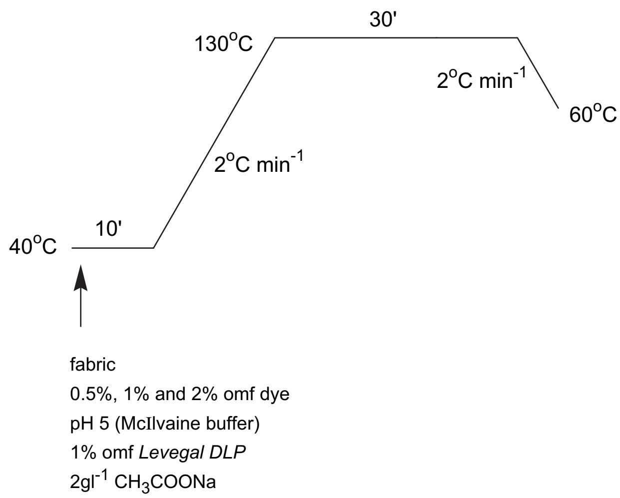


Fig. 1. Dyeing method.

to be used, especially for medium/heavy depths of shade. In addition, reduction clearing is given to some forms of polyester, regardless of depth of shade, as it removes surface-deposited oligomers [1].

The reduction clearing process suffers from two major disadvantages, in addition to its expense in itself namely:

- the use of sodium dithionite creates an environmentally unacceptable effluent which is further complicated by the presence of aromatic amines in the case of azo disperse dyes and;
- the inconvenient and expensive change in pH that accrues from the acidic dyebath to the alkaline reduction clearing process and the subsequent neutralisation of the reduction cleared substrate.

Alternative reducing agents have been proposed as well as commercial mixtures of reducing agents and dedicated auxiliaries; auxiliaries are available that can be added directly to the acidic dyebath so as to avoid the pH changes involved in the traditional reduction clear process.

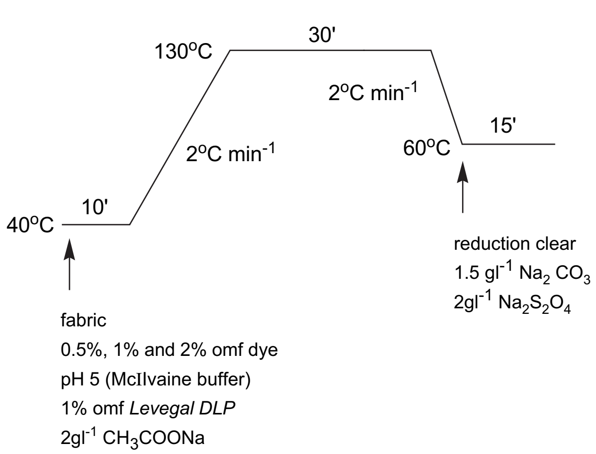


Fig. 2. Reduction clear method.

Despite the fact that the reduction clearing process has been widely used for some 50 or so years, it has been the subject of remarkably few publications. This paper seeks to establish whether or not an alternative after-treatment process can be employed for dyed polyester which does not necessitate two changes in pH and which generates a less environmentally challenged effluent by avoiding the use of reducing agents and the concomitant generation of colourless dye derivatives. This part of the paper focusses on the removal of surplus dye from dyed polyester while the removal of oligomers will be the subject of the second part of the paper.

2. Experimental

2.1. Materials

Woven polyester fabric (122 g m^{-2}), obtained from Whaleys (Bradford, UK) was scoured in a solution comprising 1 g l^{-1} *Sandozin NIN* (surfactant; Clariant) and 2 g l^{-1} Na_2CO_3 for 15 min at 60 °C using a liquor ratio of 20:1. The scoured sample was rinsed thoroughly in tap water and allowed to dry in the open air. Three disperse dyes namely, *Dianix Blue UN-SE, Dianix Yellow Brown XF* and *Dianix Cherry CC* (no C.I. generic names ascribed) were kindly supplied by DyStar and were used without purification.

2.2. Dyeing

Polyester fabric was dyed at 0.5, 1.0 and 2.0% omf depth of shade, in the presence of the proprietary anionic levelling agent *Levegal DLP* (Dystar) in 300 cm^3 capacity sealed, stainless steel dyepots housed in a Roaches *Pyrotec S* dyeing machine using the method shown in Fig. 1 using a liquor ratio of 20:1; the pH was adjusted using McIlvaine buffer [3].

2.3. Reduction clearing

After dyeing, the fabrics were rinsed in warm water and reduction cleared at 60 °C for 15 min (Fig. 2) using a 20:1 liquor ratio. The reduction cleared dyeing was rinsed, firstly in warm water and secondly in cold running water and then dried at room temperature.

