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Synthesis of reactive UV absorbers, derivatives of monochlorotriazine, for improvement in protecting properties of cellulose fabrics

Wojciech Czajkowski [a,*], Joanna Paluszkiewicz [a], Roland Stolarski [a], Mariola Kaźmierska [b], Edyta Grzesiak [b]

[a] Institute of Polymers and Dyes Technology, Ul. Zeromskiego 116, 90-543 Lodz, Poland
[b] Institute of Dyes and Organic Products, Ul. Chemikow 2/4, 95-100 Zgierz, Poland

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Abstract

A number of colourless fibre-reactive UV absorbers, derivatives of monochlorotriazine were synthesised. Reactivity with cellulose and their properties as auxiliaries increasing UV-protection factor (UPF) of treated cotton fabrics were determined. Changes in protecting properties of prepared absorbers and changes in whiteness of used textiles during prolonged exposition to light were also measured.

Keywords: Monochlorotriazine; Fibre-reactive UV absorbers; Cellulose; Ultraviolet protection factor (UPF); Whiteness of textiles

1. Introduction

In last two decades one of the often realised research programmes in the field of textile materials was works on their protective properties against sunlight UV radiation. As it is known radiation of this type emitted by sun in the range between 100 and 400 nm is subdivided into UV-C (100–280 nm), UV-B (280–315 nm) and UV-A (315–400 nm). Higher layers of the atmosphere absorb the radiation of the UV-C range which is most dangerous to living species. Human skin has to be protected against excessive radiation of the UV-B type. It was proved that the excessive radiation of this range is the origin of premature skin ageing, sunburns, allergies and even skin cancer. The UV-A radiation is less dangerous but also its overdose can result in similar effects as described above.

Among others, protection measures recommended by WHO against UV radiation, such as avoiding prolonged exposure to direct sunlight, wearing sunglasses, using cosmetics equipped with so-called sunscreens, the use of loose-fitting full-length clothes are also important [1–4].

It is obvious that protecting properties of textile garments are dependent on the transmission of the UV radiation through the particular fabric. It was already found that these properties depend on factors such as chemical composition of the particular fabric, its structural characteristics (thickness, porosity) and the presence of dyes and other textile auxiliaries. For practical purposes UPF (Ultraviolet Protection Factor) is used for protection ratings given by clothing. UPF value of 15–24 is classified as good protection, 25–39 as very good and above 40 as excellent protection against solar UV radiation [1].

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* Corresponding author. Tel.: +48 42 6313231; fax: +48 42 6362596.

E-mail addresses: woczajk@p.lodz.pl (W. Czajkowski), joanna.pal@wp.pl (J. Paluszkiewicz).

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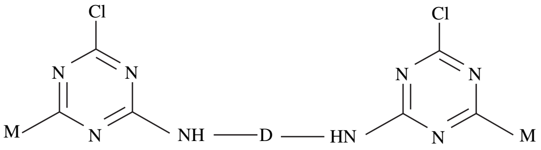


Fig. 1. Typical structure of bi-functional reactive UV absorbers for cellulose fibres, derivatives of monochlorotriazine.

Light bleached, uncoloured cotton garments which are very popular in summer do not provide sufficient protection against solar radiation so from some time now at the market are available special UV absorbers which could be applied to aqueous baths with or without the use of dyes. Especially interesting from practical point of view are absorbers containing reactive groups which could form covalent bonds with cellulose. Such products fixed on the fibre would be able to maintain its protecting properties for prolonged time [5,6].

In our earlier work bi-functional reactive colourless UV absorbers for cellulose fibres, derivatives of monochlorotriazine presented in Fig. 1 were synthesised. In these absorbers several water soluble 2-hydroxyphenylbenzotriazoles as moderators (M) were used. As bridges D, 1,4-phenylenediamine, 2,5-diaminobenzenesulphonic acid and 4,4′-diaminostilbene-2,2′-disulphonic acid were used. It was found that these substances were useful in pad-dyeing type method of application followed by fixation at 125 °C. Unfortunately with the exception of derivatives of 4,4′-diaminostilbene-2,2′-disulphonic acid, they did not exhibit sufficient affinity to cellulose fibres to use them in exhaust application methods. Moreover, derivatives of 4,4′-diaminostilbene-2,2′-disulphonic acid gave some undesired yellowish colour to treated cotton fabric [7].

