AUTEX Research Journal, Vol. 14, No 4, December 2014, DOI: 10.2478/aut-2014-0025 © AUTEX

DE GRUYTER OPEN

LIGHT CONVERSION AND SCATTERING IN UV PROTECTIVE TEXTILES

Ana Marija Grancarić*, Anita Tarbuk*, Lea Botteri

University of Zagreb, Faculty of Textile Technology, Department of Textile Chemistry and Ecology,
Prilaz baruna Filipovica 28a, HR-10000 Zagreb, CROATIA
*E-mail: amgranca@ttf.hr, anita.tarbuk@ttf.hr

Abstract:

The primary cause of skin cancer is believed to be a long exposure to solar ultraviolet radiation (UV-R) crossed with the amount of skin pigmentation in the population. It is believed that in childhood and adolescence 80% of UV-R gets absorbed, whilst in the remaining 20% gets absorbed later in the lifetime. This suggests that proper and early photoprotection may reduce the risk of subsequent occurrence of skin cancer. Textile and clothing are the most suitable interface between environment and human body. It can show UV protection, but in most cases it does not provide full sun screening properties. UV protection ability highly depends on large number of factors such as type of fibre, fabric surface and construction, type and concentration of dyestuff, fluorescent whitening agent (FWA), UV-B protective agents, as well as nanoparticles, if applied. Based on electronically excited state by energy of UV-R (usually 340–370 nm), the molecules of FWAs show the phenomenon of fluorescence giving to white textiles high whiteness of outstanding brightness by reemitting the energy at the blue region (typically 420–470 nm) of the spectrum. By absorbing UV-A radiation, optical brightened fabrics transform this radiation into blue fluorescence, which leads to better UV protection. Natural zeolites are rock-forming, microporous silicate minerals. Applied as nanoparticles to textile surface, it scatters the UV-R resulting in lower UV-A and UV-B transmission. If applied with other UV absorbing agents, e.g. FWAs, synergistic effect occurs. Silicones are inert, synthetic compounds with a variety of forms and uses. It provides a unique soft touch, is very resistant to washing and improves the property of fabric to protect against UV radiation. Therefore, the UV protective properties of cotton fabric achieved by light conversion and scattering was researched in this paper. For that purpose, the stilbene-derived FWAs were applied on cotton fabric in wide concentration range without/with the addition of natural zeolite or silicone–polydimethylsiloxane. UV protection was determined in vitro through ultraviolet protection factor. Additionally, the influence to fabric whiteness and hand was researched.

Keywords:

Fluorescence, UV protection, cotton, natural zeolite, polydimethylsiloxane (PDMS)

1. Introduction

1.1. UV Protection

The incidence of skin cancer is increasing by epidemic proportions. Basal cell cancer remains the most common skin neoplasm, and simple excision is generally curative. On the other hand, aggressive local growth and metastasis are common features of malignant melanoma, which accounts for 75% of all deaths associated with skin cancer. Its primary cause is believed to be a long exposure to solar ultraviolet radiation (UV-R) crossed with the amount of skin pigmentation in the population as well as family genetics [1-6].

Solar radiation consists of different rays, from shortest gamma rays through X-rays. The radiation that reaches the Earth's surface is a spectrum in the range of 280–3000 nm, consisting of ultraviolet (UV), visible (VIS) and infrared (IR) radiation. UV as a whole does not exceed 5% of the total energy emitted by the sun, but their impact on the organic molecules is very important and it induces significant physiological responses in all areas of life. It can be divided into UV-A (from 400 to 320 nm), UV-B (from 320 to 280 nm) and UV-C (under 280 nm). The UV-C is normally not transmitted to the Earth because it is absorbed by the stratospheric ozone layer. On the other hand, dangerous UV-B rays can cause acute and chronic reactions and damages such as erythema (sunburn), sun tanning, "photoaging", DNA and eye damage, photokeratitis and cataract, and photocarcinogenesis; increase risk factor for melanoma or cause various skin cancers [6-26]. Experts estimate about 90% of melanomas are associated with severe UV exposure and sunburns over a lifetime. Intermittent sun exposure, especially in childhood and adolescence, is considered to be a stronger risk factor for melanoma than continuous exposure [1]. It is believed that in that period of life 80% of UV-R gets absorbed, whilst in the remaining 20% gets absorbed later in the lifetime. This suggests that proper and early photoprotection may reduce the risk of subsequent occurrence of skin cancer [3].