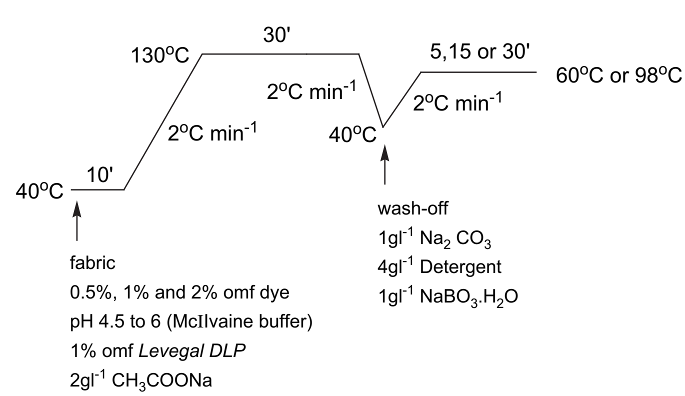


Fig. 3. Wash-off method.

2.4. Aqueous wash-off

Using the method shown in Fig. 3, dyeings were rinsed in warm water and treated at 60 or 98 °C for 5, 15 or 30 min in a solution comprising 1 g l^{-1} Na_2CO_3, 4 g l^{-1} ECE detergent and 1 g l^{-1} sodium perborate using a 20:1 liquor ratio. The washed-off dyeing was rinsed, firstly in warm water, then in cold running water and was then dried at room temperature.

2.5. Colour measurement

The CIE L^*, a^*, b^*, C^* and $h°$ colour co-ordinates were measured and K/S values calculated from the reflectance values at the appropriate λ_{max} for each dyeing, using a *Datacolor Spectroflash 600* spectrophotometer under illuminant D_{65}, using a 10° standard observer with UV component included and specular component excluded. The samples were folded so as to realise four thicknesses.

Table 1
Fastness to repeated washing of dyeings prior to reduction clearing

Dye	% omf	Number of washes	Change in shade	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	2° Acetate
Blue UN-SE	0.5	1	4/5	5	5	5	4/5	5	5
		2	4/5	5	5	5	5	5	5
		3	4/5	5	5	5	5	5	5
		4	4/5	5	5	5	5	5	5
		5	4/5	5	5	5	5	5	5
	1	1	4/5	5	5	4/5	3/4	5	5
		2	4	5	5	5	4/5	5	5
		3	3/4	5	5	5	5	5	5
		4	3/4	5	5	5	5	5	5
		5	3/4	5	5	5	5	5	5
	2	1	4/5	5	5	3/4	3	4	5
		2	4	5	5	4/5	4	5	5
		3	3/4	5	5	5	4/5	5	5
		4	3/4	5	5	5	4/5	5	5
		5	3/4	5	5	5	4/5	5	5
Yellow Brown XF	0.5	1	4/5	4	5	5	4/5	5	4/5
		2	4/5	5	5	5	5	5	5
		3	4/5	5	5	5	5	5	5
		4	4/5	5	5	5	5	5	5
		5	4/5	5	5	5	5	5	5
	1	1	4/5	4	5	5	4/5	5	4/5
		2	4/5	4/5	5	5	5	5	5
		3	4/5	5	5	5	5	5	5
		4	4/5	5	5	5	5	5	5
		5	4/5	5	5	5	5	5	5
	2	1	4/5	4	5	4/5	4/5	5	4
		2	4/5	5	5	5	5	5	5
		3	4/5	5	5	5	5	5	5
		4	4/5	5	5	5	5	5	5
		5	4/5	5	5	5	5	5	5
Cherry CC	0.5	1	4/5	5	5	4	3	5	4
		2	4	5	5	5	4/5	5	5
		3	3/4	5	5	5	5	5	5
		4	3/4	5	5	5	5	5	5
		5	3/4	5	5	5	5	5	5
	1	1	4/5	4/5	5	4	2/3	4	3
		2	4	5	5	5	4/5	5	5
		3	3/4	5	5	5	5	5	5
		4	3/4	5	5	5	5	5	5
		5	3/4	5	5	5	5	5	5
	2	1	4/5	4	5	4	2	4	3
		2	4	5	5	5	4	5	4/5
		3	3/4	5	5	5	4/5	5	5
		4	3	5	5	5	5	5	5
		5	3	5	5	5	5	5	5

Table 2
Colorimetric data prior to reduction clearing

Dye	% omf	Number of washes	*K*/*S*	*L**	*a**	*b**	*C**	*h*°	λ_{max}/nm
Blue UN-SE	0.5	0	2.6	57.1	−4.3	−32.9	33.2	262.5	620
		5	2.5	57.6	−3.5	−33.9	34.1	264.0	620
	1	0	5.6	47.1	−3.8	−34.7	34.9	263.6	620
		5	5.2	48.1	−3.1	−35.6	35.7	265.0	620
	2	0	11.1	46.3	−3.3	−35.0	35.1	264.5	620
		5	10.9	38.5	−0.94	−36.8	36.8	268.5	620
Yellow Brown XF	0.5	0	1.8	67.3	23.1	31.2	38.9	53.4	460
		5	1.6	68.8	21.7	29.4	36.5	53.5	460
	1	0	3.9	59.2	30.2	40.0	50.1	52.9	440
		5	3.9	61.0	28.4	37.9	47.4	53.2	440
	2	0	7.5	53.8	34.1	43.1	55.0	51.6	440
		5	7.1	54.7	33.2	41.5	53.2	51.3	440
Cherry CC	0.5	0	6.1	53.9	53.9	13.7	55.6	14.3	520
		5	5.2	52.5	52.5	12.3	54.0	13.2	520
	1	0	10.1	47.3	54.8	17.2	57.5	17.4	520
		5	9.2	48.8	54.7	16.3	57.1	16.6	520
	2	0	16.1	42.1	56.2	22.5	60.6	21.8	520
		5	15.9	41.6	54.7	21.4	58.8	21.4	520

