

Effectiveness of Various UV-absorbers in Dyeing of Polyester with Disperse Dyes. Part III

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ABSTRACT

The effect of various amounts of two benzotriazole (Tinuvin P and Tinuvin 327) and one benzophenone (2,4-dihydroxybenzophenone) type UV-absorbers in the dyeing of polyester fabrics with commercial samples of a red monoazo disperse dye and Viosperse Yellow GLFS was examined at various depths of dyeing (0.5, 1.75 and 3% o.w.f.). The UV-absorbers were applied to the fibre at various UV-absorber/dye molar ratios by two processes, directly in the dyeing liquor and by aftertreatment of the dyed fabrics. The dye and UV-absorber uptake, and light and sublimation fastness of the dyed fabrics aftertreated by the reduction clearing process were determined and compared with those of the corresponding samples dyed in the absence of a UV-absorber. © 1997 Elsevier Science Ltd

Keywords: UV-absorbers, dyeing of polyester, disperse dyes, lightfastness.

INTRODUCTION

In previous papers [1,2] we reported on the effect of applying UV-absorbers in the dyeing of polyester fabrics with disperse dyes, on the dye and UV-absorber uptake and on the light fastness of the dyed polyester. Light fastness improvement of polyester fabrics dyed with disperse dyes for use as automobile coloured upholstery has been noted [1] to be a subject of great interest in the textile industry and relevant literature has been noted.

In this work the commercially available UV-absorbers (UV-abs) Tinuvin P [2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole] (1), Tinuvin 327 [2-(3,5-di-t-butyl-6-hydroxyphenyl)-2H-2-chlorobenzotriazole] (2) and DHB (2,4-dihydroxybenzophenone) (3) were dispersed in the presence of surfactants and applied at various UV-abs/dye molar ratios in the dyeing of polyester fabrics. Two disperse dyes, a monoazo red (4) of low light fastness and Viosperse Yellow GLFS (C.I. Disperse Yellow 42, 5) of high light fastness (automotive dye) were used at various depths of dyeing (0.5, 1.75 and 3% o.w.f.). The dispersed UV-abs (1, 2 or 3) were applied by direct addition into the dye liquor and the dyed fabrics were then reductively cleared [3] (processes A), or the fabrics were dyed in the absence of a UV-abs, and then similarly cleared and aftertreated with the dispersed UV-abs under the same dyeing liquor ratio and heating conditions (processes B).

Dye and UV-abs uptakes were determined spectrophotometrically from the chlorobenzene extract of the finally treated dyed fabrics. The indirect determination of these uptakes described in our previous studies [2,3], i.e. by measuring spectrophotometrically the final dye liquor, was not attainable in the present work on account of the reduction clearing process used herewith (Scheme 1).

The effects of the application of the various UV-absorbers by the two processes on the final dye and UV-absorber uptake, their percentage adsorbed proportion on the final dyed fabrics and on the light and sublimation fastness of the dyed fabrics were compared with those of the corresponding reference dyeings carried out in the absence of a UV-absorber.

EXPERIMENTAL

Specimens $(9 \times 13 \text{ cm}, \text{ approx. } 3 \text{ g})$ of commercial polyester (PET) fabric were used.

UV absorbers 1, 2 (Ciba-Geigy) and 3 (Sigma) and dyes 4 and 5 were used as aqueous dispersions prepared as follows.

For UV-abs and dye dispersions: appropriate amounts of the commercial UV-abs or dye, a dispersing agent (TAMOL NN 9104, NNOK/Vultamol, sodium salt of polycondensated naphthalenesulphonic acid, M.W. approx. 6500, BASF) and/or an anionic surfactant (UL-TRAZINE NA, sodium salt of ligninesulphonic acid, M.W. approx. 17000, BORREGAARD) and water were added to a grinding mill (Sussmeyer). The pH was adjusted at 7–7.5 with 85% phosphoric acid and the mixture was stirred for 20 min. Glass ottawa type balls were added, and subsequent grinding of the UV-abs or dye was monitored until the size of the particles became less than 3 μ m. A Practical Analyser, Microtrac X100P, was used for measuring the particle size distribution.

The amounts of dyes and UV-abs quoted in this paper correspond to pure (100%) materials.

For UV-abs and dye determinations: The percentage UV-abs content in the dispersions thus obtained was determined using an HPLC Waters 990

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Scheme 1

apparatus with an integrator and a LichroCART 125-Lichrospher 100 column. $10~\mu l$ of a reference solution (25 mg of powder UV-abs in a mixture of 10 ml of dimethylformamide and 40 ml of methanol) and $10~\mu l$ of a solution of each UV-abs dispersion sample (125 mg in a mixture of 10 ml water, 10 ml dimethylformamide and 30 ml methanol) were used for the determination.

