

Application of Benzotriazole Reactive UV Absorbers to Cellulose and Determining Sun Protection of Treated Fabric Spectrophotometrically

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ABSTRACT: UV absorbers for treating cotton textiles with the aim of increased protection against harmful effects of UV component of solar radiation have been prepared by reactions of five different aminophenylsulfobenzotriazoles with the condensation product of 4-amino-phenyl-sulfatoethylsulfone and cyanuric chloride. The UV absorbers with two different reactive groups (monochlorotriazine and aromatic vinylsulfone), capable of formation of covalent bonds with hydroxyl groups of cellulose, were applied to one cellophane foil and two cotton fabrics of different porosities. This treatment increased the ultraviolet protection factor from a value of UPF = 3 to UPF = 100 and above. For attaining a high UPF value, the cotton material should exhibit low porosity. The UV absorbers with

2-hydroxyphenyl group are stable in light and do not fluoresce on the fabric on contrary to derivatives without 2-hydroxyphenyl group or with 2-methoxyphenyl group. The high photostability of absorbers is explained by the possibility to disperse the absorbed energy of UV radiation in the form of harmless energy such as IR radiation (heat) through the reversible hydrogen bond between phenolic hydroxyl group and triazine cycle. The UV filters block the effect of optical brightening agents on cotton by quenching the fluorescence. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 334–341, 2008

Key words: sun protection; UV absorbers; benzotriazoles; cellulose; cotton

INTRODUCTION

It is known that ultraviolet radiation easily penetrates through cotton textiles. Protection offered by clothes is expressed (like that provided by suntan lotions) by means of ultraviolet protection factor UPF.^{1–3} The ultraviolet protection factor expresses the multiple of time period for which an individual wearing the textiles (or using the suntan lotion) can spend in the sun without suffering from erythema as compared with the time period spent in the sun with unprotected skin. Unprotected skin has the protection factor UPF = 1. Light textiles with bulk surface density below 200 g/m² exhibit transmission of UV radiation about 30–40%. Alternatively expressed by means of protection factor, such clothing has UPF = 3–5. Individuals with sensitive skin who show onset of erythema after 30 min spending in the sun will get protection for a period of 150 min when wearing light cotton summer clothes. Dermatologists recommend a protection factor of clothes of at least

UPF = 16.⁴ For improvement of protection function of clothing, it has been suggested to apply UV absorbers to cotton textiles.^{2,5–9} Interesting representatives of UV absorbers are those synthesized by reaction of cyanuric chloride with aromatic amines containing UV chromophores. They can remove harmful UV radiation, and they also react with cotton fiber to form a firm covalent bond like that formed in the case of reactive dyes. Effective UV absorbers are expected to filter out the UV radiation in the whole range of ca. 200–400 nm.

EXPERIMENTAL

Synthesis of absorber UV-I

Preparation of azo dyestuff 4-amino-3-nitrobenzenesulfonic acid → 3-aminophenol 1

A solution of 0.50 mol 4-amino-3-nitrobenzenesulfonic acid (138 g product of technical quality 79%, sodium salt, containing 19% sodium chloride) in 500-mL water was treated with 200 g crushed ice followed by 1.25 mol hydrochloric acid (125 mL 10M HCl), whereupon a solution of 0.50 mol sodium nitrite (34.5 g) in 200-mL water was added drop by drop within 30 min. The resulting yellow solution of diazonium salt was stirred for 60 min, and then 0.50

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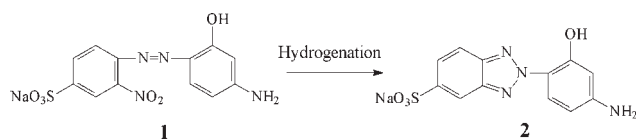


Figure 1 Synthesis of aminohydroxyphenylsulfobenzotriazole **2** by reduction of 2-nitroazo dyestuff **1**.

mol 3-aminophenol (99%, flaky solid) was added. 3-Aminophenol dissolved and a red solution resulted. Within 5 min, the red dyestuff started to separate in the form of a fine suspension. After 3-h stirring, the dyestuff was collected by filtration and washed with water. Yield 96% (free acid).

Hydrogenation of dyestuff **1** to 2-(4-amino-2-hydroxyphenyl)benzotriazol-5-sulfonic acid **2**

A solution of 0.20 mol dyestuff **1** was prepared in 600-mL water by adding 0.50 mol sodium hydroxide, whereupon 4 g of 50% aqueous paste of catalyst palladium on charcoal (3% Pd in dry matter) was added. The solution of dyestuff was hydrogenated in an autoclave at a temperature of 30°C and hydrogen pressure of 0.3 MPa for a period of 4 h. The absorbed hydrogen corresponded to the theoretical amount (0.60 mol hydrogen). After the hydrogenation, the catalyst was separated by filtration. The dark green filtrate was treated with hydrochloric acid (0.60 mol). The initially formed solution began to separate a beige precipitate within 1 min. The mixture was stirred for 30 min, and the separated aminohydroxyphenylsulfobenzotriazol (**2**) was collected by filtration. The catalytic hydrogenation gave 61% of theoretical yield. For the reaction scheme, see Figure 1.