2.6. Fastness determination

The wash fastness of the dyed samples was determined at 60 °C, using the ISO standard wash test (ISO CO6/C2S) [4] which had been modified in that dyeings were subjected to five, consecutive wash tests and, at the end of each wash test, the washed sample was rinsed thoroughly in tap water (but was not dried) and a fresh sample of SDC multifibre strip was used to assess the extent of staining for each of the five wash tests. A single, standard ISOCO6/C2S wash test was used to determine the fastness of dyeings which had been washed-off after dyeing.

Table 3
Colorimetric data for dyeings after reduction clearing

Dye	% omf	Number of washes	*K*/*S*	*L**	*a**	*b**	*C**	*h*°	λ_{max}/nm
Blue UN-SE	0.5	0	2.6	57.1	−4.3	−32.9	33.2	262.5	620
		5	2.4	58.7	−3.7	−33.9	34.1	263.6	620
	1	0	5.6	47.1	−3.8	−34.7	34.9	263.6	620
		5	4.8	49.2	−3.3	−35.5	35.6	264.6	620
	2	0	11.1	46.3	−3.3	−35.0	35.1	264.5	620
		5	10.4	38.5	−0.9	−36.8	36.8	268.5	620
Yellow Brown XF	0.5	0	1.8	67.3	23.1	31.2	38.9	53.4	460
		5	1.7	68.9	22.4	30.0	37.5	53.2	460
	1	0	3.9	59.2	30.2	40.0	50.1	52.9	440
		5	3.5	62.8	30.0	38.8	49.1	52.2	440
	2	0	7.5	53.8	34.1	43.1	55.0	51.6	440
		5	7.2	54.8	33.6	42.2	53.9	51.4	440
Cherry CC	0.5	0	6.1	53.9	53.9	13.7	55.6	14.3	520
		5	5.2	55.3	52.8	12.3	54.2	13.1	520
	1	0	10.1	47.3	54.8	17.2	57.5	17.4	520
		5	8.5	50.2	55.3	16.3	57.7	16.4	520
	2	0	16.1	42.1	56.2	22.5	60.6	21.8	520
		5	15.6	42.5	55.5	21.8	59.7	21.4	520

3. Results and discussion

The three dyes used in this work were chosen arbitrarily as being representative of typical, modern disperse dyes; *Blue UN-SE* is a mixture of azo and AQ dyes while *Yellow Brown XF* and *Cherry CC* are azo dyes. Three depths of shade were used namely, 0.5, 1 and 2% omf, as these provided typical pale/medium depth dyeings.

Table 1 shows the wash fastness data obtained for dyeings that had not been reduction cleared but, instead, at the end of dyeing, excess dye liquor had been removed from the dyeings by squeezing and the samples had then been allowed to dry in the open air. It is evident that when the dyeings were submitted to five, consecutive wash fastness tests at 60 °C they displayed poor fastness, as shown by the colour change and staining values achieved; the staining of adjacent nylon 6,6 and polyester fabrics was quite poor, in particular. It is evident (Table 1) that the fastness of the dyeings achieved for the first two or so wash tests was noticeably worse than that obtained for the subsequent wash tests. These findings were expected because