The purpose of present work was the synthesis and estimation of application and protective properties of other groups of symmetric UV absorbers, derivatives of monochlorotriazine of the structure presented in Fig. 1. As bridges D various aromatic diamines of the structures presented in Fig. 2 were used.

In synthesised absorbers as moderators M beside methoxylic group (M1) were used various aromatic amines presented in Fig. 3. The purpose of their use was to increase absorber substantivity or/and reactivity. In some cases improvement of UV-absorption properties of the final product was also expected.

2. Experimental

2.1. Characterisation of products

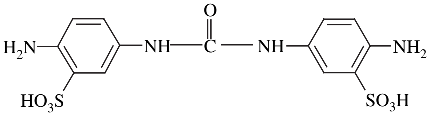
^{1}H NMR spectra were taken with a Bruker DPX − 250 instrument. The solvent used was deuterium oxide. Mass spectra were taken in dihydroxybenzoic acid matrix with a Voyager Elite spectrometer by using MALDI (matrix assisted laser desorption ionisation) technique. Spectrophotometric measurements in UV–Vis range were taken on a Perkin Elmer Lambda 40 spectrophotometer. Application tests on cotton fabrics were carried out on a Rotec (Roaches) laboratory dyeing machine by the process typical for monochlorotriazine reactive dyes. The measurements of UV transmittance were carried out with a double beam spectrophotometer Beckman DK-2A equipped with Ulbricht sphere and powered by hydrogen lamp. The use of anti-fluorescence filter was not necessary due to the absence of this phenomenon in the case of prepared absorbers. Measurements of textile whiteness were taken on a Gretag Macbeth SpectroEye spectrophotometer with the use of D_{65} illuminate and 10° additional normal observer. Lightfastness tests were carried out with the use of a Hanau Heraeus Xenotest 150S.

2.2. Synthesis of intermediates

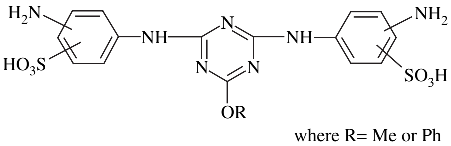
2,4-Dichloro-6-methoxy-1,3,5-triazine [8], 2,4-dichloro-6-phenoxy-1,3,5-triazine [9], 4,4′-di-aminodiphenylurea-3,3′-disulphonic acid (D1) [10] were synthesised according to literature. Benzotriazoles M4 and M5 were prepared by the oxidation of corresponding *o*-aminoazo dyes according to method described in literature [11].

2.2.1. 2-Methoxy-1,3,5-triazynyl-4,6-bis-N,N′-(1,4-diaminophenyl-3-sulphonic acid) (D2)

To the dispersion of 2,4-dichloro-6-methoxy-1,3,5-triazine (7.2 g, 0.04 mol) in ice water with 1–2 droplets of non-ionic surfactant (Rokacet 07) 2,5-diaminobenzenesulphonic acid (19.8 g a’ 94.8%, 0.1 mol) dissolved in water (100 cm^3) of pH = 7.0–7.2 (10% NaOH) was added. Condensation was carried out at 40 °C and at pH = 7.0 ± 0.2 (10% NaOH) for 2 h then at 80 °C and at the same pH for another 4 h. Product was separated



D1



D2-D5

Fig. 2. Structure of aromatic diamine bridges (Fig. 1) used in present work.

