

ULTRAVIOLET ABSORBERS INCREASING PROTECTIVE PROPERTIES OF CELLULOSE FABRICS

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Since early 1990 in such areas of the world as Australia and America, which enjoy especially sunny weather there has been increasing awareness of harmful effect of sunlight on human skin accompanied by fears of the consequences of observed damage to ozone layer of earth's atmosphere.

It is well known that solar radiation is composed of light characterised with wavelengths from the ultraviolet to infrared range. Ultraviolet radiation which reaches the surface of the earth is usually subdivided into UV-B (280-320nm) and UV-A (320-400nm) regions. Although intensity of this radiation is much lower than visible and infrared radiation the energies of UV-B and UV-A photons exceed the carbon-carbon single bond energy. It is than understandable why UV-radiation in combination with the air's oxygen is able to initiate various chemical reactions on exposed natural or synthetic organic substrates.

The most visible results of photo-oxidative degradation of natural and synthetic polymers are the loss of their mechanical properties and esthetical aspects such as loss of surface appearance and loss or changes of their colour.

Unprotected prolonged sun exposure on human skin results in various harmful effects. According to numerous medical reports ultraviolet UV-B is the major active terrestrial waveband region that causes direct photochemical damage to DNA from which gene mutation arise, therefore is one of the major factors in the development of skin cancer [1, 2].

UV-B radiation cause also erythemas (the peak of the erythema action spectrum is located at 305-310nm), skin burning which inhibit skin tanning as well as skin photoageing and immunosuppression as chronic effects.

Radiation of UV-A is known to induce skin tanning but also can cause skin damage especially to sensitive skin which is exposed for long periods. Examples of such damages are loss of skin elasticity, appearance of wrinkles and the inducement

of phototoxic and photoallergic reactions. In recent decades we spend most of our free time outdoors and in spite of public education campaigns world skin cancer rates are on the increase.

Among others protection measures recommended by dermatologists against UV radiation originating from sunlight (as well as from artificial sources) such as avoiding prolonged exposure on skin, wearing sunglasses, using cosmetics equipped with sunscreen formulations the use of textile garments is one of the most important. Since ancient times textiles in the form of clothes have been the oldest means of sun protection.

When radiation reaches a textile fabric surface it can be reflected, absorbed, transmitted through fibres or pass between fibres as it is shown on Figure 1.

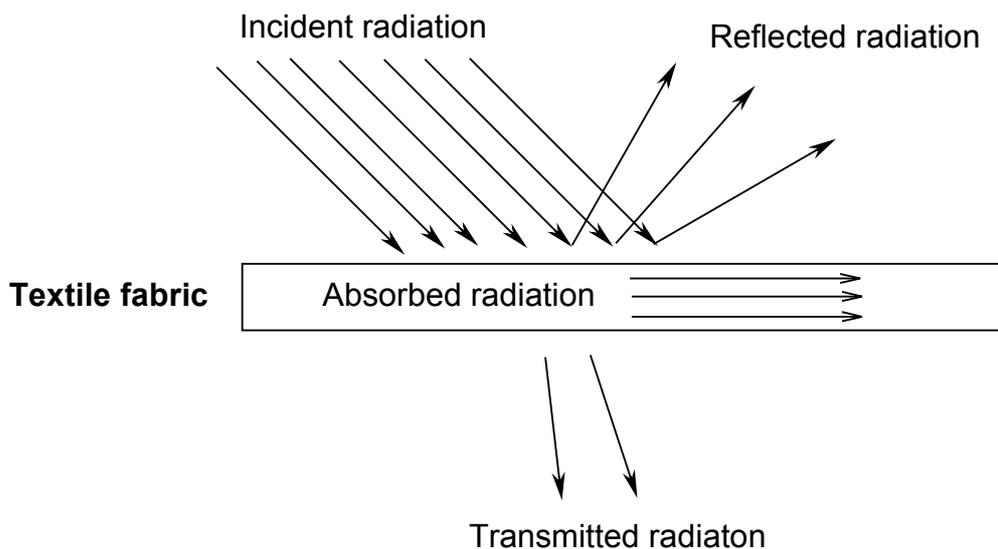


Figure 1 Interaction of sunlight with textile fabric.