Table 4
Fastness to repeated washing of dyeings after reduction clearing

Dye	% omf	Number of washes	Change in shade	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	2° Acetate
Blue UN-SE	0.5	1	4/5	5	5	5	4/5	5	5
		2	4/5	5	5	5	5	5	5
		3	4/5	5	5	5	5	5	5
		4	4/5	5	5	5	5	5	5
		5	4/5	5	5	5	5	5	5
	1	1	4/5	5	5	5	4/5	5	5
		2	4/5	5	5	5	5	5	5
		3	4/5	5	5	5	5	5	5
		4	4/5	5	5	5	5	5	5
		5	4/5	5	5	5	5	5	5
	2	1	4/5	5	5	4/5	4	5	5
		2	4/5	5	5	5	4/5	5	5
		3	4/5	5	5	5	5	5	5
		4	4/5	5	5	5	5	5	5
		5	4/5	5	5	5	4/5	5	5
Yellow Brown XF	0.5	1	4/5	5	5	5	4/5	5	5
		2	4/5	5	5	5	5	5	5
		3	4/5	5	5	5	5	5	5
		4	4/5	5	5	5	5	5	5
		5	4/5	5	5	5	5	5	5
	1	1	4/5	5	5	5	4	5	5
		2	4/5	5	5	5	5	5	5
		3	4/5	5	5	5	5	5	5
		4	4/5	5	5	5	5	5	5
		5	4/5	5	5	5	5	5	5
	2	1	4/5	4/5	5	5	4/5	5	4/5
		2	4/5	5	5	5	5	5	5
		3	4/5	5	5	5	5	5	5
		4	4/5	5	5	5	5	5	5
		5	4/5	5	5	5	5	5	5
Cherry CC	0.5	1	4/5	5	5	5	4	5	4/5
		2	4/5	5	5	5	5	5	5
		3	4/5	5	5	5	5	5	5
		4	4/5	5	5	5	5	5	5
		5	4/5	5	5	5	5	5	5
	1	1	4/5	5	5	4/5	3/4	5	4/5
		2	4	5	5	5	4/5	5	5
		3	3/4	5	5	5	5	5	5
		4	3/4	5	5	5	5	5	5
		5	3/4	5	5	5	5	5	5
	2	1	4/5	4/5	5	4/5	2/3	5	3/4
		2	4	5	5	5	4	5	5
		3	3/4	5	5	5	4/5	5	5
		4	3/4	5	5	5	5	5	5
		5	3/4	5	5	5	5	5	5

Table 5
Wash fastness of washed-off dyeings

Dye	% omf	Temp./°C	Duration/min	Change in shade[a]	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	2° Acetate
Blue UN-SE	0.5	60	5	4/5	5	5	5	4/5	5	5
			15	4/5	5	5	5	5	5	5
			30	4/5	5	5	5	5	5	5
		98	5	4/5	5	5	5	5	5	5
			15	4/5	5	5	5	5	5	5
			30	4/5	5	5	5	5	5	5
	1	60	5	4/5	5	5	4/5	4/5	5	5
			15	4/5	5	5	5	4/5	5	5
			30	4/5	5	5	5	5	5	5
		98	5	4/5	5	5	5	4/5	5	5
			15	4/5	5	5	5	4/5	5	5
			30	4/5	5	5	5	5	5	5
	2	60	5	4	5	5	4/5	3/4	5	5
			15	4/5	5	5	5	4	5	5
			30	4/5	5	5	5	4/5	5	5
		98	5	4/5	5	5	5	4	5	5
			15	4/5	5	5	5	4/5	5	5
			30	4/5	5	5	5	5	5	5
Yellow Brown XF	0.5	60	5	5	5	5	5	5	5	5
			15	5	5	5	5	5	5	5
			30	5	5	5	5	5	5	5
		98	5	5	5	5	5	5	5	5
			15	5	5	5	5	5	5	5
			30	5	5	5	5	5	5	5
	1	60	5	5	5	5	5	5	5	5
			15	5	5	5	5	5	5	5
			30	5	5	5	5	5	5	5
		98	5	5	5	5	5	5	5	5
			15	5	5	5	5	5	5	5
			30	5	5	5	5	5	5	5
	2	60	5	5	5	5	5	5	5	5
			15	5	5	5	5	5	5	5
			30	5	5	5	5	5	5	5
		98	5	5	5	5	5	5	5	5
			15	5	5	5	5	5	5	5
			30	5	5	5	5	5	5	5
Cherry CC	0.5	60	5	4/5	5	5	5	4/5	5	5
			15	4/5	5	5	5	4/5	5	5
			30	4/5	5	5	5	5	5	5
		98	5	4/5	5	5	5	4/5	5	5
			15	4/5	5	5	5	4/5	5	5
			30	4/5	5	5	5	5	5	5
	1	60	5	4	5	5	5	3/4	5	5
			15	4/5	5	5	5	4	5	5
			30	4/5	5	5	5	4/5	5	5
		98	5	4	5	5	5	4	5	5
			15	4/5	5	5	5	4/5	5	5
			30	4/5	5	5	5	4/5	5	5
	2	60	5	4	5	5	4/5	3	5	4/5
			15	4	5	5	5	3/4	5	4/5
			30	4/5	5	5	4/5	3/4	5	4/5
		98	5	4	5	5	4/5	3	5	4/5
			15	4/5	5	5	4/5	3/4	5	4/5
			30	4	5	5	4/5	4	5	4/5

[a] W.r.t to washed-off samples.