Preparation of condensation product **3** from cyanuric chloride and *p*-aminophenyl-sulfatoethylsulfone

An 1-L beaker was charged with 120-mL water, 60 g ice, 18.6 g (99%; i.e., 0.10 mol) cyanuric chloride, and 0.01 g wetting agent Slovasol O (oxethylated fatty alcohol). After 2-h stirring at the temperature of 0°C, a fine white suspension of cyanuric chloride was formed.

In the meantime, a solution of *p*-aminophenylsulfatoethylsulfone (PAFSES) was prepared in the following way: a 250-mL beaker was charged with 120-mL water and 60 g ice, and 29.4 g PAFSES (95.5%; i.e., 0.10 mol) was added. The suspension of PAFSES was treated with 44 mL 1.25M sodium carbonate added drop by drop with stirring within 40 min. The resulting violet solution contained a small amount of sediment.

Then the PAFSES solution was added to the suspension of cyanuric chloride. The obtained suspen-

sion was stirred for a period of 30 min, while adding 30 g ice. During next 4 h, 40 mL 1.25M sodium carbonate was added drop by drop to keep the pH value in the range of 2.5–4.5. The resulting condensation product of cyanuric chloride and PAFSES **3** was obtained in the form of white solution or rather very fine suspension, see Figure 2.

Condensation of intermediates **2** and **3** giving reactive absorber UV-I

A suspension of 0.10 mol condensation product of cyanuric chloride and PAFSES **3** was stirred and treated with 0.10 mol (30.6 g, acid) aminohydroxyphenylsulfobenzotriazole **2**. The suspension was stirred, while raising its temperature to 45°C. During further 2 h, 80 mL 1.25M sodium carbonate was added drop by drop to keep the pH value in the range of 4.5–5.5. The resulting solution was stirred at the temperature of 45°C for another 4 h. Finally, the pH value of the UV absorber solution was adjusted at 6.5. For the reaction scheme, see Figure 2.

Synthesis of absorber UV-II

Preparation of azo dyestuff 2-nitroaniline → 3-acetamino-4-hydroxybenzenesulfonic acid **4**

Finely ground 2-nitroaniline (14.0 g 98.5%; i.e., 0.10 mol) was stirred with 0.40 mol concentrated hydrochloric acid (40 mL, 10M HCl) overnight to obtain a fine suspension of 2-nitroaniline hydrochloride. The suspension was diluted to a volume of 150 mL by addition of 50 g ice and water, whereupon a solution of 0.10 mol sodium nitrite in 50-mL water was added drop by drop during 20 min. The obtained turbid yellow solution of diazonium salt was clarified by addition of 1 g charcoal and filtration. The excess nitrite in the filtrate was removed by addition of little amidosulfuric acid.

3-Amino-4-hydroxybenzenesulfonic acid does not resist the oxidation effect of 2-nitrobenzenediazonium salt; therefore, its amino group had to be protected by acetylation as follows: 0.10 mol (20.3 g

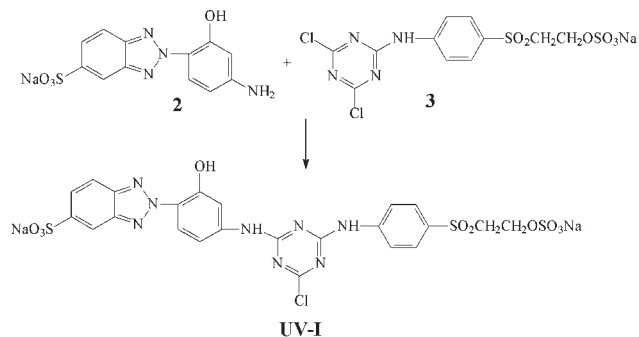


Figure 2 Synthesis of reactive absorber UV-I.

technical grade, content 93%) 3-amino-4-hydroxybenzene-sulfonic acid was dissolved in 100-mL water with addition of 0.10 mol (4 g) sodium hydroxide, whereupon 0.12 mol sodium carbonate (12.7 g) was added, followed by 0.12 mol acetic anhydride (12 mL; content 99%). The mixture was stirred with a magnetic stirrer at a temperature of 60°C for a period of 2 h; then it was cooled in ice bath, and after adding 50 g ice, the solution of 2-nitrobenzenediazonium salt was added in one portion. During next 30 min, a solution of 0.20 mol sodium carbonate in 100-mL water was added drop by drop. The suspension of red azo dyestuff was stirred for a period of 4 h, whereupon the dyestuff was collected by filtration, washed, and dried. The yield of dyestuff **4** was 34% of theoretical yield.