It is commonly known that skin-protecting properties of textiles are connected with fabric's structure and its chemical constitution and dependent on many factors such as fibre type, fabric construction, fabric weight, colour, nature of finish etc. A widely accepted method of the characterisation of the ultraviolet protecting properties of a particular fabric is the determination of UPF (Ultraviolet Protection Factor) by the irradiating sample with UV-light source and measurement of transmitted radiation by the use of special equipment and technique. European Standard EN 13758 specifies that clothing can bear a "UV-protective" label only if the UPF is higher than 40 and if

at the same time UVA transmission is less than 5%. The standard also specifies clothing design such that as much skin as possible is covered [3, 4].

Light, bleached, uncoloured cotton fabrics which are very popular in summer usually do not provide sufficient protection against solar radiation. It was reported that a typical light-coloured cotton shirt has approximate UPF value only 10. A third of examined commercial summer clothes provided an UPF factor of less than 12-15. Moreover wetting and stretching clothes which are typical during swimming and other beach activities lower level of protection.

Nowadays at the market a number of special UV absorbers for cellulose fibres which absorb light in the near UV region (290-400nm) are available. Most of these auxiliaries commercially offered are based on several chemical structures in which UV-absorbers contain specific intramolecular hydrogen bonds such as is in hydroxyphenyltriazines (1), hydroxyphenylbenzotriazoles (2), hydroxybenzophenones (3), and oxalanilides (4) presented on Figure 2.

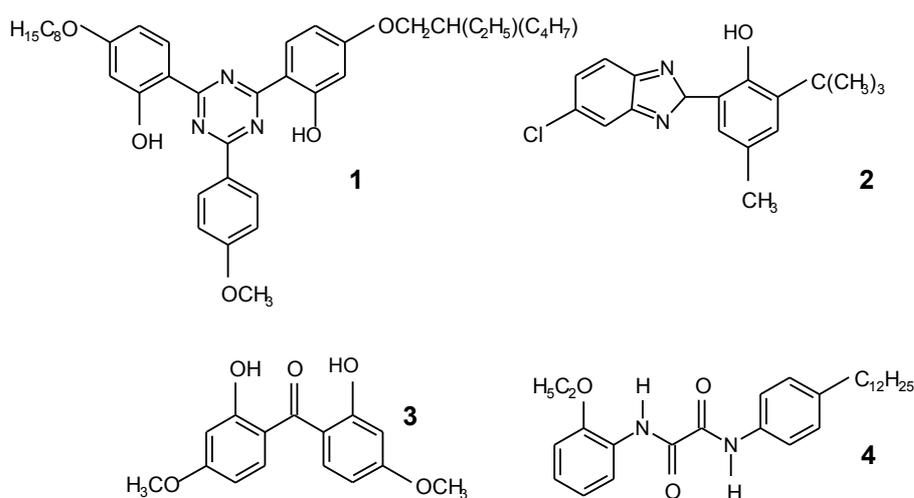


Figure 2 Examples of commercial UV-absorbers with intramolecular hydrogen bonds used to protect polymers against photodegradation.

To the second group belong compounds such as cinnamoylamides (5) or cyanoacrylates (6) presented on Figure 3 which because of a high absorption per weight also may be used for these purposes.

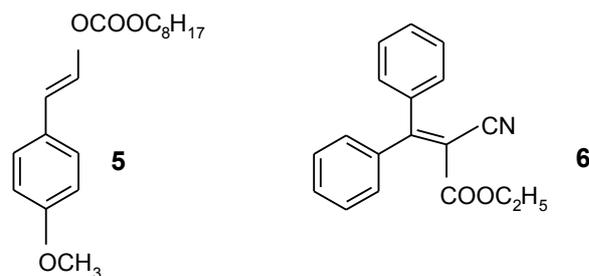


Figure 3 Examples of commercial UV-absorbers without intramolecular hydrogen bonds used to protect polymers against photodegradation.