Table 6
Colorimetric data for washed-off dyeings

Dye	Depth of shade/% omf	Wash-off temp./°C	Duration of wash-off/min	*K*/*S*	*L**	*a**	*b**	*C**	*h*°	λ_{max}/nm
Blue UN-SE	0.5	60	5	2.5	58.2	−4.0	−33.3	33.6	263.1	620
			15	2.3	58.6	−4.0	−33.1	33.3	263.1	620
			30	2.4	57.8	−3.7	−31.5	31.8	263.2	620
		98	5	2.2	58.8	−3.2	−32.9	33.1	264.3	620
			15	2.3	58.1	−4.5	−30.7	31.0	261.5	620
			30	2.2	59.2	−3.5	−32.8	33.0	263.8	620
	1.0	60	5	5.4	48.8	−3.7	−36.0	36.2	264.0	620
			15	5.0	48.9	−3.5	−35.5	35.7	264.2	620
			30	5.3	48.1	−3.2	−35.8	35.9	264.8	620
		98	5	4.9	49.1	−3.1	−36.0	36.2	265.0	620
			15	4.9	49.2	−3.3	−36.1	36.2	264.6	620
			30	4.7	49.5	−3.4	−35.4	35.6	264.5	620
	2.0	60	5	11.3	37.9	−1.5	−36.1	36.1	267.5	620
			15	9.3	40.3	−2.2	−35.7	35.7	266.3	620
			30	9.7	39.7	−2.1	−35.7	35.7	266.5	620
		98	5	9.8	40.1	−1.2	−37.1	37.2	268.0	620
			15	9.7	40.0	−1.2	−37.2	37.2	268.0	620
			30	9.6	40.2	−0.7	−37.8	37.8	268.8	620
Yellow Brown XF	0.5	60	5	1.8	68.6	22.1	31.1	38.1	54.5	460
			15	1.8	69.2	23.7	31.9	39.7	53.3	460
			30	1.7	69.2	23.3	31.4	39.1	53.3	460
		98	5	1.7	69.2	22.7	30.5	38.0	53.2	460
			15	1.6	69.4	22.5	30.3	37.8	53.4	460
			30	1.6	69.7	22.9	30.4	38.1	53.0	460
	1.0	60	5	3.9	62.7	30.3	39.5	49.8	52.4	440
			15	3.9	64.5	27.3	36.9	45.9	53.4	440
			30	3.8	61.3	28.3	38.2	47.6	53.4	440
		98	5	3.6	62.8	30.2	39.2	49.5	52.4	440
			15	3.5	63.2	30.2	39.1	49.4	52.3	440
			30	3.3	63.3	28.2	37.9	47.3	53.3	440
	2.0	60	5	7.4	54.9	33.6	42.8	54.5	51.8	440
			15	7.4	54.8	33.9	42.7	54.6	51.5	440
			30	7.4	53.6	34.8	43.4	55.7	51.2	440
		98	5	7.2	55.4	34.7	43.0	55.3	51.0	440
			15	7.2	55.4	34.7	43.0	55.3	51.0	440
			30	7.1	55.5	34.8	43.0	55.4	51.0	440
Cherry CC	0.5	60	5	5.3	53.5	49.1	10.1	50.1	11.6	520
			15	5.8	53.3	51.4	11.8	52.7	12.9	520
			30	4.2	56.6	49.3	9.2	50.1	10.6	520
		98	5	4.8	56.3	52.7	11.6	54.0	12.4	520
			15	5.3	55.2	53.2	12.2	54.6	12.9	520
			30	3.8	57.4	47.8	7.3	48.3	8.6	520
	1.0	60	5	9.9	48.4	55.4	17.0	57.9	17.1	520
			15	10.0	48.2	55.2	17.0	57.8	17.1	520
			30	10.0	47.9	54.4	16.3	56.8	16.7	520
		98	5	10.7	47.1	54.2	17.6	57.0	17.9	520
			15	9.0	49.4	54.5	16.3	56.9	16.7	520
			30	9.1	49.1	54.5	16.6	57.0	17.0	520
	2.0	60	5	15.3	42.2	54.0	20.3	57.8	20.6	520
			15	16.0	41.3	53.4	20.3	57.2	20.8	520
			30	15.1	43.1	55.3	20.8	59.1	20.6	520
		98	5	16.3	41.8	54.6	21.2	58.6	21.2	520
			15	14.4	44.5	56.7	21.5	60.7	20.7	520
			30	14.5	43.8	55.8	21.0	59.7	20.6	520