Reduction and concomitant deacetylation of dyestuff **4** giving the respective aminosulfo-benzotriazole **5**

A mixture of 0.10 mol (33.8 g) dyestuff **4**, 300-mL water and 24 g sodium hydroxide (0.60 mol) was stirred by means of a magnetic stirrer, and 30 g zinc powder was added in portions during a period of 3 h. The mixture was stirred for another 4 h and filtered. The filtrate was acidified with hydrochloric acid to pH 1.7. The resulting gray suspension was filtered to give 9.5 g aminosulfo-benzotriazole **5**. The reduction in alkaline medium was accompanied by deacetylation of amino group, see reaction scheme in Figure 3.

Condensation of intermediates **3** and **5** giving reactive absorber UV-II

The reaction of benzotriazole **5** with condensation product **3** of cyanuric chloride and PAFSES gave absorber UV-II. The procedure was identical with that described above for absorber UV-I.

Preparation of further UV absorbers

Further substituted benzotriazoles **6–8** were prepared in similar way; for their formulas, see Figure 4. Their condensation reactions with intermediate **3** gave absorbers UV-III, UV-IV, and UV-V. For formulas of all the absorbers prepared, see Figure 5.

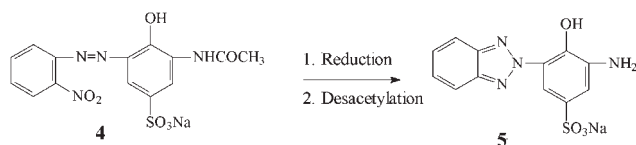


Figure 3 Reduction with simultaneous deacetylation of **4** to give the respective benzotriazole **5**.

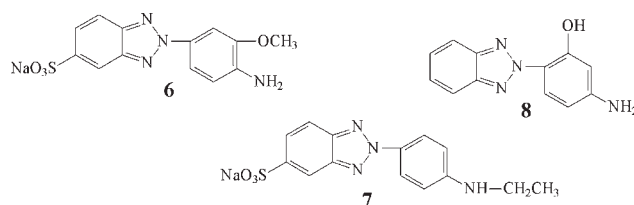


Figure 4 The other benzotriazoles synthesized.

Application of UV absorbers to cotton fabric and cellophane foil

Determination of rate of exhaustion of UV absorber from bath by cellulose

The application was carried out by the procedure corresponding to dyeing with reactive dyes from aqueous bath: 5 g mixture of cotton fabrics and a ribbon of cellophane foil were dyed with the UV absorbers in a 250-mL flask placed on laboratory shaker with water bath at the temperature of 60°C. The substrates and the UV absorber (0.2–2% relative to weight of the cellulose material) dissolved in 50-mL water were shaken for a period of 20 min, whereupon a solution of 3.75 g NaCl in 25-mL water was added and the shaking was continued for another 20 min (bath ratio 1 : 15). Then, 1.5 g sodium carbonate in the form of 7.5 mL 1.25M Na₂CO₃ was added, and the shaking was continued for another 60 min. After the finished application, the cellulose substrate was gradually washed with total amount of 600-mL water. The exhausted bath and rinsing water were transferred into a graduated

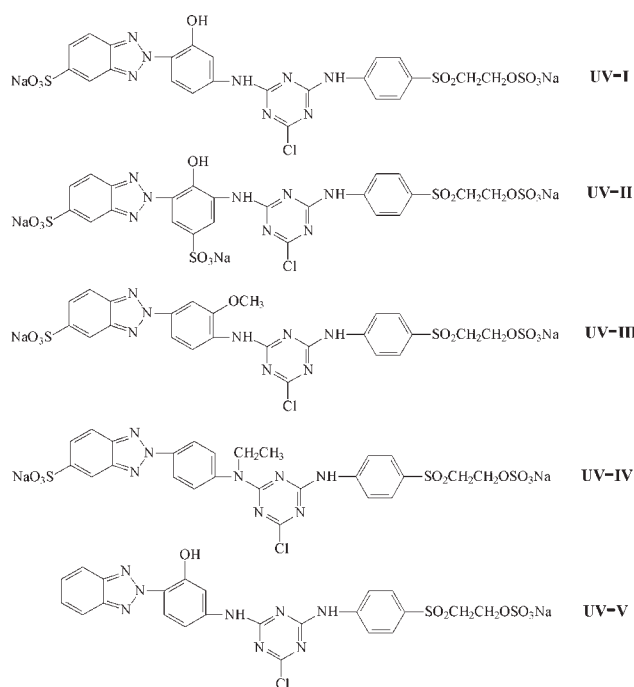


Figure 5 A survey of UV absorbers synthesized.