In order to meet requirements of the industrial practice a typical UV-absorber designed for cellulose should be water-soluble, show an appropriate affinity to the fibre and lack of added colour. Therefore in application terms it could be regarded as “colourless dye” of the “direct” or “reactive”-type.

“Direct dye” type UV-absorbers which may be applied by the same methods as direct dyes are recently recommended by patent literature for the use as the components of a laundry detergents or laundry pre- and aftertreatment. Applied by consumers in each washing cycle or final rinse aftertreatment these products progressively increase protecting properties of textiles. Simultaneously they also give another beneficial effect improving light fastness of dyed textile material [5, 6]. These compounds as it is shown on Figure 4 are often of a basic or cationic character in order to provide them an appropriate affinity to negative-ionised cellulose fibre.

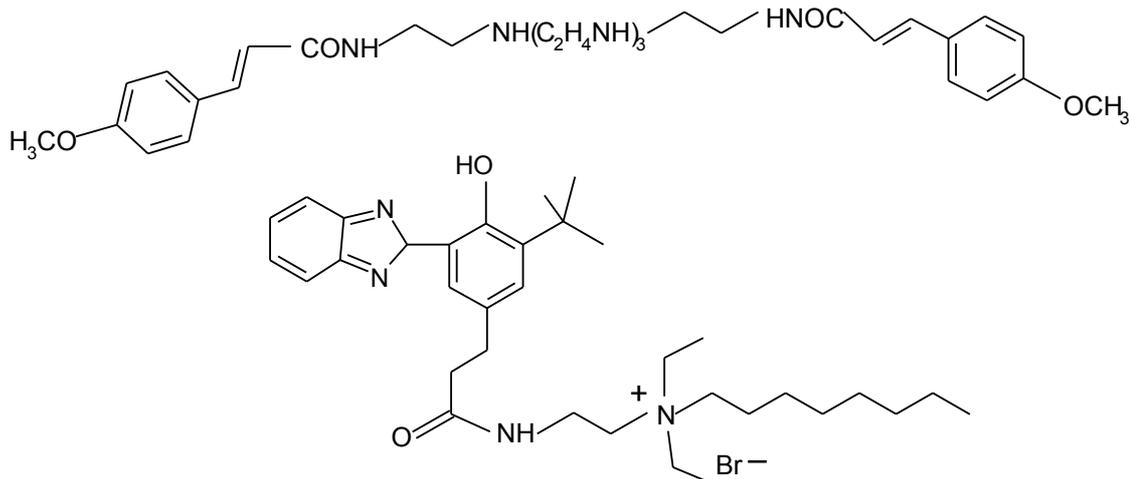


Figure 4 Examples of basic and cationic “direct-type” UV-absorbers designed as additives to a laundry detergents or laundry aftertreatment chemicals

UV-absorbers containing reactive groups seem to be especially interesting in industrial-scale applications. Such products could form covalent bonds with cellulose after fixation on the fibre and then would be able to maintain protecting properties of “dyed” fabric for prolonged time. Analogically, as it is practiced in the case of modern reactive dyes, introduction of two or more reactive systems to a UV-absorber molecule provide high fixation efficiency. Similarly as in the case of commercial reactive dyes these polyfunctional reactive absorbers may be of a homo-functional or hetero-functional type. The first one group usually contains monochlorotriazine residues reacting with cellulose fibre at the temperature about 80°C or sulphatoethylsulphone groups which react with the fibre at the temperature of 60°C. Absorbers of the second group usually contain both types of reactive systems and therefore can be applied at the temperature range of 60-80°C. Reactive UV-absorbers can be applied from aqueous baths separately or as an additional component of dyeing bath during dyeing with the use of various brands of commercial reactive dyes present on the market.