Table 7
Colorimetric data for washed-off dyeings after a single wash test

Dye	% omf	Temp./°C	Duration/min	*K/S*	L^*	a^*	b^*	C^*	h^o	λ_{max}/nm
Blue UN-SE	0.5	60	5	2.2	59.6	−3.7	−33.3	33.5	263.6	620
			15	2.2	58.8	−3.7	−33.6	33.8	263.6	620
			30	2.3	58.4	−3.4	−32.5	32.6	263.9	620
		98	5	2.3	58.5	−3.1	−33.4	33.5	264.6	620
			15	2.4	58.1	−3.8	−32.2	32.4	263.1	620
			30	2.2	59.3	−3.5	−32.8	33	263.8	620
	1	60	5	4.9	49.5	−3.8	−36.1	36.3	263.9	620
			15	4.8	49.6	−3.5	−35.8	35.9	264.3	620
			30	5.3	48.3	−3.3	−36.1	36.2	264.7	620
		98	5	4.9	49.4	−3.3	−35.9	36.1	264.6	620
			15	4.5	50.6	−3.8	−35.8	36	263.9	620
			30	4.6	50	−3.5	−35.5	35.7	264.2	620
	2	60	5	9.8	39.9	−1.5	−37.1	37.1	267.6	620
			15	9.0	40.4	−2.6	−34.4	34.5	265.5	620
			30	9.6	39.8	−2.3	−35.4	35.5	266.2	620
		98	5	9.5	40.2	−1.4	−37.0	37	267.7	620
			15	9.7	40.0	−1.4	−37.1	37.1	267.7	620
			30	9.3	40.4	−1.4	−37.3	37.3	268.4	620
Yellow Brown XF	0.5	60	5	1.8	68.9	22.7	31.5	38.8	54.2	460
			15	1.9	69.6	24.3	33.9	41.7	54.3	460
			30	1.7	69.9	23.8	31.7	39.7	53.9	460
		98	5	1.6	69.6	23.2	30.6	38.4	52.8	460
			15	1.8	69.7	23.1	33.1	40.3	55.1	460
			30	1.7	69.7	23.3	31.1	38.9	53.8	460
	1	60	5	3.6	63.3	30.5	40.0	50.3	52.7	440
			15	3.8	61.7	29.1	38.5	48.2	52.9	440
			30	4.1	61.3	29.4	39.6	49.3	53.3	440
		98	5	3.7	62.8	30.8	40.1	50.6	52.4	440
			15	3.5	63.3	30.5	39.2	49.7	52	440
			30	2.7	65.6	27.3	37.0	46.0	53.5	440
	2	60	5	7.2	55.2	33.9	42.8	54.6	51.5	440
			15	7.0	55.5	34.3	42.9	54.9	51.3	440
			30	7.2	55.7	34.3	43.6	55.5	51.7	440
		98	5	7.0	55.7	35.1	43.2	55.5	50.7	440
			15	7.1	55.7	35.2	43.2	55.7	50.8	440
			30	6.8	56.1	35.2	43.1	55.7	50.7	440
Cherry CC	0.5	60	5	5.2	54.2	50.2	11.0	51.3	12.3	520
			15	5.1	54.7	51.1	11.0	52.3	12.1	520
			30	4.9	55.5	51.1	10.4	52.2	11.5	520
		98	5	4.6	56.6	52.4	11.1	53.6	12	520
			15	5.5	54.7	53.8	12.8	55.3	13.4	520
			30	5.3	53.8	50.3	10.1	51.3	11.3	520
	1	60	5	10.7	47.6	56	17.7	58.7	17.5	520
			15	10.7	47.6	55.7	17.5	58.4	17.4	520
			30	9.2	48.9	54.8	16.1	57.2	16.4	520
		98	5	7.9	48.7	51.8	17.5	54.7	18.7	520
			15	8.5	50.1	55.2	16.9	57.5	16.2	520
			30	9.9	48.1	54.9	17.7	57.6	17.8	520
	2	60	5	15.2	42.3	54.5	20.7	58.3	20.8	520
			15	11.7	43.4	52.6	19.3	56	20.1	520
			30	14.3	43.6	55.4	20.5	59.1	20.3	520
		98	5	13.3	43.9	54.8	22.6	59.3	22.4	520
			15	13.7	44.9	57	21.3	60.8	20.5	520
			30	13.8	44.4	56.3	21.6	60.3	20.9	520

surplus dye had not been removed from the dyeings by reduction clearing; the observation that the fastness of the dyeings improved with increasing number of wash tests can be attributed to the first two or so washes having removed surplus dye. Table 2 shows the corresponding colorimetric data for the dyeings which had not been reduction cleared and which had been subjected to five wash tests. The, sometimes quite marked, change in depth of shade which the dyeings had undergone as a result of repeated washing is clearly shown by the lower *K*/*S* values of the five times washed samples. Despite the reduction in depth of shade that repeated washing imparted, it is apparent that the colour (hue and chroma) of the dyeings was largely unaffected by washing as evidenced by a comparison of the $L^*a^*b^*C^*$ and h^o values of the zero and five times washed dyeings; this finding is supported by the fact that the λ_{max} of the dyeings were unchanged by repeated washing.

Table 3 shows the colorimetric data obtained for dyeings which had been reduction cleared and subjected to five repeated wash tests. Washing obviously reduced the depth of shade of the dyeings (as shown by the respective *K*/*S* values for zero and five washes) but, as observed for the effect of washing on dyeings which had not been reduction cleared (Table 2), the colour of the dyeings was mostly unaffected by washing, as evidenced by the respective $L^*a^*b^*C^*$ and h^o values of the dyeings and the λ_{max} of the zero and five times washed samples. The corresponding wash fastness data (Table 4) show that the reduction cleared dyeings displayed moderate fastness to repeated washing, especially in the case of the staining of adjacent nylon 6,6 and polyester fabrics. It is evident (Table 4) that the fastness of the dyeings achieved for the first two or so wash tests was generally worse than that obtained for subsequent wash tests.