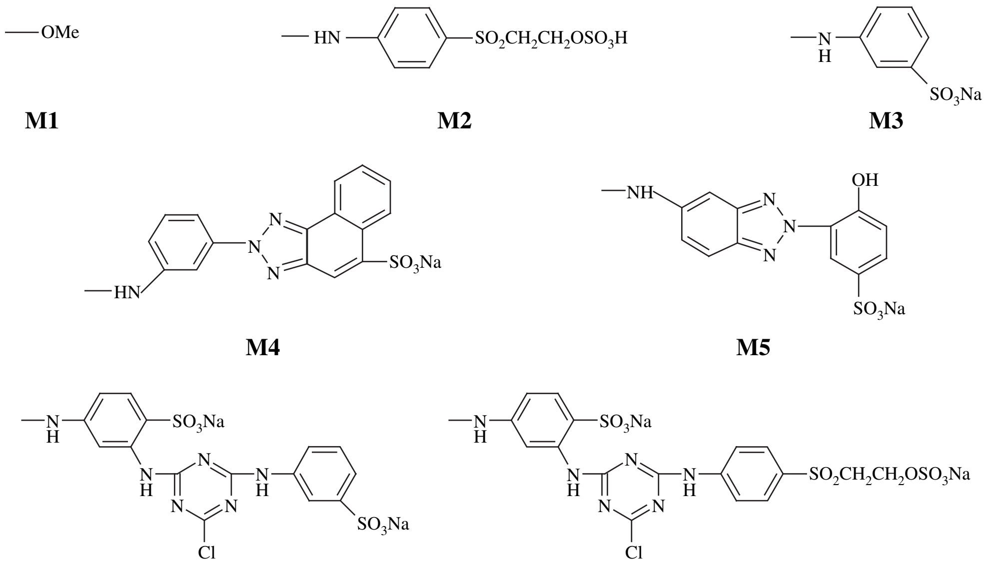


Fig. 3. Structure of moderators (M) used in UV absorbers synthesised in present work and presented in Fig. 1.

by salting out with NaCl (10% vol.), filtered out and purified by dissolving in hot water (150 cm^3), salting out with NaCl (20% vol.), filtered out and washed on the filter with saturated brine till colourless effluent was formed. Finally, after drying 18.2 g product containing 75.5% of diamine (65.2% theoretical yield) was obtained. Product was homogeneous as it was found by TLC analysis (eluents, *n*-butanol, ethanol, acetic acid, water – 30:20:1:5; Merck Kieselgel 60 F_{254} plate). Its structure was confirmed by ^1H NMR analysis of the sample acetylated with acetic anhydride. [$COCH_3$, 2.21 ppm, s, 6H; (Cj)–OCH_3, 4.34 ppm, s, 3H; Ar–H, 7.63–8.73 ppm, m, 6H].

Diamines D3, D4 and D5 were prepared and analyzed in similar way.

2.3. Synthesis of absorbers A1–A11

All absorbers were prepared by the method described below as in the example of Absorber 2.

2.3.1. UV absorber A2

Solution of 0.01 mol (5.2 g a’ 77%) 4,4′-diaminodiphenylurea-3,3′-disulphonic acid (D1) in 80 cm^3 of hot water containing 3 cm^3 of 30% sodium hydroxide was slowly added to cyanuric chloride (3.8 g, 0.021 mol) dispersed in ice water with the use of non-ionic surfactant the same as in Example 1. Temperature of 0–5 °C and pH 3–4 were maintained during this operation. Reaction pH was then increased to 6.2–6.5 by adding 10% Na_2CO_3 solution. Final reaction volume was 800 cm^3. Reaction end point was estimated by TLC (Merck Cellulose F_{254} plate; ethyl acetate:*n*-propanol:water 1:6:2 as the eluent). The excess of cyanuric chloride was filtered out and solution of 4-(β-hydroxyethyl)sulphonylaniline (M2) (0.02 mol i.e. 5.86 g a’ 96%) in 20 cm^3 warm water with addition of 10 cm^3 10% Na_2CO_3 (to slight alkaline pH at Brilliant Yellow paper) was added to the filtrate. Second condensation was carried out at a temperature of 35–40 °C and at pH = 6.0–6.5 (10% Na_2CO_3). Reaction was considered as completed after the disappearance of free amine in the reaction mixture (test on the filter paper with Ehrlich reagent). Product was separated by salting out with potassium chloride (20% vol.), filtered, stabilised with phosphate buffer (pH = 7.0) and dried at 40–50 °C. Finally 24.1 g of grey powder of approximated purity 75% was obtained (estimated by analysis of active chlorine content by potentiometric titration of hydrolysed and unhydrolysed samples with 0.1 N $AgNO_3$ solution). Structure of the product was confirmed by mass spectroscopy during which molecular ions *m*/*z* 1322 [M (3K, Na salt)–H]$^-$, *m*/*z* 1300 [M – Na]$^-$ and *m*/*z* 1183 [M – 3K – Na]$^-$ were detected.

Details of the synthesis of other absorbers prepared in similar way are given elsewhere [12].