On figure 5 are presented examples of such-type products synthesised in our laboratory [7]. Both absorbers may be classified in the group of light stabilisers without hydrogen bridges. It may be also observed that absorber A1 is of a homobifunctional and A2 of a heteropolyfunctional-reactive type.

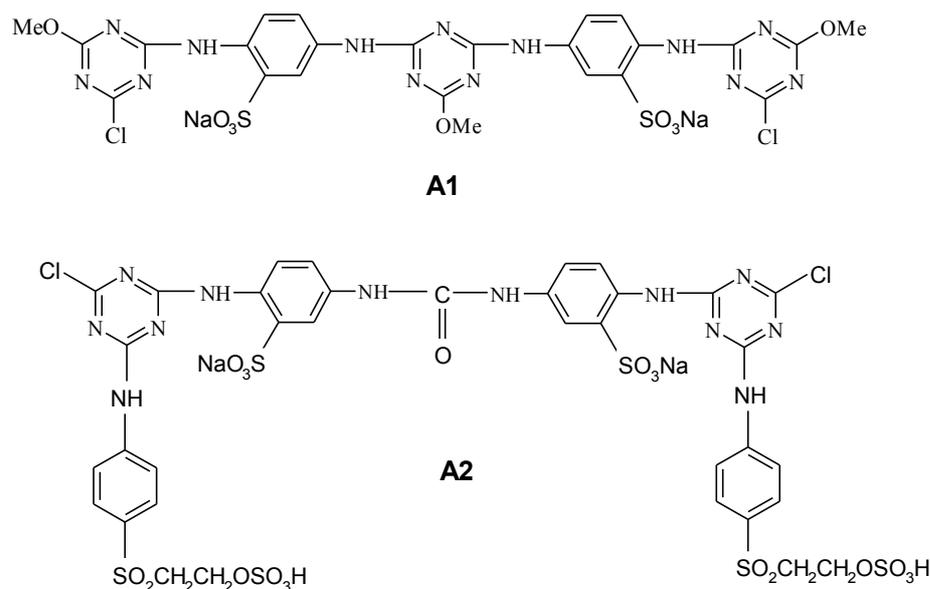


Figure 5 Polyfunctional reactive UV-absorbers synthesised at the Institute of Polymer and Dye Technology of the Technical University of Lodz.

Both presented absorbers are characterised by good light stability, and after application to cotton fabrics increased their UV-protection properties as it can be observed on Figure 6.

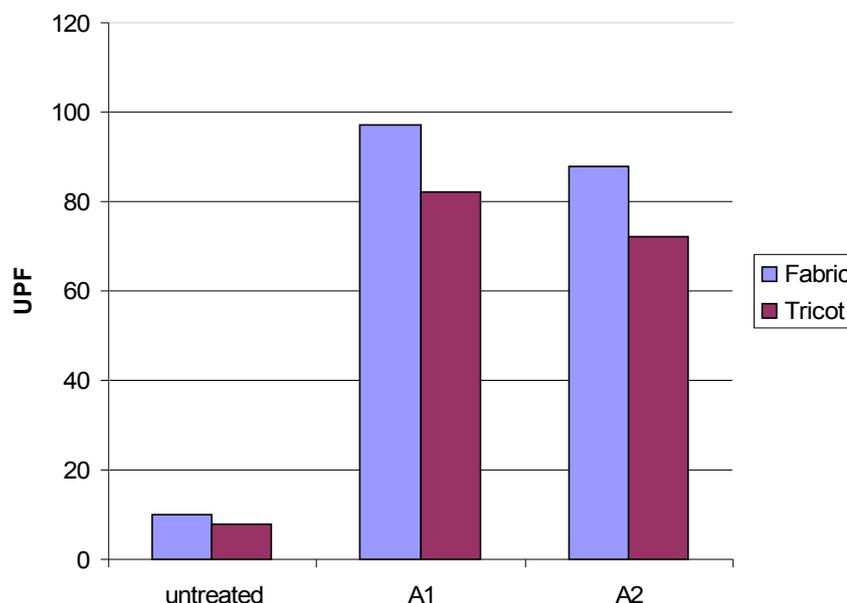


Figure 6 Protecting properties of samples of the cotton fabric and the cotton tricot treated with absorbers A1 and A2 (1% owf, 80°C, bath ratio 1:15, 50g/dm³ Na₂SO₄, 20g/dm³ Na₂CO₃)