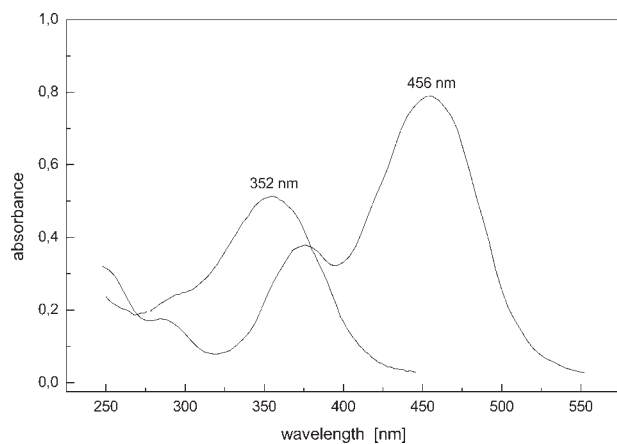


Figure 6 UV-Vis spectra of 2-nitroazo dyestuff **1** ($\lambda_{\text{max}} = 456$ nm) and the corresponding benzotriazole **2** ($\lambda_{\text{max}} = 352$ nm); 1-cm cell, aqueous solution 10 mg/L.

flask, the pH value of the solution was adjusted at 7 by addition of concentrated acetic acid, and the volume was made up to 1 L. The concentration of UV absorber in solution was measured spectrophotometrically, and the portion of UV absorber that had not been fixed to the cellulose substrate was calculated.

Application of optical brightening agent

Cotton fabric (2.2 g; treated with 0.5% of particular UV absorber) was processed in a 66-mL bath with addition of 0.8% Rylux BAK (Color Index: Fluoresc. Bright. 113, stilbene type) and 0.33 g sodium chloride at the temperature of 40°C for a period of 20 min.

Determination of ultraviolet protection factor of textiles "in vitro"

The measurement of transmission of UV radiation through the fabrics in the wavelength interval of

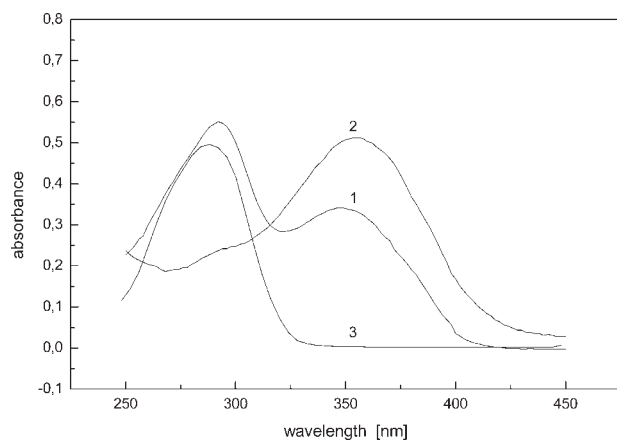


Figure 7 UV-Vis spectra of aqueous solution (10 mg/L, 1-cm cell, pH = 6.5): curve 1—absorber UV-I; curve 2—benzotriazole of formula 2; curve 3—condensation product of cyanuric chloride and PAFSES; formula 3.

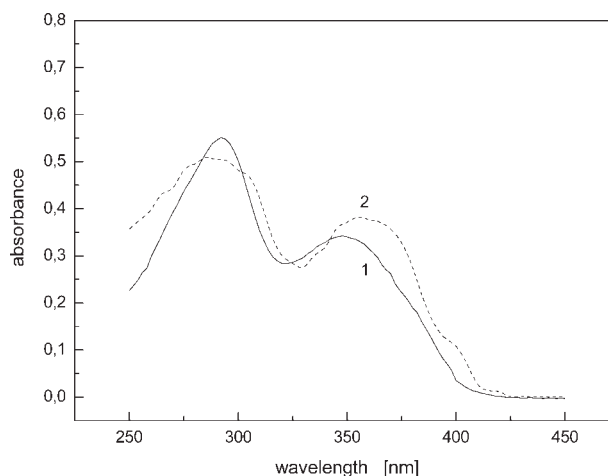


Figure 8 UV spectra of reactive absorber UV-I: curve 1—in water (1-cm cell, 10 mg/L); curve 2—on a treated cellophane foil 150 μm (0.1% UV-I).

290–400 nm was carried out in 5-nm steps using a spectrophotometer Varian Cary Solascreen 50 with an extension called Fabric Protection Factor. Cary 50 is a dual-beam xenon flash lamp spectrophotometer with resolution ± 0.5 nm. The extension enables measurements of diffusion transmission spectra. The measurements of fabric samples that fluoresce were carried out with attached filter Schott UG 11, which is a part of the spectrophotometer set. The ultraviolet protection factor was calculated in accordance with Australian standard¹ using the values of spectral distribution of solar radiation valid for Southern Europe.³ The transmission spectra of solutions of UV absorbers were measured by means of a cell extension.

RESULTS AND DISCUSSION

Benzotriazole-type UV absorbers are widely used for stabilization of macromolecular substances against light (foils, fibers, coating compositions). However, the benzotriazoles designed for plastics are insoluble in water, often containing bulky hydrophobic alkyl substituents. The treatment of cotton presumes application of absorbers from aqueous solutions. An intermediate for preparation of reactive UV absorber must contain, besides groups imparting water solubility, also amino group attached to aromatic ring

TABLE I
Spectral Characteristics of Aminobenzotriazoles

Aminobenzotriazole formula	Wavelength λ_{max} (nm)	Extinction coefficient, E (L/cm g)
2	352	51.0
5	347	47.0
6	354	61.4
7	360	63.3
8	365	47.3