2.4. Spectroscopic measurements and application tests

Spectroscopic data of the prepared absorbers in the region of 250–500 nm were measured in water (concentrations of 2×10^{-5} mol/dm^3). Results are presented in Table 1 and in Figs. 4–6.

Table 1
Structure and spectral properties of absorbers A1–A11

Absorber	Diamine (D)	Moderator (M)	λ_{max} (nm)	Approximate[a] ε_{max} (dm^3/mol cm)
A1	D1	M1	290.8	4.31×10^4
A2	D1	M2	288.5	5.53×10^4
A3	D1	M3	277.1	5.01×10^4
A4	D1	M4	275.7	15.44×10^4
A5	D1	M5	295.0	5.17×10^4
A6	D1	M6	278.2	14.80×10^4
A7	D1	M7	280.7	16.86×10^4
A8	D2	M1	287.5	6.14×10^4
A9	D3	M1	273.3	7.25×10^4
A10	D4	M1	285.0	5.80×10^4
A11	D5	M1	273.8	7.34×10^4

[a] Absorber percentage estimated by analysis of active chlorine content in analysed sample.

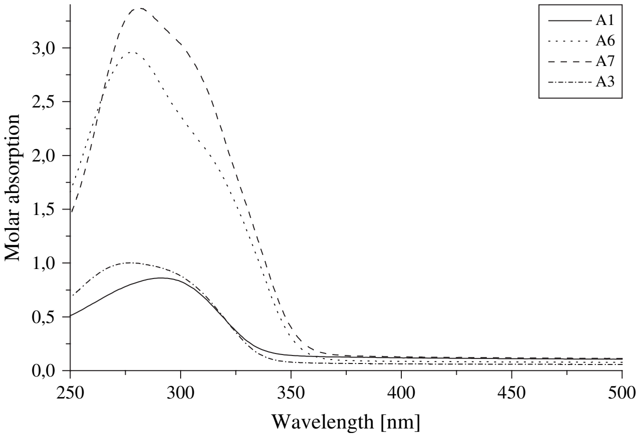


Fig. 5. Absorption spectra of A1, A3, A6 and A7 absorbers (water, concentration 2×10^{-5} mol/dm^3, cuvette thickness 1 cm).

All prepared absorbers were subjected to application tests during which bleached cotton with the linen weave, weighing 104 g/m^2 (Fabric 1) and bleached cotton satin, weighing 119 g/m^2 (Fabric 2) were used. UV absorbers were applied on fabrics by the exhaust method, similarly as in the case of monochlorotriazine reactive dyes (80 °C, dyebath ratio 1:15, 50 g/dm^3 Na_2SO_4 and 20 g/dm^3 Na_2CO_3). The percentage degrees of exhaustion was calculated from spectral measurements according to the formula:

$$E = \left(1 - \frac{B_2}{B_1}\right) \times 100\%$$

where, B_1 – light absorption of the dyebath at absorber λ_{max} before and after application test (B_2). Results of these measurements are listed in Table 2.

All used and treated textiles were examined for their protecting properties by method given in appropriate European Standard [13]. The UPF factor was calculated according to the formula:

$$\mathrm{UPF} = \frac{\sum_{\lambda=290}^{\lambda=400} E(\lambda)\varepsilon(\lambda)\Delta\lambda}{\sum_{\lambda=290}^{\lambda=400} E(\lambda)T_i(\lambda)\varepsilon(\lambda)\Delta\lambda}$$

where, $E(\lambda)$ is the solar spectral irradiance [W/m^2 nm], $\varepsilon(\lambda)$ the erythema action spectrum, $T_i(\lambda)$ the spectral transmittance of sample i at the wavelength λ and $\Delta\lambda$ is the interval of wavelength [nm].

Results of these measurements are graphically presented in Fig. 7.