A mixture (v/v) of (a) 90 parts of methanol and 10 parts of aqueous 4% acetic acid, (b) 95 parts of acetonitrile and 5 parts of aqueous 4% acetic acid, or (c) 40 parts of acetonitrile and 60 parts of aqueous 4% acetic acid, was used as eluant for the determination of 1, 2 or 3, respectively. The dispersed UV-abs preparations were found to contain 8.0% 1, 11.8% 2 or 17.6% 3 (w/w). Dilution of these in distilled water at a concentration 2% w/v were made and maintained in the dark prior to use.

The percentage content of pure (100%) dye in the dispersion sample was determined spectrophotometrically using a mixture of dimethylformamide/distilled water/acetic acid (87:10:3 v/v) as solvent, and reference solutions of pure dye. The dispersion samples of the red dye 4 were found to contain 50.0%; and of the yellow dye 60.6% (w/w) pure dye. These dispersions were diluted in distilled water at a concentration of 2% (w/v) and kept in the dark until use.

Dyeings of polyester fabrics were carried out in a Rotadyer apparatus (John Jeffreys Ltd, Rochdale-Banbury) with a liquor ratio of 20:1 at pH 5 using a sodium acetate-acetic acid buffer solution and the appropriate volume of the dispersion (2%, w/w) of the dye and of the UV-abs (process A), or only of the dye (process B). The dyebath was heated at 60°C for 10 min, then the temperature was raised gradually to 135°C within 35 min and maintained at this level for 1 h. The dyed fabrics were rinsed with distilled water, squeezed and heated in an aqueous solution (20:1 o.w.f.) containing 1 g/litre dispersing agent, 3 g/litre sodium bisulphite and 1.6 g/litre sodium hydroxide, at 80°C for 20 min (reduction clearing) [3]. The fabrics were then successively rinsed with distilled water and squeezed. Dyeings from process A were finally dried at <100°C, and those dyed in the absence of a UV-abs (process B) were aftertreated with an aqueous suspension of the appropriate amount of a UV-abs dispersion (2%, w/w) under the same liquor ratio and heating conditions as the dyeing process and then rinsed, squeezed and dried as above.

Determination of dye and UV-abs uptake was effected by Soxhlet extraction with chlorobenzene dye and UV-abs from the final fabrics from processes A and B, and measuring the absorbances of an aliquot of the chlorobenzene solution at the λ_{max} of the dye (504 nm for 4 or 422.8 nm for 5) and at $\lambda=354$ nm for both 1 (λ_{max} 354 nm) and 2 (λ_{max} 288 nm) or at 327 nm for 3 (λ_{max} 290 nm). Determinations of 2 and 3 were obtained by measuring the

absorbance at 354 nm or 327 nm, respectively, instead of at their λ_{max} (288 nm or 290 nm, respectively) to avoid the interference of the strong absorbance at 288 nm, due to ester oligomers extracted from the polyester fabric (as was proved by a blank test).

Measurements were recorded with a Shimadzu UV-2101 PC spectrophotometer using chlorobenzene as the reference. Calculations of UV-abs content in the presence of dye were done as described previously [2].

All determinations were made in duplicate and the results given are the mean values of the two measurements.

Light fastness tests were carried out according to ISO 105/BS 1006: 1992 BO2 [4] in a Suntest Hanau (Heraeus) apparatus with a Xenon lamp (Black panel temperature $50\pm2^{\circ}\text{C}$). The colour change was estimated against the blue standard scale 1–8 in a Verivide Colour cabinet (Leslie Hubble) with a D_{65} lamp.

Sublimation fastness tests were carried out according to ISO 105-PO1-1978 [5] in a Fixotest (Heraeus) apparatus at temperatures of 180 and 210°C.

RESULTS AND DISCUSSION

The dyeing results obtained with dyes 4 and 5 in the absence of a UV-abs (reference samples) and by application (process A or B) of the UV-abs 1, 2 and 3, are given in Tables 1-3, respectively.

Reference samples

The percentage proportion of the dye finally adsorbed on the fabric, for the range of the applied depths (0.5–3% o.w.f.), was high for the red dye 4 (95.0–80.1) and comparatively moderate for the yellow dye 5 (46.7–48.1). However, the light fastness of the fabrics dyed with 5 at all three applied depths was found to have the same rating (6), which was much higher than those dyed with 4. In contrast, the latter showed an increasing light fastness with the increase in the depth of dyeing, as is usually observed.

The sublimation fastness with respect to colour change (cc) did not show a clear dependence on the dyeing depth and was approximately similar for both the red and the yellow samples at both temperatures, being in most cases somewhat lower at the higher temperature of 210°C. However, the colour staining rating (cs) was generally lower for the red samples than for the yellow samples, and a significant decrease with increase in the dyeing depth was clearly observed at 210°C for both dyes.