When the data in Table 4 are compared with that obtained for the dyeings which had not been reduction cleared (Table 1), it is apparent that the reduction cleared samples displayed higher fastness than their non-reduction cleared counterparts, especially for the first two or so washes. This can be attributed to reduction clearing having removed surplus dye from the dyeings prior to repeated wash testing. Further comparison of the data in Tables 1 and 4 reveals that the fastness of both the reduction cleared and non-reduction cleared dyeings was virtually identical after four and five washes. Also, comparison of the colorimetric data in Tables 2 and 3 shows that the colour strength of the reduction cleared and non-reduction cleared dyeings after five washes were not too dissimilar, with the non-reduction cleared dyeings having slightly higher colour strength. In addition, the λ_{max} values of the reduction cleared and non-reduction cleared dyeings were identical for each of the depths of shade used after five washes and there was little, if any, meaningful difference in the chroma and hue of the respective dyeings after repeated washing.

The results presented thus far indicate that whilst reduction clearing removed surplus dye from each of the three depths of shade used, this dye removal did not impart higher wash fastness to the dyeings after five repeated washes. Indeed, the only difference between the reduction cleared and non-reduction cleared dyeings after five washes was that the former dyeings were of lower colour strength. Thus, as it appeared that the five repeated washes had removed surplus dye from the dyeings, it was decided to investigate if the reduction clearing process could be replaced by a simpler wash-off treatment that used ECE detergent (as employed in the ISO wash test used in this work).

Table 8
Comparison of the colorimetric data for dyeings after reduction clearing and after wash-off for 15 min at 98 °C

Dye	% omf	Treatment	*K*/*S*	L^*	a^*	b^*	C^*	h^o	λ_{max}/nm
Blue UN-SE	0.5	Red. clearing	2.7	56.7	−3.9	−33.4	33.4	263.1	620
		Wash-off	2.3	58.1	−4.5	−30.7	31.0	261.5	620
	1	Red. clearing	5.2	46.3	−3.3	−35.0	35.1	264.5	620
		Wash-off	4.9	49.2	−3.3	−36.1	36.2	264.6	620
	2	Red. clearing	10.8	46.2	−3.3	−35.1	35.1	264.5	620
		Wash-off	9.7	40.0	−1.2	−37.2	37.2	268.0	620
Yellow Brown XF	0.5	Red. clearing	1.8	67.5	23.1	31.2	38.8	53.2	460
		Wash-off	1.6	69.4	22.5	30.3	37.8	53.4	460
	1	Red. clearing	3.6	61.4	31.3	40.0	50.8	51.9	440
		Wash-off	3.5	63.2	30.2	39.1	49.4	52.3	440
	2	Red. clearing	7.4	53.4	34.1	42.6	54.6	51.3	440
		Wash-off	7.2	55.4	34.7	43.0	55.3	51.0	440
Cherry CC	0.5	Red. clearing	5.9	53.2	54.2	14.4	56.1	14.8	520
		Wash-off	5.3	55.2	53.2	12.2	54.6	12.9	520
	1	Red. clearing	9.3	48.4	55.2	16.8	57.7	16.9	520
		Wash-off	9.0	49.4	54.5	16.3	56.9	16.7	520
	2	Red. clearing	15.6	42.0	55.6	22.0	59.8	21.6	520
		Wash-off	14.4	44.5	56.7	21.5	60.7	20.7	520

Table 9
Fastness of dyeings after reduction clearing and after wash-off for 15 min at 98 °C

Dye	% omf	Treatment	Change in shade	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	2° Acetate
Blue UN-SE	0.5	Red. clearing	4/5	5	5	5	4/5	5	5
		Wash-off	4/5	5	5	5	5	5	5
	1	Red. clearing	4/5	5	5	5	4/5	5	5
		Wash-off	4/5	5	5	5	4/5	5	5
	2	Red. clearing	4/5	5	5	4/5	4	5	5
		Wash-off	4/5	5	5	5	4/5	5	5
Yellow Brown XF	0.5	Red. clearing	4/5	5	5	5	4/5	5	5
		Wash-off	5	5	5	5	5	5	5
	1	Red. clearing	4/5	5	5	5	4	5	5
		Wash-off	5	5	5	5	5	5	5
	2	Red. clearing	4/5	4/5	5	5	4/5	5	4/5
		Wash-off	5	5	5	5	5	5	5
Cherry CC	0.5	Red. clearing	4/5	5	5	5	4	5	4/5
		Wash-off	4/5	5	5	5	4/5	5	5
	1	Red. clearing	4/5	5	5	4/5	3/4	5	4/5
		Wash-off	4/5	5	5	5	4/5	5	5
	2	Red. clearing	4/5	4/5	5	4/5	2/3	5	3/4
		Wash-off	4/5	5	5	4/5	3/4	5	4/5