TABLE II
Specification of Reactive UV Absorbers

UV absorber formula	UV A region λ_{\max} (nm)	UV A region extinction coefficient E (L/g cm)	UV B region λ_{\max} (nm)	UV B region extinction coefficient, E (L/g cm)	Solubility in water (25°C) (g/L)
UV-I	348	34.3	292	55.2	150
UV-II	337	17.8	292	55.2	80
UV-III	348	31.5	292	49.4	180
UV-IV	320	39.6	292	61.7	190
UV-V	350	37.4	292	48.3	7

that is capable of reaction with cyanuric chloride. A simple variant of synthesis of suitable benzotriazole derivatives consists in reduction of *o*-nitro-substituted azo dyestuffs (compounds **1**, **2** or **4**, **5**, reaction scheme Figs. 1 and 3). The syntheses make use of accessible starting materials. The preparation of azo dyes and their subsequent reduction giving the respective benzotriazoles take place in aqueous medium and give good yields.

Reduction of nitro group at *o*-position to azo group and the concomitant triazole ring closure are accompanied by changes in the UV-Vis spectra. The intensive band of the red dyestuff **1** disappears and the band of benzotriazole **2** appears in the UV region with its maximum at 352 nm, see Figure 6.

In analogy to UV-I (which was obtained by condensation of the respective benzotriazole **2** with the condensation product **3** of cyanuric chloride and PAFSES in aqueous medium, see reaction scheme in Fig. 2), the other UV absorbers were prepared by reactions of the corresponding benzotriazoles **5**, **6**, **7**, **8** with the same condensation product **3**.

The UV spectrum of UV-I exhibits two absorbance maxima at 290 and 350 nm with a saddle at 320 nm. The spectrum covers the whole UV region from 290 to 400 nm. The UV spectrum of the absorber is virtually composed from the spectra of the intermediates, i.e., benzotriazole **2** and condensation product **3** of cyanuric chloride (Fig. 7). The UV B region (290–320 nm) covers in its absorption the condensation product **3** and the UV A region (320–400 nm) covers the benzotriazole **2** incorporated in the molecule of UV-I.

The UV absorber carries two different reactive groupings: monochlorotriazine and sulfatoethylsulfone. Hence, the application of the absorber to sub-

strate involves formation of covalent bonds with hydroxyl groups of cellulose and immobilization of UV absorber at the fiber. From the standpoint of the reaction with cellulose, the character of UV absorber corresponds to that of bifunctional reactive dyestuffs with monochlorotriazine and aromatic vinyl sulfone groupings (commercial assortments Sumifix Supra (Sumitomo) or Diamira SN (Mitsubishi)).

The formation of covalent bond between UV absorber and hydroxyl group of cellulose is also reflected in UV spectrum. A comparison of spectrum of aqueous solution of UV-I with that of treated cellophane foil is presented in Figure 8.

The reaction with cellulose is connected with a bathochromic shift by ca. 15 nm toward higher wavelengths. This effect is unfavorable, because the absorption already slightly extends into visible region, and the cotton fabric treated with UV-I appears as slightly yellowish.

Altogether five water-soluble reactive UV absorbers with benzotriazole chromophore have been prepared. Chemical structures of the absorbers are presented in Figure 5. For the formulas of their corresponding aminophenylbenzotriazoles **2**, **5**, **6**, **7**, **8**, see Figs. 2–4.

The wavelengths of absorption maxima, λ_{\max} , of the aminophenylbenzotriazoles synthesized lie in the region of 347–360 nm, and their extinction coefficients, E , vary in the interval from 47 to 63 L/cm g, see Table I.

Water solubility of the UV absorbers at room temperature is in the range of 80–190 g/L. To achieve a sufficient solubility in water, the molecule must contain, besides the solubilizing sulfatoethylsulfonic group, still another sulfonic acid group. Absorber

TABLE III
Results of Application of Reactive UV Absorbers in the Amount of 2% Relative to Weight of Dry Cellulose Substrate and on Cellophane Foil 150 μ m and Cotton Fabric I

UV absorber formula	Fixation on fabric I (%)	Fluorescence of fabric I	Effect on optical brightening	UPF foil	UPF fabric I
UV-I	86	No fluorescence	Strong quenching	147	102
UV-II	72	No fluorescence	Slight quenching	100	179
UV-III	66	Strong fluorescence	No quenching	21	33
UV-IV	84	Strong fluorescence	No quenching	31	28
UV-V	84	No fluorescence	Strong quenching	50	58

UV-V, which does not contain the additional sulfonic acid group in the benzotriazole moiety, exhibits a water solubility of 7 g/L only; Table II.

The UV absorbers synthesized resemble bifunctional reactive dyestuffs, and they were applied to cellulose substrate using a procedure common in dyeing with bifunctional reactive dyes, Table III. With the application from a 2% aqueous bath, the fixation ratio reaches ca. 80%, which is a value close to those attained with bifunctional reactive dyes. The absorbers were tested on cellophane (thickness 150 μm) and also applied to cotton fabric I, which is a densely woven shirting material of 130 g/m^2 density.

