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UV-absorbers in the dyeing of polyester with disperse dyes

E.G. Tsatsaroni*, I.C. Eleftheriadis

Department of Chemical Technology and Industrial Chemistry, School of Chemistry, Aristotle University, 541 24 Thessaloniki, Greece

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Abstract

The effect of the benzotriazole type UV-absorbers Tinuvin P and Tinuvin 327 and 2.4-dihydroxy benzophenone in the dyeing of polyester fibres with Viosperse Blue RFS, an azodye of low light fastness at various depths of dyeing and UV-absorber amounts was studied using different application procedures. The dye and UV-absorber uptake and the light and sublimation fastness of the dyed samples were determined and compared to those obtained for the corresponding samples dyed in absence of a UV-absorber. The effectiveness of 2-(2-hydroxy-5-carboxy-phenyl)-2*H*-benzotriazole in improving the light fastness of polyester fibres dyed with C.I. Disperse Blue 77, Red 86, Yellow 42 and Viosperse Red BS was also studied and compared to that of the above commercial benzotriazole type UV-absorbers. The latter was applied to the fibre in various molar ratios to the dye using two different application procedures: directly in the dyebath and by aftertreatment of the dyed fabrics.

Keywords: UV-absorbers; Polyester fibres; Disperse dyes; Light fastness

1. Introduction

In previous papers [1–4] the effect of using various amounts of commercial UV-absorbers of the benzotriazole and benzophenone type was extensively examined and discussed.

In this work a further study of the application of the same UV-absorbers in the dyeing of polyester fibres with a disperse dye of low light fastness was studied further. Improvement of the light fastness value is of crucial importance in the textile industry since polyester fabrics dyed with disperse dyes are widely used in automobile coloured upholstery and are exposed to direct sunlight and temperatures above 50 °C.

Furthermore the use of 2-(2-hydroxy-5-carboxy-phenyl)-2*H*-benzotriazole [5], a molecule designed to meet the requirements of a UV-absorber both in regard to its adsorption on polyester and even more importantly, its compatibility with disperse dyes containing particular groups in their molecule, was studied and the results were compared to those obtained in our previous papers [1–4] and discussed.

2. Experimental

Specimens $10^{-2}\times10^{-2}$ m^2 (10×10 cm^2) approx 2×10^{-3} kg (2 g) of commercial polyester (PET)

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* Corresponding author. Tel.: +32-310-997855; fax: +32-310-997769.

E-mail address: tsatsaro@chem.auth.gr (E.G. Tsatsaroni).

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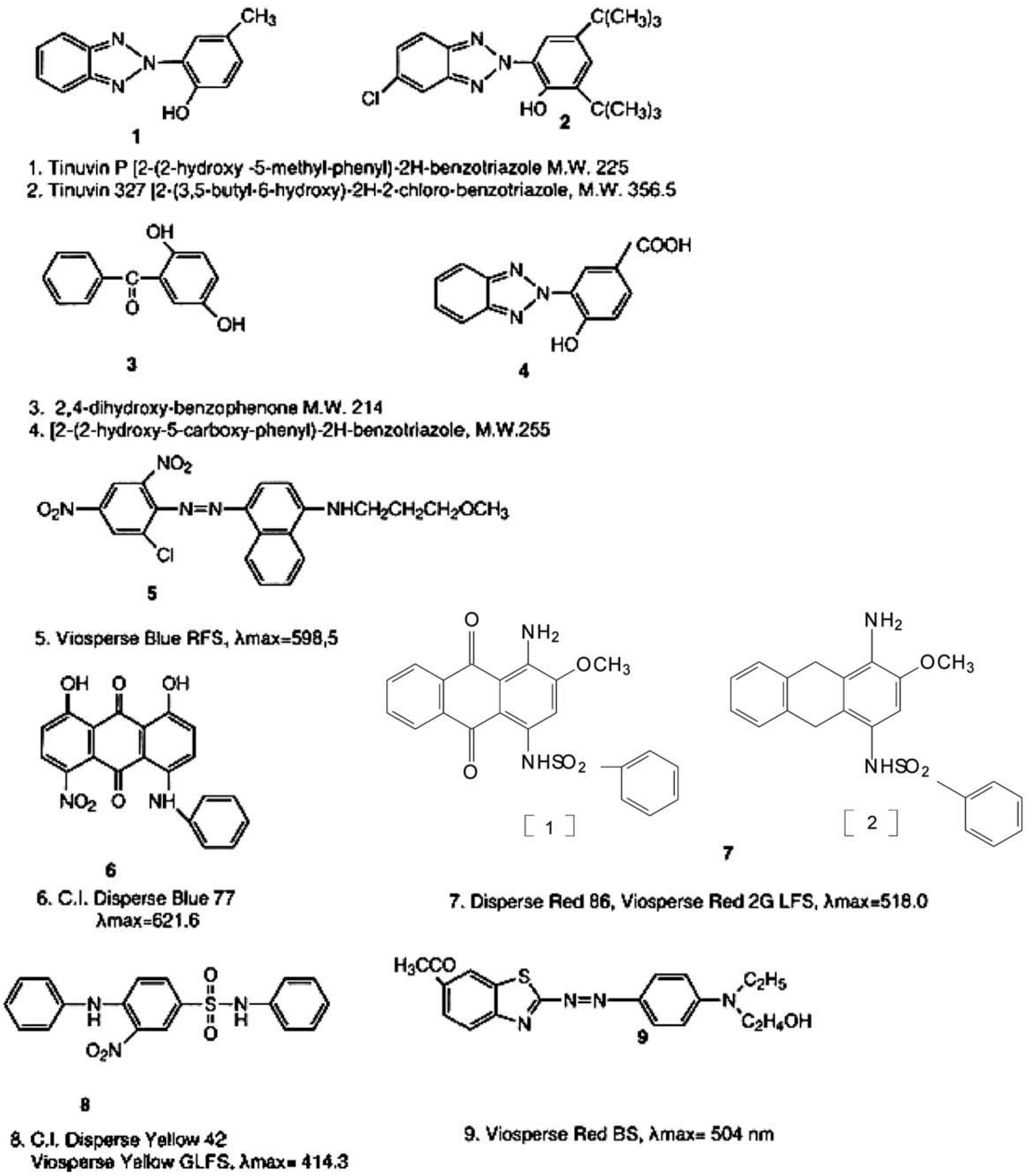