Textile and clothing are the most suitable interface between environment and human body. It can reflect, absorb and scatter solar wavelengths (Figure 1), but in most cases, it does not provide full sun screening properties [10]. Literature sources claim that only one-third of the spring and summer collections tested give off proper UV protection [11,12]. UV protection ability highly depends on large number of factors such as type of fibre, fabric surface and construction, type and concentration of dyestuff, fluorescent whitening agent (FWA), UV-B protective agents, as well as nanoparticles, if applied [6, 13-32].

Textile finishing agents for UV protection can be incorporated into the fibre matrix, or it can be applied to the surface of the fabric [15]. Usually, sun protection effect is achieved through the use of UV absorbers [14-18]. Molecules of UV absorbers, such as benzotriazole and phenyl benzotriazole, are able to absorb the damaging UV-R range of 290–360 nm and convert it into harmless heat energy. Latest research declare that FWAs and UV absorbers can be applied in washing [27,28].

1.2. Light conversion

When P. Krais in 1929 discovered fluorescent compound *Aesculin* by water extraction from wild chestnut, he wrote “About the new white ...“. It was the new white indeed, never seen before such high whiteness degree. However, he could never assume that this UV-A absorption of FWAs would result in better UV protection as well [6, 15-17, 26, 27]. Based on electronically excited state by energy of UV-R (usually 340–370 nm), the molecules of FWAs show the phenomenon of fluorescence giving to white textiles high whiteness of outstanding brightness by reemitting the energy at the blue region (typically 420–470 nm) of the spectrum. This phenomenon can be explained by modified diagram according to Jablonski (Fig. 2) [33]. An electronically excited molecule can lose its energy by emission of radiation, which is known as “luminescence”. One of these kinds of emission is fluorescence. According to Fig. 2, fluorescence is an emission process occurring from lowest excited state (S_1) to the ground state (S_0). The frequency of fluorescence radiation is lower than that of excitation light (which is known Stokes Law). For the same compound, an ideal emission should be the mirror image of the absorption band system.

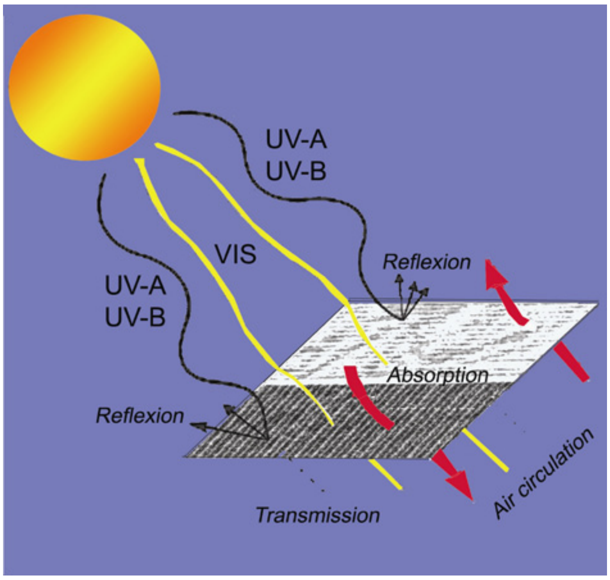


Figure 1. UV radiation in contact with textile fabric.