Fabric I (untreated) transmits 40% of visible radiation and about 30% of ultraviolet radiation; hence, the ultraviolet protection factor only is $\text{UPF} = 3$. The application of sun modification using the UV absorbers markedly decreases the transparency of fabric in the UV region of spectrum, Figure 9. The application of 0.35% **UV-I** relative to weight of dry fabric increased the protection factor to 14. With application of 2% **UV-I**, the increase in protection reached $\text{UPF} = 102$. The protection factor of 100 means that the fabric with this treatment transmits only 1% of the incident ultraviolet radiation. A similar application of 2% **UV-II** increased the protection factor to as much as $\text{UPF} = 179$.

The application of UV absorber also resulted in a slight transparency decrease for visible radiation (400–650 nm). This decrease is connected with the shrinking of the fabric taking place during the application in water and decrease in its porosity.

Absorber **UV-I** was also used for treating fabric II with lower texture density and higher porosity (simple fabric with calico weave; the bulk surface density of 120 g/m^2). However, the protection factor achieved on fabric II was not higher than 24 (Fig.

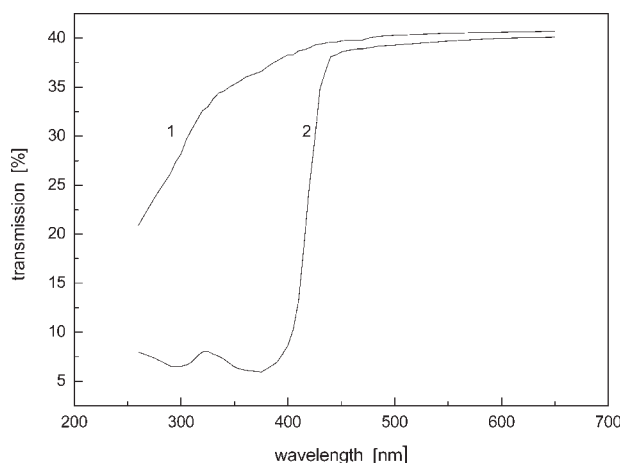


Figure 9 Transparency of cotton fabric I for UV-Vis radiation: curve 1—original untreated fabric I, $\text{UPF} = 3$; curve 2—fabric I treated with 0.35% **UV-I**, $\text{UPF} = 14$.

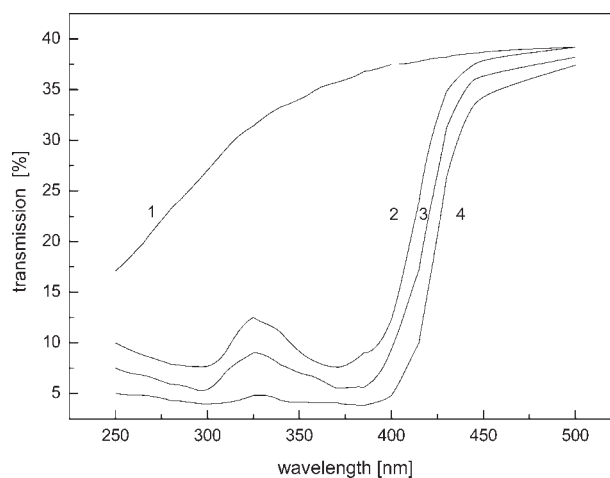


Figure 10 Curves of transparency of fabric II for UV radiation after application of **UV-I**: curve 1—untreated fabric, 0% **UV-I** ($\text{UPF} = 3$); curve 2—0.2% **UV-I** ($\text{UPF} = 11$); curve 3—1% **UV-I** ($\text{UPF} = 15$); curve 4—2% **UV-I** ($\text{UPF} = 24$).

10). Even the dose of 2% gave treated fabric II with the UV radiation transparency of 4–5%.

The dependences of protection factor on concentration of **UV-I** for cotton fabrics I and II and for cellophane foil are presented in Figure 11.

In the cases of the cellophane foil and fabric I, the dose of 2% **UV-I** will cause an almost full optical saturation for ultraviolet rays. Out of the amount used (i.e., 2%) only 80% is fixed to the substrate (i.e., 1.6% **UV-I**; the exhaustion of absorber from water bath is incomplete).

With fabric II, it is impossible to reach high values of protection factor. The reason lies in the higher porosity of the fabric, which contains uncovered spots allowing direct penetration of radiation.

From the dependence shown in Figure 11 it can be deduced that fabric I possesses porosity below 1%, while fabric II has the porosity of 4%.

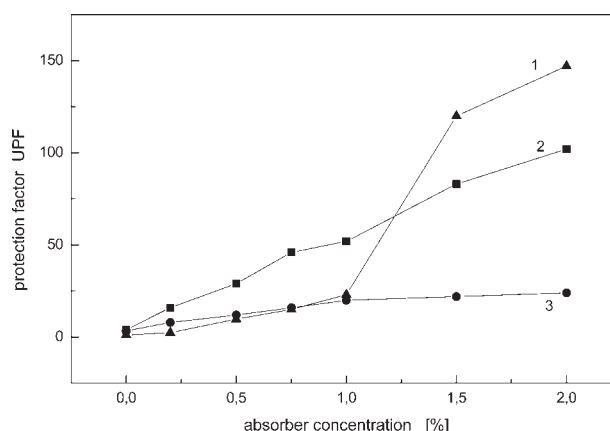


Figure 11 Dependence of UPF of foil and fabrics I and II upon dose of **UV-I** in bath: curve 1—cellophane foil; curve 2—fabric I; curve 3—fabric II.