Dye and UV-abs Uptake, and Light and Sublimation Fastness of Fabrics Dyed with 4 and 5 at Various Depths Applying Various Molar Ratios of Tinuvin P (1)/Dye, by Initial Addition (Process A) or by Aftertreatment (B) TABLE 1

)	N	7. 17	7117								
2)		Depin of dyeing % o.w.f.)	UV-abs/dye molar ratio (% o.w.f. I)	UV-abs applic. proc.	Dye (g) per 100 g dyed fabric (% of initial dye)	UV-abs (g) per 100 g dyed fabric (% of initial UV-abs)	I/dye Light molar ratio fastn.	ht Sul n. (.	Sublimation (180°C)	Fasi (210	Fastness (210°C)
							fabric	\mathcal{S}	so :	$\mathcal{Z}_{\mathcal{C}}$	cs
4 (Red)	-	0.50	1	1	0.48 ± 0.01 (95.3 ± 1.5)	J				4	,
	7	0.50	0.50 (0.16)	∢	0.22 ± 0.03 (44.8 ± 6.2)	0.07 + 0.00 (43.2 + 2.3)				ĵ.	າ ູ່
	m	0.50	0.50(0.16)	В	(7.0 ± 9.00)	$0.08 \pm 0.00 (43.2 \pm 2.3)$	0.00			1 .	4
	4	0.50	2.00 (0.63)) ⊲	(46.2 ± 0.1)	0.08 ± 0.00 (51.4 ± 1.5)				4-5	co
	v	0 20		ζ Δ	(40.2 ± 1.9)	$0.3/\pm 0.03$ (59.6 ± 5.2)				4-5	3
	٧ (2.50	3	٩	(34.4 ± 1.5)	$0.39 \pm 0.04 \ (61.8 \pm 7.2)$				4-5	4
	0 1	27.1	1 3	1 -	$1.52 \pm 0.03 \ (86.9 \pm 1.7)$	I				4	
	~ c	C	1.25 (1.38)	∢	$0.75 \pm 0.06 \ (42.8 \pm 3.2)$	$0.69 \pm 0.05 (50.2 \pm 3.6)$, 4	, ,
	×	1.75	1.25 (1.38)	8	_	$0.81 \pm 0.06 \ (58.4 \pm 4.3)$	1.85			. 4 . 4	, <u>,</u> ,
	7	3.00	I	I	$2.40 \pm 0.00 (80.1 \pm 0.1)$	· 1				, v	, c
	10	3.00	0.50 (0.95)	∢	_	0 43 + 0 03 (45 4 + 3 1)				1	٧.
	=	3.00	0.50 (0.95)	В	_	$0.47 \pm 0.09 (49.5 \pm 0.1)$	0.57			1 .	7-1
	12	3.00	2.00 (3.79)	ا ⊲	+3 (4)	1 88 + 0 04 (49.3 ± 0.4)				4	7
	13	3.00	2 00 (3 70)	; 0	1 2 3 5 5	1.00 ± 0.04 (49.6 ± 1.2)				4- 5	7
5 (Vel.)	; -	95.0	3	a	_	$1.97 \pm 0.20 \ (52.0 \pm 4.3)$				4-5	7
()	٠ ,	0.50		•	_	1				ς.	4
	٦,	0.50	0.50 (0.15)	۷ı	_	$0.11 \pm 0.00 (76.3 \pm 2.0)$				2-4	. 4
	ი •	0.50	0.50 (0.15)	В	_	$0.12 \pm 0.00 (77.7 \pm 2.9)$				34	4
	4 '	0.50	2.00 (0.61)	¥	_	$0.49 \pm 0.01 \ (80.6 \pm 0.2)$, v	٠ ٦
	ο ν	0.50	2.00 (0.61)	œ	_	$0.48 \pm 0.00 \ (79.6 \pm 0.5)$	3.42 6	, v	. 4	· •	۲ 4
	، د	5.75	1	I	$0.84 \pm 0.07 \ (48.0 \pm 3.9)$					2.4	۰,
	_ (1.75	1.25 (1.33)	∢	$0.88 \pm 0.02 \ (50.5 \pm 1.0)$	$0.88 \pm 0.04 \ (66.2 \pm 3.0)$				ď	ر د
	∞	1.75	1.25 (1.33)	В	$0.69 \pm 0.05 (39.3 \pm 3.2)$	$0.87 \pm 0.03 (65.2 \pm 2.4)$	2 07			o v	ţ -
	6	3.00	1	t	1.40 ± 0.03 (46.7 ± 1.0)					, ,	t (
	10	3.00	0.50 (0.91)	∢	_	(6.51 ± 1.2)				Ĵ,	5- 7
	Ξ	3.00	0.50 (0.91)	~	(40.1 ± 1.1)	$0.50 \pm 0.01 \ (02.1 \pm 1.3)$				n	4
	12	3.00	2 00 (3 66)	>	(42.1 ± 1.1)	$0.04 \pm 0.01 \ (/0.3 \pm 0.6)$				S	۲
	7 7	200	2.00 (3.00)	< 4	$\pm 0.06 (48.1 \pm 2.0)$	$2.51 \pm 0.07 \ (68.6 \pm 2.0)$	2.85 7	S		2	2–3
		3.00	7.00 (3.00)	27	$1.23 \pm 0.09 \ (41.0 \pm 3.3)$	$2.67 \pm 0.13 \ (73.0 \pm 3.5)$	3.56 7	S		v	7
								')	r 3