Whiteness of all textile samples was measured twice, directly after introducing UV-absorbers and after their exposition to UV radiation by the use of Xenotest apparatus. The latter measurements were accompanied in selected cases by repeated measurements of UPF

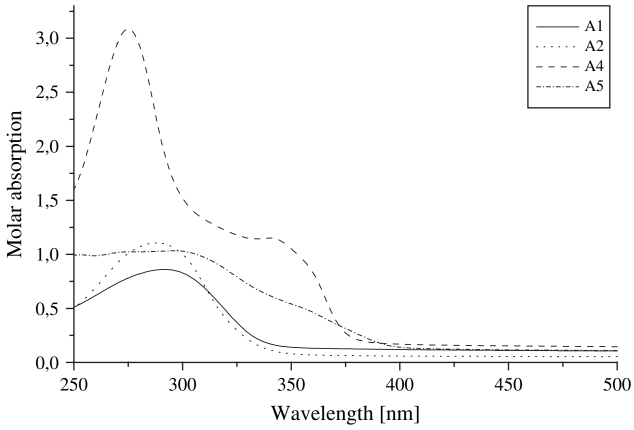


Fig. 4. Absorption spectra of A1, A2, A4 and A5 absorbers (water, concentration 2×10^{-5} mol/dm^3, cuvette thickness 1 cm).

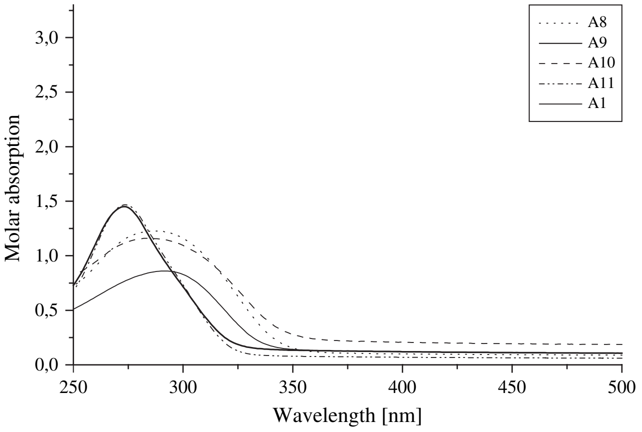


Fig. 6. Absorption spectra of A1, A8, A9, A10 and A11 absorbers (water, concentration 2×10^{-5} mol/dm^3, cuvette thickness 1 cm).

Table 2
Exhaustion degrees of absorbers A1–A11 on cellulose fabrics (%)

Absorber	Concentration of UV-absorber in application bath[a]		
	Fabric 1		Fabric 2
	1%	2%	1%
A1	53.2	52.9	63.0
A2	85.2	84.7	83.8
A3	77.6	71.4	70.0
A4	86.9	66.5	78.7
A5	76.9	72.1	69.0
A6	72.1	66.4	63.1
A7	80.7	76.7	79.7
A8	83.0	74.9	75.2
A9	68.9	66.5	52.1
A10	87.8	68.3	76.6
A11	63.6	60.9	47.1

[a] On the weight of the fabric.

factor. Results of these measurements are graphically presented in Figs. 8–10.

3. Discussion

In Figs. 4–6 are presented UV–Vis spectra of all prepared products which were grouped according to their structures and compared with the simplest one A1. As it can be seen from these figures and the data in Table 1 all of the prepared products absorb light in the range of 270–300 nm specific for typical UV absorbers. Compounds A4 and A5, including benzotriazole and naphthotriazole systems in their molecule exhibit additional absorption in the range of 350–360 nm. The presence of additional triazine rings in absorbers A6 and A7 yields higher molar absorption coefficient. Derivatives of 4,4′-diaminodiphenylurea-3,3′-disulphonic acid (A1–A7) in comparison look more interesting than absorbers A8–A11 obtained with the use of diaminodiphenylmethoxytriazine and diaminodiphenylphenoxytriazine.

Substantivity of prepared absorbers was estimated during application tests as mentioned in Section 2.4. Percentage exhaustion values of absorbers A1–A11 on used cotton fabrics are enlisted in Table 2. It can be seen that in some cases (A2, A4, A7, A8 and A10) these values are close to 80%. Such results are similar to those received in the case of typical reactive dyes designed for exhaustion dyeing of cellulose fibres. As it was expected among derivatives of diaminodiphenyltriazine (A8–A11), higher affinity to cotton fabric exhibits more linear absorbers A8 and A10 based on 2,5-diaminobenzenesulphonic acid. Some differences in exhaustion degrees on both samples of used fabric may be also noticed.

Results of the measurements of spectral transmittance of unprotected and protected fabrics are graphically presented in Fig. 7. It can be noticed that all of the used absorbers radically increase UV protecting properties of examined fabrics. It can be noticed that as it was earlier reported physical properties of particular fabric are in practice one of the most important factors. In the case of Fabric 1 which is more penetrable by UV radiation the highest received values are in the “good” range and increases absorber’s concentration from 1% to 2% and give only slight improvement in protecting properties. Unprotected Fabric 2 absorbs UV radiation in greater degree and in its case all applied products except A9 and A11 gave “good” and “very good” protecting properties.