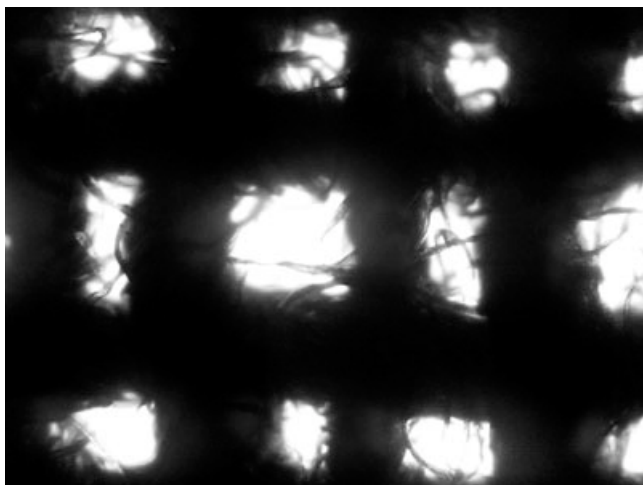


Figure 12 Photograph of fabric I dyed with 8% Ostazin black V-N, magnification $\times 130$.

If the latter fabric is dyed, e.g., with black reactive dye, the pores in it can be seen by means of a microscope (see Figs. 12 and 13). The pores observed in fabrics I and II have the dimensions of ca. $16 \mu\text{m} \times 50 \mu\text{m}$ and ca. $30 \mu\text{m} \times 60 \mu\text{m}$, respectively.

In the case of fabric II dyed with 8% Ostazin black V-N (mixed reactive dye produced by Synthesia Comp., Czech Rep.), the diffusion transmission spectrum was measured over the whole range of wavelengths present in the solar radiation, see Figure 14. This intensively colored fabric has a transparency for radiation from 3.5 to 4.5%. The ultraviolet protection factor of such black colored fabric II is $\text{UPF} = 28$.

The UV absorbers containing a 2-hydroxyphenyl group, i.e., UV-I, UV-II, and UV-V are photostable. Fabric I treated with 0.35% UV-I, exposed in a Xenotest apparatus, retained its protection factor without any change even after irradiation that corresponds to



Figure 13 Photograph of fabric II dyed with 8% Ostazin black V-N, magnification $\times 130$.

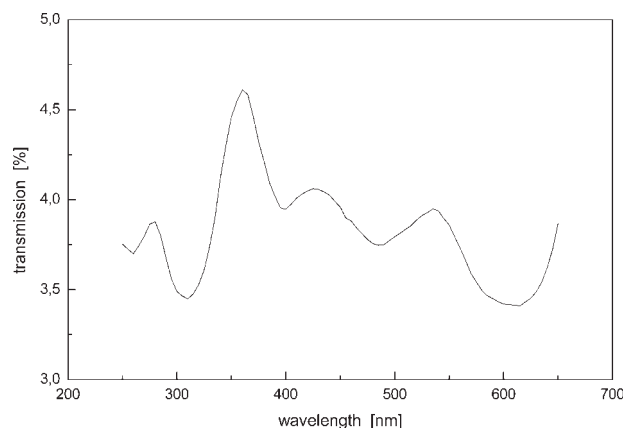


Figure 14 Diffusion transmission spectrum of fabric II dyed with 8% Ostazin black V-N, $\text{UPF} = 28$.

dyestuffs with the light fastness degree equal to 7. The high photostability of absorbers of this type is explained by the possibility to disperse the absorbed energy of UV radiation in the form of harmless energy such as IR radiation (heat) through the reversible hydrogen bond between phenolic hydroxyl group and triazine cycle, see Figure 15. No emission of the absorbed energy is observed in the UV-Vis region, and the products show no fluorescence after the irradiation with UV rays, see Table III.

On the other hand, in the case of absorbers UV-III and UV-IV, which do not possess the 2-hydroxyphenyl group in their molecules, the absorbed energy is released by radiation in UV-VIS region by means of fluorescence, see Table III. The preparations of this type exhibit low photostability (Xenotest 2–3). After exposure to direct solar radiation, the fabrics treated with UV-III and UV-IV rapidly lost their ability to eliminate UV radiation because of photolysis of the UV absorber. Then, their fluorescence during irradiation with UV rays also disappeared.

UV absorbers are designed to be used for treatment of undyed textiles or those dyed in light hues. Such products should be brightened by optical brighteners (Fluorescent Brightening Agents-FB). The optical brightening agents of stilbene type form a current component of washing powders. They absorb radiation in near UV A region, i.e. in the wavelength range of 360–380 nm, and they emit fluorescence radiation in the wavelength range of 410–450 nm, which imparts brilliant snow-white aspect to the

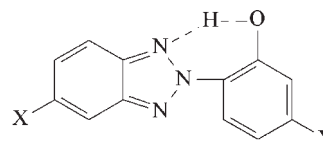


Figure 15 Formation of hydrogen bond between phenolic hydroxyl group and triazine ring.