Dye and UV-abs Uptake, and Light and Sublimation Fastness of Fabrics Dyed with 4 and 5 at Various Depths Applying Various Molar Ratios of Tinuvin 327 (2)/Dye, by Initial Addition (Process A) or by Aftertreatment (B) TABLE 2

						• !						
Дуе	No.	Depth of dyeing (% o.w.f.)	UV-abs/dye molar ratio (% o.w.f. 2)	UV-abs applic. proc.	Dye (g) per 100 g dyed fabric (% of initial dye)	UV-abs (g) per 100 g dyed fabric (% initial UV-abs)	2/dye molar ratio on	Light fastn.	Light Sublimation fastn. (180°C)	oation °C)	Fastness (210°C)	ess C)
				1			dyed fabric	•	22	so	22	cs
4 (Red)	-	0.50		1	$0.48 \pm 0.01 \ (95.3 \pm 1.5)$	1		2	4-5	4-5	4-5	3
,	7	0.50	0.50 (0.25)	A	$0.40 \pm 0.01 \ (80.8 \pm 1.6)$	$0.19 \pm 0.00 (76.2 \pm 0.2)$	0.47	2–3	S	4-5	4-5	3
	ĸ	0.50	0.50(0.50)	В		$0.18 \pm 0.01 \ (71.6 \pm 2.2)$	0.47	2–3	5	4-5	4-5	e
	4	0.50	2.00 (1.00)	¥	$0.38 \pm 0.01 \ (75.6 \pm 3.1)$	$0.69 \pm 0.01 \ (68.9 \pm 0.8)$	1.81	2-3	2	4-5	4-5	2–3
	2	0.50	2.00 (1.00)	æ	$0.32 \pm 0.03 (64.6 \pm 5.4)$	$0.49 \pm 0.07 \ (49.0 \pm 7.5)$	1.53	2–3	5	4-5	4-5	c
	9	1.75	ı	١	$1.52 \pm 0.03 \ (86.9 \pm 1.7)$	I	1	2-3	S	4-5	4-5	2–3
	7	1.75	1.25 (2.19)	∢	$1.09 \pm 0.15 (62.3 \pm 9.0)$	$0.61 \pm 0.02 \ (27.8 \pm 1.1)$	0.56	æ	2	4	4-5	7
	∞	1.75	1.25 (2.19)	B	$0.94 \pm 0.07 (53.9 \pm 4.0)$	$0.64 \pm 0.14 \ (28.9 \pm 6.3)$	89.0	ю	S	4-5	4-5	2-3
	6	3.00	ı	ì	$2.40 \pm 0.00 \ (80.1 \pm 0.1)$	1	١	n	5	4	4-5	7
	01	3.00	0.50 (1.50)	¥	_	$0.62 \pm 0.02 \ (41.4 \pm 1.4)$		%	S	<u>ښ</u>	4-5	2-3
	Ξ	3.00	0.50(1.50)	B	$1.88 \pm 0.09 (62.7 \pm 3.1)$	$0.74 \pm 0.17 (49.3 \pm 11.4)$		ю	5	4	4-5	7
	12	3.00	2.00 (6.00)	¥	$2.19 \pm 0.05 \ (73.0 \pm 1.6)$	$0.73 \pm 0.00 (12.2 \pm 0.0)$	0.33	ж 4	2	4	4-5	1-2
	13	3.00	2.00 (6.00)	æ	$1.87 \pm 0.08 \ (62.2 \pm 2.6)$	$0.78 \pm 0.01 \ (13.0 \pm 0.2)$		٣ 4	2	4	4-5	7
5 (Yel.)		0.50	ı	ı	$0.24 \pm 0.00 \ (48.1 \pm 0.0)$	ı	1	9	S	S	S	4
	7	0.50	0.50(0.24)	A	$0.32 \pm 0.01 \ (63.6 \pm 1.2)$	$0.21 \pm 0.00 (89.1 \pm 0.0)$	89.0	6-7	2	4-5	2	4
	3	0.50	0.50 (0.24)	В	_	$0.21 \pm 0.00 (86.2 \pm 0.0)$	1.28	6-7	2	4-5	2	4
	4	0.50	2.00 (0.96)	¥	_	$0.60 \pm 0.02 \ (62.6 \pm 2.0)$	2.07	6-7	2	4-5	2	4
	2	0.50	2.00 (0.96)	м	±0.01	$0.56 \pm 0.03 \ (58.3 \pm 3.0)$	3.41	2-9	2	4-5	2	4
	9	1.75	ſ	1	0.07 (48.0	I	l	9	S	2	4- 5	æ
	7	1.75	1.25 (2.11)	∢	$0.90 \pm 0.04 \ (51.3 \pm 2.1)$	$\pm 0.00 (31.1 \pm$	92.0	6-7	S	4-5	5	m
	∞	1.75	1.25 (2.11)	В	$0.54 \pm 0.01 \ (30.6 \pm 0.5)$	$0.52 \pm 0.08 \ (24.6 \pm 3.7)$	1.00	2-9	2	4-5	2	%
	6	3.00	. 1	I	$1.40 \pm 0.03 \ (46.7 \pm 1.0)$		ı	9	\$	4-5	4-5	2-3
	10	3.00	0.50 (1.45)	¥	$1.36 \pm 0.25 \ (45.4 \pm 8.4)$	$0.75 \pm 0.01 \ (51.5 \pm 1.1)$	0.57	7	S	4-5	2	7
	Ξ	3.00	0.50(1.45)	В	$0.88 \pm 0.03 \ (29.5 \pm 0.9)$	$0.67 \pm 0.03 \ (46.4 \pm 2.0)$	0.79	6-7	S	4-5	S	Э
	12	3.00	2.00 (5.79)	¥	$0.98 \pm 0.08 \ (32.7 \pm 2.6)$	$0.72 \pm 0.01 \ (12.4 \pm 0.1)$	92.0	7	2	4-5	2	Э
	13	3.00	2.00 (5.79)	В	$0.84 \pm 0.02 \ (28.0 \pm 0.7)$	$0.84 \pm 0.03 \ (14.6 \pm 0.5)$	1.04	6-7	2	4-5	5	33
	!											