It is obvious that one of the most expected and important characteristic of uncoloured textile garments is retaining their white colour during use. As it could be foreseen all of the synthesised absorbers introduced into examined fabrics decrease their whiteness although not in the same degree. This phenomenon is especially visible on “more white” Fabric 1 where decrease of

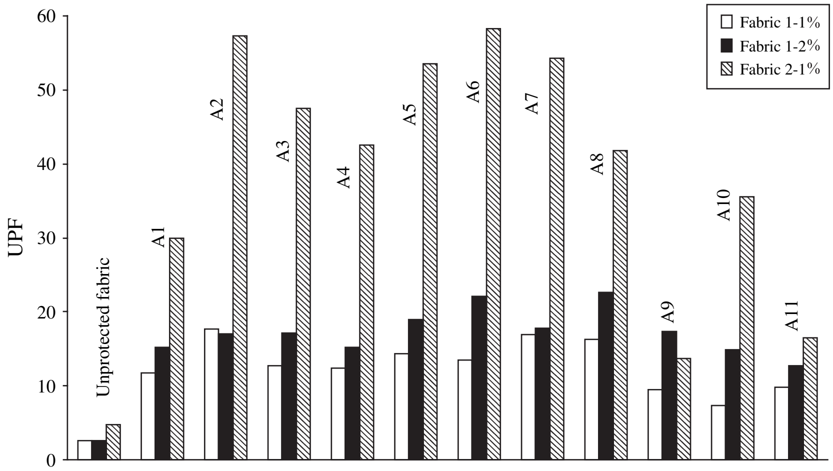


Fig. 7. Protecting properties of cellulose fabrics (UPF) as function of percentage concentration of absorbers A1–A11 in application bath.

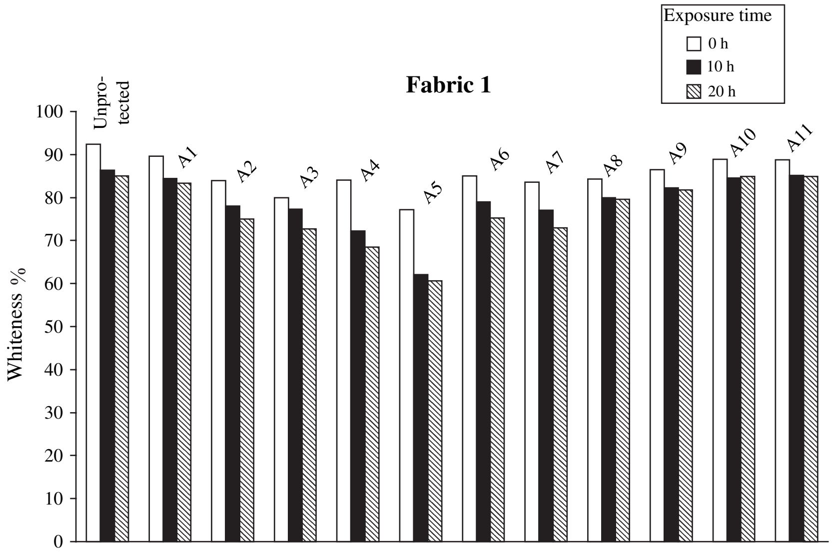


Fig. 8. Whiteness degree of the Fabric 1 protected with absorbers A1–A11 as function of Xenotest lamp irradiation time.

initial textile whiteness varies from several to dozen percent in the case of absorber A5. Only several percent decrease of whiteness can be detected on "less white" Fabric 2. After exposition to radiation of Xenotest lamp (Figs. 8 and 9) decrease in initial whiteness of unprotected Fabric 1 is visible due to its ageing. On the opposite way some whitening of Fabric 2 probably due to its UV-bleaching can be observed. Most of the prepared absorbers exhibit satisfactory lightfastness except absorbers A4 and A5 probably because of premature photodestruction of their triazole residues. Good application and fastness properties have some multi-triazine absorbers such as A9–A11 and even (rather unexpectedly) very simple bis-triazine absorber A1.