1. Tinuvin P [2-(2-hydroxy -5-methyl-phenyl)-2H-benzotriazole M.W. 225
2. Tinuvin 327 [2-(3,5-butyl-6-hydroxy)-2H-2-chloro-benzotriazole, M.W. 356.5

3. 2,4-dihydroxy-benzophenone M.W. 214
4. [2-(2-hydroxy-5-carboxy-phenyl)-2H-benzotriazole, M.W.255

5. Viosperse Blue RFS, λmax=598,5

6. C.I. Disperse Blue 77
λmax=621.6

7. Disperse Red 86, Viosperse Red 2G LFS, λmax=518.0

8. C.I. Disperse Yellow 42
Viosperse Yellow GLFS, λmax= 414.3

9. Viosperse Red BS, λmax= 504 nm

Scheme 1. Dyes and UV-absorbers used.

fabric were used. UV-absorbers and dyes used are given in Scheme 1.

UV-absorbers (UV-abs) **1**, **2** (Ciba-Geigy), **3** (Sigma) and **4** and dyes 5–9 (Yorkshire Hellas) were used as aqueous dispersions prepared as follows.

Appropriate amounts of the commercial UV-abs or dye, a dispersing agent (TAMOL NN 9104, NNOK/Vultamol, sodium salt of polyandensated naphthalenesulphonic acid, M.W. approx. 6500, BASF) and/or an anionic surfactant (ULTRAZINE NA, sodium salt of lignine sulphonic acid, M.W. approx. 17,000, BORREGAARD) and water were added to a grinding mill (Susmeyer). The pH was adjusted at 7–7.5 with 85% phosphoric acid and the mixture was stirred for 1.2×10^2 s (20 min). Glass otawa 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 μm. A practical Analyser, Microtrac X 100 P was used for measuring the particle size distribution.

The percentage UV-abs content in the dispersions obtained was determined using an HPLC Waters 990 apparatus with an integrator and a LichroCART 125-Lichrosphor 100 column. The dispersed UV-abs preparations were found to contain **1**: 8.0%, **2**: 1.8% and **3**: 17.6% (w/w).

The percentage content of pure dye in the dispersion sample was determined spectrophotometrically using a mixture of dimethyl formamide/distilled water/acetic acid (87:10:3 v/v) as solvent and reference solution of pure dye. The dispersion samples of the dyes **5**, **6**, **7**, **8** and **9** were found to contain 40.0, 36.5, 43.2, 60.6 and 50.5% (w/w) pure dye.