Dye and UV-abs Uptake, and Light and Sublimation Fastness of Fabrics Dyed with 4 and 5 at Various Depths Applying Various Molar Ratios of DHB (3)/Dye, by Initial Addition (Process A) or by Aftertreatment (B) TABLE 3

20	Дуе	No.	Depth of dyeing (% o.w.f.)	UV-abs/dye molar ratio (% o.w.f. 3)	UV-abs applic. proc.	Dye (g) per 100 g dyed fabric (% initial dye)	UV-abs (g) per 100 g dyed fabric (% of initial UV-abs)	3/dye molar ratio on	Light fastn.	Sublimation (180°C)	ation C)	Fastness (210°C)	ness C)
1 0.50 - - 0.48 ± 0.01 (95.3 ± 1.5) - 2 4-5 4-5 4-5 4-5 4-5 4-5 4-5 4-5 5 4-5 5 4-5 5 4-5 5 4-5 5 4-5 5 4-5 5 4-5 5 4-5 5 4-5 5 4-5 5 5 4-5 4-5 5 5 5 5 5 5 5 5 5 5 4-5 5 5 5 5 5 5 5 5 5 4-5 5 5 4-5 5 5 4-5 5 5 4-5 5 4-5 5 4-5 5 4-5 5 4-5 5 4							,	dyed fabric		cc	CS	cc	cs
2 0.50 (0.15) A 0.36±0.04 (73.1±6.8) 0.07±0.01 (49.8±6.5) 0.35 2 5 4.5 5 4 5 5 6 0.50 (0.15) B 0.36±0.01 (72.0±3.0) 0.06±0.02 (41.7±11.6) 0.30 2 5 4.5 5 5 6 0.50 0.50 (0.160) B 0.34±0.01 (66.8±1.7) 0.28±0.00 (36.2±0.5) 1.11 2 5 5 4.5 5 6 1.75 1.25 (1.31) A 1.12±0.01 (66.8±1.7) 0.18±0.01 (29.7±1.3) 0.84 2 5 4.5 5 4.5 5 1.75 1.25 (1.31) A 1.12±0.01 (67.8±11.4) 0.18±0.01 (29.7±1.3) 0.84 2 5 4.5 5 4.5 5 1.75 1.25 (1.31) A 1.12±0.01 (67.8±11.4) 0.18±0.01 (29.7±1.3) 0.84 2 5 4.5 5 1.25 (1.31) A 1.12±0.01 (67.8±11.4) 0.18±0.01 (29.2±2.5) 0.49 3 5 4 5 4 5 1.25 (1.31) A 1.12±0.01 (66.1±0.0) 0.32±0.00 (24.6±0.0) 0.45 3 4 4.5 4.5 1.25 (1.31) A 1.99±0.15 (66.5±5.2) 0.25±0.03 (24.8±0.0) 0.20 3.4 4.5 4 4.5 1.30 0.50 (0.90) B 1.62±0.00 (67.1±0.0) 0.32±0.00 (24.6±0.0) 0.20 3.4 4.5 4 4.5 1.30 0.50 (0.90) B 1.62±0.00 (43.8±0.3) 0.20 3.4 4.5 4 4.5 1.30 0.50 (0.360) A 1.99±0.15 (66.5±5.2) 0.25±0.03 (29.8±3.9) 0.20 3.4 4.5 4 4.5 1.30 0.50 (0.360) A 1.99±0.15 (66.5±5.2) 0.25±0.03 (29.8±3.9) 0.20 3.4 4.5 4 4.5 1.30 0.50 (0.360) A 1.99±0.15 (66.5±0.2) 0.20±0.03 (29.8±3.9) 0.20 0.30 0.30 0.30 0.30 0.30 0.30 0.30	4 (Red)	-	0.50	I	1	±0.01			,		4.5	4.5	~