Several samples of protected and UV-irradiated fabrics were selected to repeat measurements of ultraviolet protection factor. As it was expected after 20 h of exposition slight decrease in UPF values can be observed but on Fabric 2 they still remain in "very good" to "excellent" range. In the case of absorbers A8 and A10 after prolonged exposition to 80 h even some increase in protecting properties are noticeable. It is difficult to fully explain such behaviour. Probably some degradation products of mentioned absorbers retain on the fibre and their presence is responsible for observed phenomenon. This effect might be also the result of UV-absorption by photo-chemical decomposition products of the fibre itself.

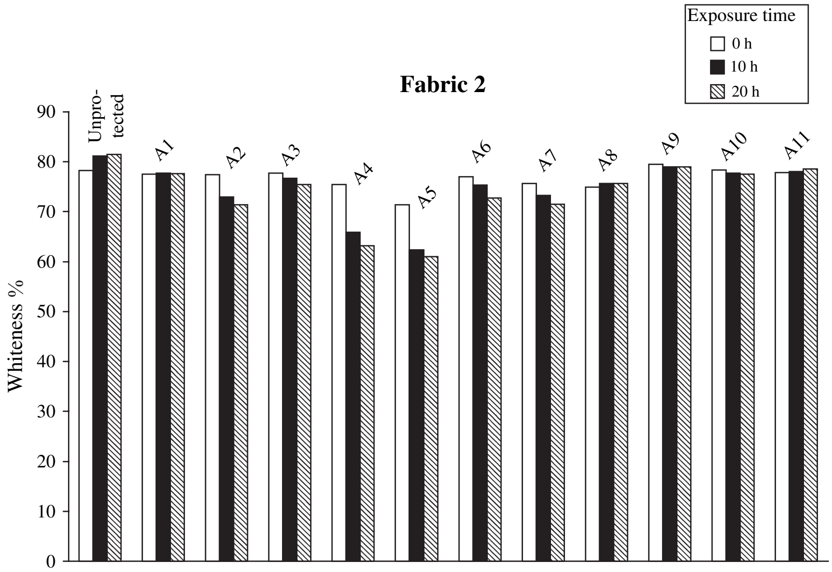


Fig. 9. Whiteness degree of the Fabric 2 protected with absorbers A1–A11 as function of Xenotest lamp irradiation time.

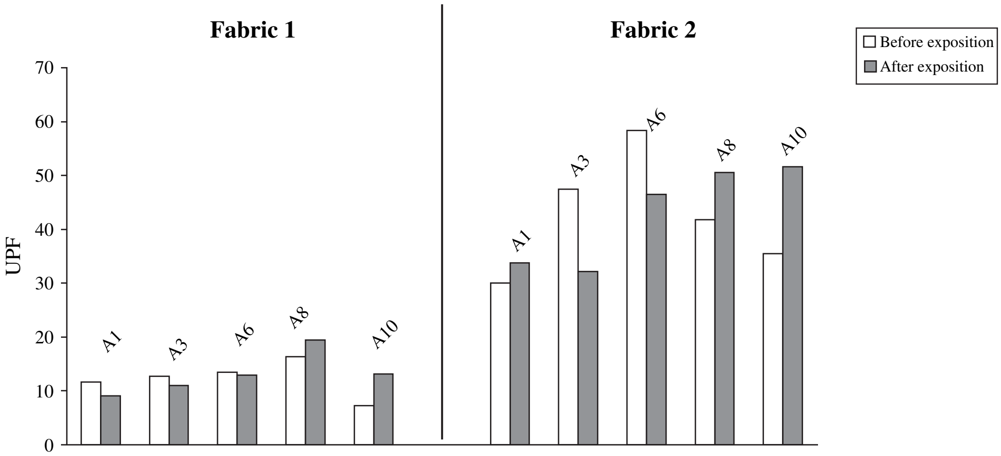


Fig. 10. Protecting properties (UPF) of Fabric 1 and Fabric 2 treated with selected absorbers before and after exposition to Xenotest.

The results of above presented work show that even relatively simple derivatives of symmetrical trichlorotriazine which is the intermediate commonly used in industrial synthesis of fibre-reactive dyes may be considered as practically valuable absorbers increasing protecting properties of uncoloured cellulose fabrics against solar UV-radiation.

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