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

Dyeings were carried out in a Rotadyer apparatus (John Jeffreys Ltd., Rochdale Banbury) with a liquor ratio 10:1 in the presence of the UV-absorber in various molar ratios (dye:UV-abs) at pH 5 using a sodium acetate-acetic acid buffer solution. Reference samples (without UV-absorber treatment) were also dyed. The dyebath was to 333 K (60 °C) within 2.1×10^3 s (35 min) and maintained at this level for 3.6×10^3 s (1 h). After dyeing, rinsing and squeezing of the samples reduction clearing was carried out by heating in an aqueous solution (10:1 on the weight of the fibre, o.w.f.) containing 1 kg/m^3 (g/l) dispersing agent 3 kg/m^3 (g/l) sodium bisulphite and 6 kg/m^3 (g/l) sodium hydroxide at 353 K (80 °C) for 1.2×10^3 s (20 min) [6]. The fabrics were then successively rinsed and squeezed.

After treatment of the dyed samples with the UV-absorbers was also made.

Determination of dye and UV-absorber uptake was carried out by Soxhlet extracting the dye and UV-absorber with chlorobenzene from the final fabrics and measuring the absorbances of the chorobenzene solutions at the $\lambda_{\max}$ of the dyes and at $\lambda = 354$ nm for 1, 2 and 4 or at 327 nm for 3. Determinations of **2**, **3** and **4** were obtained by measuring the absorbance at the above wave lengths instead of their $\lambda_{\max}$ (288, 290 and 295 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). Calculations of the UV-absorber content in the presence of dye were done by subtracting the absorbances of the dyes at 354 or 327 nm (depending on the UV-abs measured), which were determined by correlating the absorbance of the dyes at their $\lambda_{\max}$ and at the above wavelengths.

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

A reflectance spectrometer Macbeth CE 3000 [UV and specular component included, large area view 25.4×10.4 m (25.5 mm) diameter] was used for the colorimetric measurements on the dyed samples. K/S value given by the reflectance spectrometer is directly correlated with the dye concentration on the dye substrate according to the Kubelka–Munk equation:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} = a.c$$

where K = absorbance coefficient, S = scattering coefficient, R = reflectance ratio, a = constant, c = dye concentration.

Light fastness tests were carried out according to ISO 105/BS 1006: 1992 BO2 in a Suntest Hanau (Heraeus) apparatus with a Xenon lamp (black panel temperature 323±2 K, 50±2 °C). The colour change was estimated agains the blue standard scale 1–8 in a Verivide Colour cabinet (Leslie Hubble) with a D_{65} Lamp [9].

Sublimation fastness tests were carried out according to ISO 105-P01-1978 [9] in a Fixotest (Heraeus) apparatus at temperatures of 453 and 483 K (180 and 210 °C).

Table 1
Dye and UV-abs uptake and light and sublimation fastness of fabrics dyed with Viosperse Blue RFS in absence and/or presence of various amounts of the UV-abs **2**–**4** (direct application D or after treatment A)

Depth of dyeing (% o.w.f.)	UV-abs	UV-abs/dye molar ratio mol. mol $^{-1}$	UV-aps application procedure	% ads dye (Soxhlet extracted)	% ads UV-abs	Light fastness	Sublimation fastness			
							180 °C		210 °C	
							CC	CS	CC	CS
1.5	–	–	–	86.0	–	3–4	5	5	5	3–4
	Tin P	1:1	D	76.6	52.8	4	5	5	5	3–4
		1:1	A	75.3	47.2	4	5	5	5	4
		1:2	D	71.3	72.0	4	5	5	5	3–4
		1:2	A	71.3	68.0	4	5	5	5	4
2.5	–	–	–	73.6	–	4	5	4–5	5	3–4
		1:1	D	78.4	46.4	5	5	5	5	3
		1:1	A	72.0	44.0	4–5	5	4–5	5	2–3
		1:2	D	80.8	72.0	5	5	5	5	3
		1:2	A	73.2	60.0	4–5	5	4–5	5	2–3
1.5	–	–	–	86.0	–	3–4	5	5	5	3–4
	Tin 327	1:1	D	87.3	96.0	4	5	5	5	3–4
		1:1	A	89.3	52.8	4–5	5	5	5	3–4
		1:2	D	91.3	98.0	4	5	5	5	3–4
		1:2	A	81.3	80.0	4–5	5	5	5	3–4
2.5	–	–	–	73.6	–	4	5	4–5	5	3–4
		1:1	D	86.0	74.0	5–6	5	4–5	5	2–3
		1:1	A	72.0	68.0	4–5	5	5	5	3–4
		1:2	D	72.0	96.0	5–6	5	5	5	3
		1:2	A	70.0	68.8	4–5	5	4–5	5	2–3
1.5	–	–	–	86.0	–	3–4	5	5	5	3–4
	DHB	1:1	D	76.6	20.6	3–4	5	5	5	4
		1:1	A	85.3	26.4	3–4	5	5	5	3–4
		1:2	D	71.3	28.0	3–4	5	5	5	4
		1:2	A	71.3	30.0	3–4	5	5	5	4
2.5	–	–	–	73.6	–	4	5	4–5	5	3–4
		1:1	D	66.8	22.4	4	5	5	5	3
		1:1	A	71.6	32.0	4–5	5	4–5	5	2–3
		1:2	D	68.0	42.0	4	5	4–5	5	2–3
		1:2	A	72.0	42.0	4–5	5	5	5	3