It was earlier mentioned that protecting properties of a particular textile garment are also connected with its colour and nature of its finishing. Synthetic dyes and several others textile auxiliaries especially such as optical brighteners are characterised by their own significant absorption in ultraviolet region. It is then obvious that the use of optical brighteners as UV-absorbers increasing UPF value of the textile has been already proposed. Because typical optical brighteners are usually effective in absorbing radiation in the UV-A range several new structures were produced which absorb ultraviolet radiation both in the UV-A and UV-B ranges.

Examples of such-type products given by patent literature are presented on Figure 7 [8, 9]. It can be noticed that as was mentioned above in application terms one of the products could be regarded as “direct dye-type” and the second as “reactive dye type”. According to quoted patents these substances increase both whiteness and UPF value of the textile.

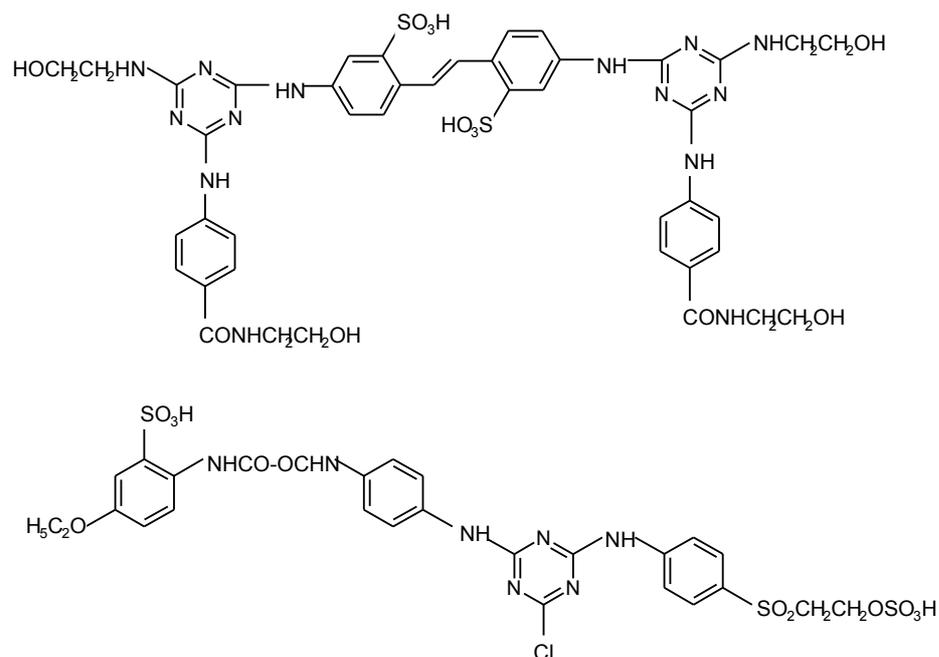


Figure 7 Optical brighteners increasing UV-protection properties of cellulose-made textiles.

Similarly a synthesis of dyes with built-in UV-absorber moiety was reported in groups of direct [10] and reactive dyes for cotton [11] although the main purpose of this work was to increase the lightfastness of newly-prepared colorants or to prevent the photodegradation of dyed fibres.

In our earlier work on the reactive dye derivatives of C.I. Reactive Red 198 which contained built-in 2'-hydroxyphenylbenzotriazole UV-absorber residue in their molecules it was found that cotton fabric dyed with new colorants exhibited approximately 10% higher UPF-factor values in comparison with the same fabric coloured with model dye. A disadvantage of the synthesised dyes was their moderate affinity to cellulose fibre which limited their application in typical exhaust methods [12].