Accordingly, dyeings were subjected to a single, wash-off treatment and the effects of varying both the temperature (60 and 98 °C) and duration (5, 15 and 30 min) of this wash-off on the fastness of the dyeings to a single wash fastness test at 60 °C were studied; the results are shown in Table 5. Firstly, it is evident that the dyeings displayed moderate/poor fastness at each of the two wash-off temperatures and each of the three lengths of time of wash-off used, as shown by the colour change and staining values achieved. As observed previously for the repeated washing of both the reduction cleared and non-reduction cleared dyeings, the nylon 6,6 and polyester fabrics were the most stained of the six adjacent fabrics. In terms of the duration of wash-off, it is apparent that the extent of staining of adjacent materials generally increased in the order: $5 > 15 > 30$ min. In the context of the temperature of wash-off, Table 5 shows that there was little, if any, difference between 60 and 98 °C in terms of the wash fastness of the dyeings. The corresponding colorimetric data for the washed-off dyeings (Table 6) reveal that the colour strength of the dyeings was lower when wash-off had been carried out at 98 °C, which can be attributed to more dye having been removed during wash-off due to greater dye diffusion and higher fibre swelling imparted by the greater kinetic energy at 98 °C. Table 6 also reveals that in terms of the duration of wash-off, the colour strength of the dyeings generally followed the order: $5 > 15 = 30$ min. The data in Table 6 also show that neither the λ_{max} nor the chroma and hue of the dyeings were generally affected by either the duration or temperature of wash-off.

As this part of the study aimed to determine if the reduction clearing process could be replaced by a simpler wash-off treatment (Table 7) that used ECE detergent, a comparison is needed of the wash fastness and colorimetric characteristics of the dyeings that were obtained as a result of reduction clearing and wash-off. Table 8 shows the colorimetric data obtained for dyeings which had been reduction cleared, these results having been taken from Table 3 (zero number of washes) as well as data for dyeings which had been washed-off for 15 min at 98 °C, these data having been taken from Table 6. It is clear from Table 8 that the colour strength of the washed-off samples was slightly lower than that of the reduction cleared samples but that there was no difference between the λ_{max} of the washed-off and reduction cleared dyeings; in addition, there was little difference between the hue and chroma of the reduction cleared and washed-off dyeings. The corresponding results (Table 9) for the fastness of the dyeings show that the washed-off dyeings displayed slightly higher fastness than their reduction cleared counterparts. Thus, Tables 8 and 9 clearly show that, in terms of fastness and colorimetric characteristics, the reduction clearing treatment can be replaced by a single wash-off at 98 °C for 15 min.

As previously mentioned, the use of sodium dithionite in traditional reduction clearing creates an environmentally unacceptable effluent. As an indication of the nature of the environmental impact of reduction clear treatment, Table 10 compares the BOD, COD and TOC data achieved [5] for the reduction clearing process and 98 °C for 15 min wash-off process. The somewhat high values recorded for the traditional,

Table 10
Environmental indicators

Parameter	Reduction clearing process	98 °C, 15 min wash-off
BOD/mg l O^{-1}	1420	76.5
COD total/mg l O^{-1}	4190	1490
TOC/mg l^{-1}	334	298
Suspended solids/mg l^{-1}	363	66

sulfide-based reduction clear process contrast, markedly, with those obtained for the wash-off treatment devised in this work. Environmentally, reduction clearing poses an additional problem due to the generation of aromatic amines in the case of azo disperse dyes; clearly, the replacement of a reduction clearing treatment with the single, wash-off treatment used herein negates this environmentally unacceptable problem.

4. Conclusions

The comparison of the colorimetric data obtained for dyeings which had been reduction cleared with that secured for dyeings which had been washed-off for 15 min at 98 °C clearly shows that while the colour strength of the washed-off samples was slightly lower than that of the reduction cleared samples, there was no difference between the λ_{max} of the washed-off and reduction cleared dyeings; in addition, there was little difference between the hue and chroma of the reduction cleared and washed-off dyeings. The washed-off dyeings displayed slightly higher fastness than their reduction cleared counterparts. Thus, in terms of fastness and colorimetric characteristics, the traditional reduction clearing treatment can be replaced by a single, detergent-based wash-off at 98 °C for 15 min. This enables a major reduction to be achieved in terms of the BOD, COD, TOC and suspended solids that can be generated during a typical traditional reduction clearing treatment for disperse dyes on polyester; it also offers the potential of avoiding the environmentally unacceptable generation of aromatic amines.

References

[1] Burkinshaw SM. Chemical principles of synthetic fibre dyeing. London: Blackie; 1990.
[2] Fern AS, Hadfield HR. J Soc Dyers Colour 1955;71:840.
[3] Vogel A. Textbook of quantitative inorganic analysis. London: Longmans; 1944.
[4] Methods of test for the colour fastness of textiles and leather. 5th ed. Bradford: Society of Dyers and Colourists; 1990.
[5] Eclipse Scientific Group, Ashford, Kent.