3. Results and discussion

The results of the use of Tinuvin P and 327 and DHB (dihydroxybenzophenone) in the dyeing of Viosperse Blue RFS are given in Table 1.

From Table 1 the following conclusions were reached.

The dye uptake is high in both depths of dyeing for the reference samples. Addition of the UV-absorbers affects the dye uptake, though not significantly, in different ways depending on the UV-absorber, the application method (addition in the dyebath or aftertreatment) and the quantity of the UV-abs used (UV-abs/dye molar ratio).

Thus addition of the two benzotriazole UV-absorbers Tinuvin P and 327 in the dyebath results in an increase in dye uptake compared to the reference sample in almost all the cases, while duplication of the UV-abs/dye molar ratio (equimolar quantity dye and UV-abs) results in a further increase in dye uptake. It seems like the presence of these two compounds in the dyebath during the dyeing favours the dye migration from the dye liquor onto the fibre.

The same was not observed while using DHB, whose presence in the dye bath, as well as increase in molar ratio DHB/dye results in lower dye uptake values compared to the reference sample.

This different behaviour could be related with the differences in the molecular structures of the three compounds. 2,4-Dihydroxybenzophenone with the two polar hydroxy substituents has the lowest affinity to the nonionic blue disperse dye with a competitive action to this. On the contrary the benzotriazole UV-absorber and mainly the Tinuvin 327 with the two bulky *tert*-butyl substituents in its molecule have higher affinity to the dye acting as "carriers" and improving the dye uptake on the fibre.

Dye uptake in the case of aftertreatment of the dyed samples with the UV-absorber is always lower than the reference sample due to dye desorption in some extent in the aftertreatment liquor.

Regarding the UV-absorbers uptake on the polyester fibre Tinuvin 327 shows the highest and DHB the lowest uptake. The same structural reasons mentioned above affect the affinity of the three UV-absorbers with the hydrophobic polyester fibre. Thus in most cases DHB does not improve the light fastness of the dyed samples while in the case of Tinuvin P and 327 light fastness of the corresponding samples is 0.5–1 units higher than the reference sample, depending on the UV-abs application procedure, the applied quantity and the depth of dyeing.

Viosperse Blue is a dye of relatively low light fasness on polyester (3–4 and 4 of the blue wool standard scale 1–8 at 1.5 and 2.5% o.w.f.). Low light fastness values are observed in all cases for similar 2-nitro-substituted dyes [7,8] and can be related to a partially delocalised structure in which electron density on the a-nitrogen atom facilitates the oxidative degradation of the excited state [8].

Addition of a UV-absorber did not affect the high sublimation fastness of the samples at 180 °C, either the colour change or the colour staining. At 210 °C the medium fastness in staining was affected by the presence of a UV-abs: in most cases addition of the UV-abs by aftertreatment resulted in a slight increase in the value of the corresponding reference sample, while in some cases a decrease 1–1.5 units in the grey scale was observed.

The results of the use of 2-(2-hydroxy-5-carboxy-phenyl)-2*H*-benzotriazole **4** in the dyeing of polyester fabrics with the dyes **6–9** are given in Table 2.

Table 2 shows that light fastness values of the dyed sample with the dyes **6–8** are not affected by the presence of the UV-abs, since those dyes are of very high light fastness (7 or >7 units of the blue standards scale 1–8). In order to examine the effectiveness of the 2-(2-hydroxy-5-carboxy-phenyl)-2*H*-benzotriazole in improving the light fastness of the dyed samples it was necessary to use a low light fastness disperse dye such as Viosperse Red BS **9**. In this case the addition of the UV-absorber to the dyeing resulted in an improvement (0.5–1 units) of light fastness value of the dyed samples in both molar ratios dye/UV-abs and application procedures (direct addition to the dyebath or aftertreatment of the dyed fabric).

This improvement in light fastness was observed for Viosperse Red BS although the% adsorption of the UV-absorber on the fabric is generally low, compared to the uptake of Tinuvin P, Tinuvin 327 and DHB when used in the dyeing of polyester fibres with the dyes **7–9** as observed in previous papers [1–4] and the dye **6**.