The purpose of the other work, which results are now in press, was to examine the properties of more substantive symmetric homobifunctional monochlorotriazine yellow and red dyes of a Procion HE – type of the general structure presented in Figure 8.

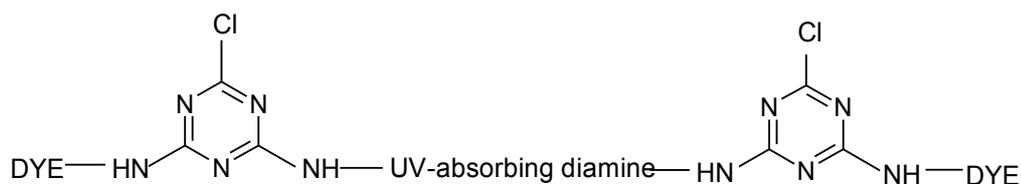


Figure 8 General structures of the homobifunctional monochlorotriazine reactive dyes containing aromatic diamine bridges characterised by increased UV-absorption

During preparing these dyes typical intermediates used in industrial practice as diamine bridges, such as *p*-phenylenediamine or *o*-phenylenediamine were substituted by 4,4'-diaminostilbene-2,2'-disulphonic acid, 4,4'-diamino-3,3'-disulphodipenylurea and 2-methoxy-1,3,5-triazynyl-4,6-bis-N1,N1'-(1,4-diaminophenyl-3-sulphonic) acid. It can be noticed that the latter two diamines were the same as used earlier in synthesis of colourless reactive UV-absorbers shown on Figure 5.

It was found that all the new dyes gave very similar levels of fixation and dyeing efficiency when compared with the model dyes. The presence of the special UV-absorbing diamine in the dye molecule usually resulted in a significant increase of the measured UPF value [13]. Introducing the appropriate residues to the molecule of the reactive dye may be then also considered as the method of increasing UV-protection properties of dyed textiles. Moreover, coloration of cellulose fabrics with the use of specially tailored dyes could eliminate the necessity of using additional UV-absorber auxiliaries, and therefore decrease the number of chemicals used in the dyehouse. This fact should be considered while designing new reactive dyes, although introducing UV-absorbing residues to dyes characterised by a different structure than that presented in Figure 8 would probably require more pronounced efforts. In the case of the currently manufactured dyes, the “colorant + UV-absorber auxiliary” method might still be probably the most convenient way of improving the UV-protection properties of dyed textiles.

According to literature review most of single-used organic auxiliaries do not ensure complete protection both in UV-B and UV-A regions because each substance due to its chemical structure absorb only UV-light of specific wavelength range. In such cases when complete protection is necessary usually a mixture of two broad-

spectrum organic absorbers are offered. More frequently also for this purpose a combination of organic and inorganic absorbers is used.

Inorganic UV absorbers such as titanium dioxide and zinc oxide applied as pigments especially in the form of nanoparticles were already used for UV protection of textiles. TiO₂ dispersed in hydrolyzed modified alkoxy silane and applied to cotton fabric provided good UV protection allowing also for good air permeability, acceptable strength and crease recovery [14]. Good protection properties provided also cotton fabric with nano-scale layer of TiO₂ deposited by sol-gel method [15].

It was found that the combined use of organic UV absorbers and mentioned above inorganic pigments leads to a more effective UV-protection than the separate use of organic and inorganic UV absorbers. Patent literature suggests introducing such combined mixture to textile finishes, laundry detergents or fabric conditioner compositions [16]. Good results were also described in the work on optimised UV protective coatings with the full absorption of virtually all UV light prepared by the sol-gel technique comprising the use both organic and inorganic UV-absorbers [17, 18]. One may expect then that some of the developed and described above methods will be successfully commercialised in the nearest future.

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