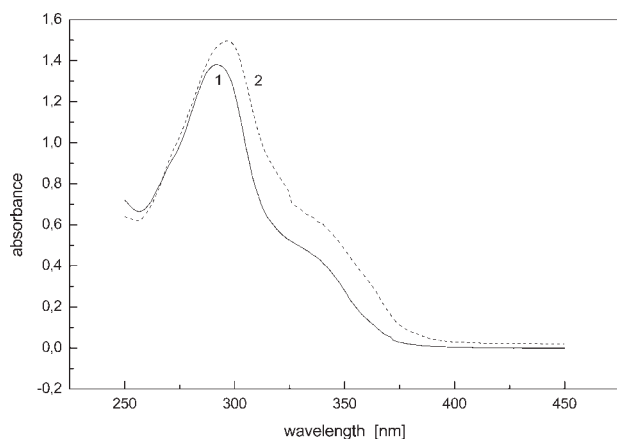


Figure 16 Spectrum of absorber UV-II: curve 1—aqueous solution 25 mg/L, 1-cm cell; curve 2—cellophane foil 150 μm , 0.4%.

cotton fabric. Broadband UV absorbers also absorb the wavelength necessary for the operation of FB, and thus the effect of optical brightening is suppressed. If the UV absorber is designed in such a way that its absorption spectrum does not cover the range of 360–400 nm, then the effect of optical brightening will be retained. Thus the absorption of wavelength in the range of 360–400 nm can be reserved for FB agents. This wavelength region is less dangerous and its elimination is not necessary for attaining high values of protection factor of the textile material. In the case of benzotriazole-type UV absorbers it is possible to use suitable positional rearrangement of substituents in order to lower absorption in the wavelength range of 360–400 nm. Such properties are present in absorber UV-II, see Figure 16.

The application of absorber UV-II gives a fabric that can be optically brightened and thereby attains perfect whiteness.

If the absorption spectrum of UV absorbers is shifted to the UV B region (below ca. 350 nm), then the effectiveness of most FB agents for cellulose fibers is retained. These products are components of washing powders, and their presence on fiber is repeatedly renewed during washing. Thus, a combination of UV absorber for UV B region with optical brighter covers the whole UV region (A and B) and, in addition to that, the capability of optical brightening remains retained. This combination of absorbers with effectiveness in the UV B range together with

FB agents obviously represents the optimum variant for utility value of textiles.¹⁰

CONCLUSIONS

UV absorbers for cellulose textiles can markedly increase UPF and, hence, fundamentally improve protection of humans against harmful effects of UV component of solar radiation. The importance of such protection will probably increase in connection with civilization effects resulting in gradual thinning of ozone layer of the Earth and formation of ozone holes.

One of possible solutions to this problem is the application of UV absorbers to cellulose fibers, the absorbers having a character of bifunctional reactive dyes, i.e., possess the ability to form firm covalent bond with the cellulose fiber, which results in a permanent effect of treatment that cannot be washed out. This requirement is best met by a combination of monochlorotriazine and vinylsulfone reactive groupings, which can easily be obtained by reaction of cyanuric chloride with PAFSES. The second reactive atom of chlorine in cyanuric chloride is used for binding the chromophore.

UV chromophores of benzotriazole type with a phenolic hydroxyl group at *o*-position with respect to the triazole ring are highly photostable and relatively easily available by reduction of the corresponding azo dyes containing a nitro group at *o*-position to azo group.

Suitable variation of substituents can affect spectral and other properties of the UV absorbers. It is possible to prepare broadband UV absorbers covering the whole UV range, or only its UV B section, resulting in retained possibility of optical brightening by means of FB Agents.

References

1. Australia/New Zealand Standard AS/NZ 4399 (1996).
2. Thompson, B. L.; Pailthorpe, L. T. Pat. EP 0,655,061 (1993).
3. Diffey, B. L.; Robson, J. J Soc Cosmet Chem 1989, 40, 127.
4. Georgouras, K. E.; Stanford, D. G.; Pailthorpe, M. T. Aust J Dermatol 1997, 38 (Suppl 1), 79.
5. Mura, J. L. Pat. GB 2,287,467 (1995).
6. Fuso, F.; Reinert, G. Pat. EP 0,704,444 (1996).
7. Reinehr, D.; Eckhart, C.; Hochberg, R.; Kaufmann, W.; Metzger G. Pat. EP 0,728,749 (1996).
8. Isharani, J. V.; Hung, W. M.; Su, K. C. U.S. Pat. 5,700,394 (1997).
9. Isharani, J. V.; Hung, W. M.; Su, K. C. Pat. EP 0,717,140 (1995).
10. Palacin, F. Melliand Textilberichte 1997, 78, 519.