3 0.50 0.05 (0.15) B 0.36 ± 0.01 (72.0±3.0) 0.06 ± 0.02 (41.7±11.6) 0.30 2 4 5 4 0.50 2.00 (0.60) A 0.33 ± 0.01 (65.4±1.7) 0.22 ± 0.00 (36.2±0.5) 1.11 2 5 4.5 5 6 1.75 1.25 (1.31) A 1.12±0.13 (64.3±7.3) 0.33±0.03 (25.2±2.5) 0.49 3 4 5 4.5 4 5 <td></td> <td>7</td> <td>0.50</td> <td>0.50 (0.15)</td> <td>¥</td> <td></td> <td>(49.8 ±</td> <td>0.35</td> <td>1 C</td> <td></td> <td>2 4</td> <td>ر ا</td> <td>ה ני</td>		7	0.50	0.50 (0.15)	¥		(49.8 ±	0.35	1 C		2 4	ر ا	ה ני
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6 1.75		S,	0.50	2.00 (0.60)	В	$0.34 \pm 0.01 \ (67.8 \pm 11.4)$	$0.18 \pm 0.01 (29.7 \pm 1.3)$	0.84	1 7		. 4) v	,
7 1.75 1.25 (1.31) A 1.12±0.13 (64.3±7.3) 0.33±0.03 (25.2±2.5) 0.49 3 5 4 5 4 5 3 300 0.50 (0.90) B 1.17±0.00 (67.1±0.0) 0.32±0.00 (24.6±0.0) 0.45 3 4.5 4.5 4.5 1.25 (1.31) B 1.17±0.00 (67.1±0.0) 0.32±0.00 (24.6±0.0) 0.45 3 4.5 4.5 4.5 1.25 (0.90) B 1.02±0.00 (63.6±5.2) 0.25±0.03 (28.2±3.0) 0.20 3-4 4-5 4.5 1.2 (0.90) B 1.62±0.09 (63.2±3.1) 0.26±0.03 (29.0±3.9) 0.26 3-4 4.5 4.5 1.2 (0.90) B 1.62±0.09 (63.2±3.1) 0.26±0.03 (29.0±3.9) 0.26 3-4 4.5 1.2 (0.90) B 1.47±0.01 (49.1±0.3) 1.01±0.11 (28.2±3.2) 1.14 3-4 5 4 4.5 1.0 0.50 (0.36) B 1.47±0.01 (49.1±0.3) 1.01±0.11 (28.2±3.2) 1.14 3-4 5 4 4.5 1.0 0.50 (0.36) B 1.47±0.01 (49.1±0.3) 1.01±0.11 (28.2±3.2) 1.14 3-4 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5		9	1.75	I	1	$1.52 \pm 0.03 \ (86.9 \pm 1.7)$		i	2-3		2	4.5	, <mark>,</mark>
8 1.75 1.25 (1.31) B 1.17±0.00 (67.1±0.0) 0.32±0.00 (24.6±0.0) 0.45 3 4-5 4-5 4-5 3.00 3.00		7	1.75	1.25 (1.31)	V	$1.12 \pm 0.13 (64.3 \pm 7.3)$	$0.33 \pm 0.03 (25.2 \pm 2.5)$	0.49	, w		, 4	, v	1 C
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$		7	3.00	8	¥	$2.08 \pm 0.14 \ (69.3 \pm 4.8)$	$1.00 \pm 0.15 (27.9 \pm 4.3)$	0.80	34		4	4-5	2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		<u>.</u>	3.00	8	В	$1.47 \pm 0.01 \ (49.1 \pm 0.3)$	$1.01 \pm 0.11 \ (28.2 \pm 3.2)$	1.14	6		4	4-5	2-3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5 (Yel.)	- ·	0.50	t	j	$0.24 \pm 0.00 \ (48.1 \pm 0.0)$	· ·	t	9		ς.	