The low UV-absorber **4** uptake on polyester in all cases can be attributed to the low affinity of this compound with polyester compared to Tinuvin P, Tinuvin 327 and DHB due to the existence of the ionic carboxy group in its molecule.

Regarding the dye uptake this is medium for the dyes Direct Yellow 42, Viosperse Red BS and Direct Blue 77, while Direct Red 86 shows a high dye uptake. While addition of the UV-absorber during the dyeing does not affect significantly the uptake of Viosperse Red BS and Direct Yellow 42 in the case of Direct Blue 77 the presence of the UV-absorber in equimolar quantity to the dye resulted in a significant increase in dye uptake. Duplication of the UV-abs quantity (molar ratio dye/UV-abs = 1/2) resulted in a further increase in dye uptake. This could be related to the molecular structure of both the UV-absorber and the dye. Addition of the 2-(2-hydroxy-5-carboxy-phenyl)-2*H*-benzotriazole 4 with the acid carboxy group in the molecule could enhance the uptake of Disperse Blue 77 with the –NHPh group of higher basicity

Table 2
Dye and UV-abs uptake and light fastness of fabrics dyed with dyes **6**–**9** in absence and/or presence of various amounts of 2-(2-hydroxy-5-carboxy-phenyl)-2*H*-benzotriazole 1 (direct application D or aftertreatment A)

Dye	Dye/UV-abs	UV-abs	% ads dye	*K*/*S* value	% ads UV-abs	Light fastness
Viosperse Red BS 9 (VRBS)	–	–	47.0	20.37	–	2
	1:1	D	44.1	19.36	6.7	2–3
	1:2	D	45.6	19.93	6.9	3
	1:1	A	42.2	19.56	6.9	2–3
	1:2	A	44.5	19.59	10.0	2–3
CI Disperse Blue 77 6 (DB 77)	–	–	58.1	6.39	–	>7
	1:1	D	63.0	7.17	11.2	>7
	1:2	D	82.0	9.38	12.4	>7
	1:1	A	54.0	6.22	10.8	>7
	1:2	A	53.0	6.07	16.4	>7
C.I. Disperse Red 86 7 (DR 86)	–	–	83.6	9.11	–	7
	1:1	D	78.0	8.51	12.1	>7
	1:2	D	80.5	8.97	6.9	>7
	1:1	A	68.3	7.52	12.6	>7
	1:2	A	71.6	7.42	8.5	>7
C.I. Disperse Yellow 42 8 (DY 42)	–	–	48.0	6.50	–	7
	1:1	D	47.9	6.49	8.8	7
	1:2	D	42.9	6.09	4.7	7
	1:1	A	42.2	5.33	11.5	7
	1:2	A	41.9	5.77	7.7	7

than the –$NHSO_2Ph$ and –SO_2NHPh groups of Direct Red 86 and Direct Yellow 42, respectively.

Dye uptake in the case of aftertreatment of the dyed samples is again lower than of the reference samples due to small dye desorption in the aftertreatment liquor.

Comparison of the results in Table 2 with those obtained with the same dyes and the UV-absorbers Tinuvin P, Tinuvin 327 and DHB [1–4] shows that there is a general agreement in the order of dye uptake values for the dyes Direct Yellow 42, Direct Red 86 Viosperse Red BS, although they do not conform to a pattern regarding the application procedure and the UV-absorber amount used.

This order in dye uptake (determined by dye extraction of the fibre) is in satisfactory agreement with the corresponding *K*/*S* values in Table 2.

4. Conclusions

The use of 2-(2-hydroxy-5-carboxy-phenyl)-2*H*-benzotriazole in the dyeing of polyester fibres with disperse dyes results in an improvement of light fastness value of the low light fastness Viosperse Red BS, thus establishing its usefulness as a UV-absorber of the benzotriazole series. The presence of the carboxy substituent in the phenyl ring may affect the uptake of the dyes used, as well as its uptake on the non-polar polyester fibre.

In contrast, the molecular structure of the two other benzotriazole UV-absorbers, Tinuvin P and 327 [2-(2-hydroxy-5-methyl-phenyl) 2*H*-benzotriazole and 2-(3,5-butyl-6-hydroxy)-2*H*-2-chlorobenzotriazole respectively] as well as 2,4-dihydroxy-benzophenone favours their uptake on the polyester fibre when used in conjunction with Viosperse Blue 77 improving in most cases the light fastness of the dyed samples. However, the light fastness values of the samples still remain low, because of the high susceptibility of this dye to photodegradation.

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