S	, 4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		7	0.50	0.50(0.14)	V	52.4 ± 3.3	$0.06 \pm 0.00 \ (39.5 \pm 0.2)$	0.40	2-9		4-5	· v	- 4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		· ·	0.50	0.50 (0.14)	—	46.1 ± 0.5	$0.06 \pm 0.00 \ (42.2 \pm 1.0)$	0.45	6- 7		4-5	S	4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		4 '	0.50	2.00 (0.58)	V	44.9 ± 1.0	0.17 ± 0.01 (29.7 ± 1.0)	1.33	7-9		5	v	4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		· 0	0.50	8	В	45.6 ± 0.5	$0.11 \pm 0.00 (18.2 \pm 0.1)$	0.82	2-9		1 5	, v.	- 4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		9	1.75		1	48.0 ± 3.9)	` I	I	9		ر د	4.5	٠,
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		7	1.75	1.25 (1.27)	¥	$0.94 \pm 0.01 \ (53.7 \pm 0.4)$	$0.33 \pm 0.02 (26.2 \pm 1.3)$	09.0	1-9		4	, v	, (r
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		∞ ·	1.75	1.25 (1.27)	മ	$0.69 \pm 0.06 \ (39.3 \pm 3.2)$	$0.31 \pm 0.05 (24.6 \pm 3.7)$	0.77	6-7		. 1	, v	, ~
$3.00 0.50 (0.87)$ A $1.67 \pm 0.06 (55.7 \pm 1.9) 0.21 \pm 0.09 (23.7 \pm 0.1)$ 0.22 $6 \pm 7 5 4 5$ 3.00 0.50 (0.87) B 1.26 ± 0.03 (42.1 ± 1.1) 0.18 ± 0.01 (20.9 ± 1.5) 0.25 $6 \pm 7 5 4 5$ 3.00 2.00 (3.48) A 1.76 ± 0.10 (58.7 ± 3.4) 0.71 ± 0.02 (20.3 ± 0.6) 0.70 7 5 3 ± 4 5 3.00 2.00 (3.48) B 1.23 ± 0.10 (41.0 ± 3.3) 0.86 ± 0.00 (24.6 ± 0.0) 1.21 7 5 4 5		6	3.00	ſ	ı	$1.40 \pm 0.03 (46.7 \pm 1.0)$	` I	1	٠		, , ,	4,4	2,7
$3.00 0.50 (0.87) \mathbf{B} 1.26 \pm 0.03 (42.1 \pm 1.1) 0.18 \pm 0.01 (20.9 \pm 1.5) 0.25 6-7 5 4 5 \\ 3.00 2.00 (3.48) \mathbf{A} 1.76 \pm 0.10 (58.7 \pm 3.4) 0.71 \pm 0.02 (20.3 \pm 0.6) 0.70 7 5 3-4 5 \\ 3.00 2.00 (3.48) \mathbf{B} 1.23 \pm 0.10 (41.0 \pm 3.3) 0.86 \pm 0.00 (24.6 \pm 0.0) 1.21 7 5 4 5 $		10	3.00	0.50(0.87)	¥	± 0.06	$0.21 \pm 0.09 (23.7 \pm 0.1)$	0.22	5-7		, 4		1 C
$3.00 2.00 (3.48) A 1.76 \pm 0.10 (58.7 \pm 3.4) 0.71 \pm 0.02 (20.3 \pm 0.6) 0.70 7 5 3-4 5$ $3.00 2.00 (3.48) B 1.23 \pm 0.10 (41.0 \pm 3.3) 0.86 \pm 0.00 (24.6 \pm 0.0) 1.21 7 5 4 5$		=	3.00	0.50 (0.87)	æ	$\pm 0.03 (42.1 \pm 1.1)$	$0.18 \pm 0.01 \ (20.9 \pm 1.5)$	0.25	2-9		. 4	, v	, ~
3.00 2.00 (3.48) B 1.23 ± 0.10 (41.0±3.3) 0.86 ± 0.00 (24.6±0.0) 1.21 7 5 4 5		12	3.00	2.00 (3.48)	¥	$\pm 0.10 (58.7 \pm 3.4)$	20.3	0.70	, ~		. 7	, v	ر 1.
		13	3.00	2.00 (3.48)	æ	$\pm 0.10 (41.0 \pm 3.3)$	24.6	1.21	7		. 4	· •	, ~

Effectiveness of UV-abs

Dyeing with 4

Dye and UV-abs uptake. Application of the three UV-abs in all dyeings with the red dye 4 resulted in a significantly reduced uptake of the dye compared with the corresponding reference samples (Tables 1-3). Generally, 1 caused a greater reduction in dye uptake than 3 and 2. Comparing the two UV-abs application processes it is concluded that process A resulted mostly in a slightly higher dye content on the fabric, due to a slight dye desorption during the after treatment (B).

Among the three UV-abs, 1 (M.W. 225) showed the highest and 2 (M.W. 365.5) the lowest percentage adsorption of their initial amounts for an equivalent UV-abs/dye molar ratio and application process. Regarding the UV-abs uptake, no substantial difference was correspondingly observed between the two application processes for each of the three UV-abs. An increase of the UV-abs/dye molar ratio for the same depth of dyeing resulted in a proportional increase of the final uptake of 1 and 3 and a smaller increase in the final uptake of 2 which has highest molecular weight. The UV-abs/dye molar ratio on the final fabrics was higher than the initially applied one in almost all cases of 1, whereas it was significantly lower in all cases of 2 and 3.

Light fastness of the dyed fabrics. Application of the UV-abs resulted in a slight increase (0.5 grade) in the light fastness of the fabrics dyed with dye 4, with the exception for that of 1 (Table 1) and 2 (Table 2) at the dyeing depth of 0.5%, where no increase was observed, probably on account of their low dye uptake. This is in agreement with previous results [1] where the content of 1 on the dyed fabric (<0.30% o.w.f.) did not result in a light fastness improvement.

A four-fold increase of UV-abs/dye molar ratio did not correspondingly affect the light fastness, which appeared the same in all cases (Tables 1-3). These results are consistent with those of previous work [1], where only a significantly high increase in molar ratio (4-15) caused a variation in light fastness improvement.

No difference regarding the light fastness improvement was observed in this work between the two UV-abs application processes. This is in disagreement with previous results [1], where application of 1 by aftertreatment of the fabrics dyed with 4 seemed to be more advantageous than by process A. This disagreement could be attributed to the different dyeing conditions, such as the use of dispersing agents for the dye and UV-abs and the application of the reduction clearing process in the present work.

Comparing the activity of the three UV-abs (1-3) on the light fastness improvement, it is concluded that 3 was the most active since, with a lower percentage content of it on the fabric relative to that of 1 and 2, this resulted in the same light fastness improvement.

Dyeing with 5

Dye and UV-abs uptake. Application of 1 and 2 by process A did not affect in most cases the final uptake of Viosperse Yellow GLFS (5) (Tables 1 and 2). In contrast, process B resulted in a lower dye content on the fabric in all cases of 2 and in a slightly lower one in some cases of 1. The UV-abs (1 or 2)/dye molar ratio for the same depth of dyeing and application method did not in the main, affect the final dye uptake. The content of 1 and 2 on the fabric was found independent of the application process used, and proportional to the UV-abs/dye molar ratio for 1 and less proportional for 2. In general the percentage amount of 1 on the fibre was found to be higher than that of 2 (which has a higher molecular weight) and also higher than in the corresponding dyeing with dye 4 (Table 1). The UV-abs/dye molar ratio on the final fabrics was higher than the initially applied one in all cases of 1, and was highest on the aftertreated samples by process B, as in dyeing with the red dye 4, whereas this ratio for 2 was found to have wide fluctuations.

Application of 3 by process A did not significantly affect the dye uptake, as was the case for 1 and 2. Aftertreatment with 3 at a dyeing depth of 0.5% o.w.f. did not affect (or slightly decreased) the adsorbed amount of dye, as with 1, whereas at higher dyeing depths (1.75 and 3% o.w.f.) it resulted in a significant decrease in dye content, similarly to 2.

Variation of the 3/Yellow GLFS molar ratio for the same depth of dyeing and application method, did not significantly affect the dye content on the fabric, as in the case of 1 and 2.

Regarding the amounts of 3 finally adsorbed on the fibre, the two application processes A and B had practically the same result, as was also observed for 1 and 2.

The percentage amount of the benzophenone UV-abs (3) finally adsorbed was, in all cases, significantly lower than that of 1, and in most cases than that of 2. These results are in agreement with those obtained with the red dye 4 (Table 2).

Light fastness of the dyed fabrics. Application of the UV-abs 1 by process A or B at depths of dyeing of 0.5% o.w.f. for both molar ratios (0.5 and 2.0) did not improve the light fastness, probably due to its low content on the fabric (0.49%, w/w), similar to results obtained for corresponding samples dyed with 4 (Table 1). However, an improvement in light fastness of 1 grade

was obtained compared with that of reference samples in all cases at dyeing depths 1.75% and 3.00% o.w.f., where its content on the fibre was higher than 0.49% w/w.

Application of 2 resulted in an improvement in light fastness by 1 grade in the samples of process A and depth of dyeing 3% o.w.f., and by 0.5 grade in all other cases. This effectiveness of 2 at dyeing depths 0.5% o.w.f., in contrast to 1, could be attributed, from one point of view, to its higher content on the fibre, compared with that of 1 (Tables 1 and 2).

Application of 3 resulted in a light fastness improvement by 1 grade in the samples of the highest dyeing depth (3% o.w.f.) and highest applied 3/5 molar ratio (2.00), but by 0.5 grade in all other cases.

Comparison of the activity of the three UV-abs in the light fastness, in relation to their content on the fabric and their initially applied quantity, lead to the conclusion that 3 was more active than 1 and 2 at dyeing depths 0.5% o.w.f., whereas a similar conclusion pertained for all dyeings with dye 4 (Tables 1-3). However, considering the initial quantity of the UV-abs at the higher dyeing depths, 1 appeared rather more effective with respect to light fastness than 3, on account of the much higher content of the former on the fabric (Tables 1 and 3).

Sublimation fastness of the dyed fabrics (dyes 4 and 5). Generally the sublimation fastness of the dyed samples was either not affected, or only slightly affected, by the application of the three UV-abs. No substantial differences in sublimation fastness were observed between the two application processes of the UV-abs and the applied UV-abs/dye molar ratios in all corresponding dyeings with both the red and yellow dyes (Tables 1–3).

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