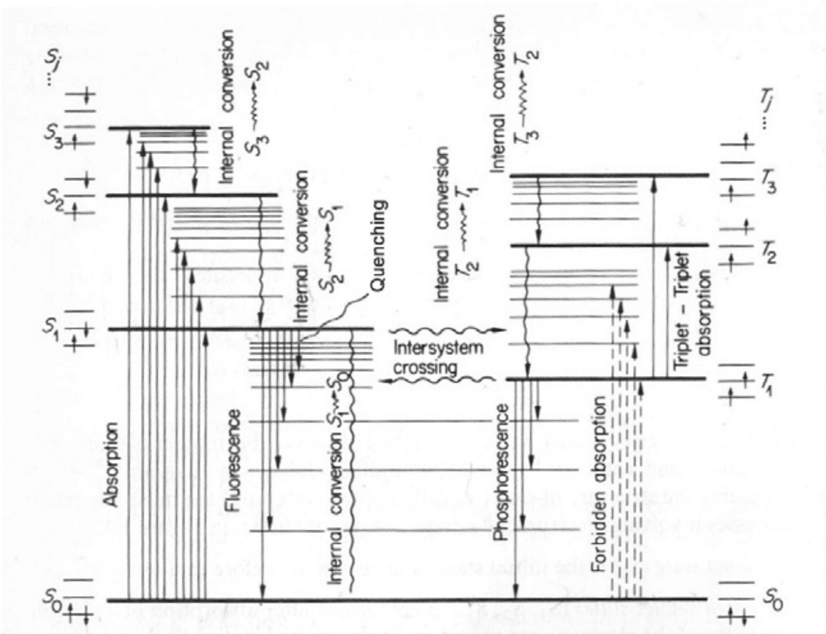


Figure 2. Modified Jablonski diagram [33].

There are many organic compounds for the application on textiles like stilbene, bis-benzoxazole, cumarine and pyrazoline derivates and many others. It is well known that fluorescent compounds show the high fluorescence intensity at low concentration on textile and other materials. Recently, FWAs showed the good prevention of harmful UV rays. By absorbing UV-A radiation, optical brightened fabrics transform this radiation into blue fluorescence, lowering UV transmission, contributing to high ultraviolet protection factor (UPF), which results in better UV protection.

1.3. Light scattering

The presence of inorganic pigments in the fibres also allows better scattering of light from the substrate, thus providing better protection [13]. Titanium dioxide (TiO_2), which is used as a delustering agent, and other ceramic materials have an absorption capacity in the UV region of 280–400 nm reflecting visible and infrared rays. Incorporation of TiO_2 into fibre matrix improves the UV blocking capacity of the fibre [31,32]. Good skin protection thereby can be achieved by the textile itself, if the fabric is sufficiently dense. Introducing the nanoparticles in textile finishing led to UV protection by coating the surface of textiles and clothing with nano particles of titanium and zinc oxide [29,30], and nowadays, of natural zeolite clinoptilolite [22-24].

Natural zeolites are rock-forming, microporous silicate minerals that act as strong adsorbents and ion-exchangers, having multiple uses in medicine and industry, agriculture, water purification and detergents. Zeolites are nontoxic substance, excellent for proteins and small molecules such as glucose adsorption; even absorbs toxins, mould and caesium. It has positive effect on the metabolism of living organisms and its anticancerogenic, antiviral, antimetastatic and antioxidant effect. Clinoptilolite can be grinded by a certain tribomechanical processing in a patented machine (Patent: PCT/1B99/00757) by obtaining particles on a submicron level (micro and nanoparticles) yielding all the above-mentioned properties. When applied externally in powder form, it has been found to quicken the healing of wounds and surgical incisions and act as proven bactericides and fungicides as well. Applied as nanoparticles to textile surface, it scatters the UV-R, resulting in lower UV-A and UV-B transmission. If applied with other UV absorbing agents, e.g. FWAs, synergistic effect occurs.

Silicones are inert, synthetic compounds with a variety of forms and uses. They provide a unique soft touch, are very resistant to washing and improve the fabric protection against UV radiation [34].

Therefore, the UV protective properties of cotton fabric achieved by light conversion and scattering by application of FWA, natural zeolite and silicone were researched in this paper.

2. Experimental

2.1. Materials

Chemically bleached cotton fabric was used. It was plain weave fabric of 100% cotton yarn of 25 tex and surface mass 240 g/m^2.

FWAs chemically based on stilbene disulphonic acid triazine derivative (Uvitex RSB, Ciba-Geigy AG) shown in Figure 3 and 4,4′-bis(2- sulphostyryl)-biphenyl disodium salt (C.I. Fluorescent Brigthener 351, Uvitex NFW, Ciba-Geigy AG) shown in Figure 4 were applied in wide concentration range (c_1 = 1 g/l; c_2 = 5 g/l; c_3 = 10 g/l; c_4 = 50 g/l) by pad-dry procedure to achieve high whiteness degree and UV protection. Padding was performed at wet pick up of 100%, in bath containing 5 g/l corn starch, 10 g/l glycerol, 20 g/l Na_2SO_4 dried at T = 100°C for t = 90 s, with the addition of 5 g/l of activated natural zeolite micro and nanoparticles (Z), made by tribomechanical activation in Tribomin d.o.o. Osijek; or 10 g/l of silicone – polydimethylsiloxane (PDMS) with amino-alkyl groups (Softycon SRN, Textilcolor). Labels and treatments are presented in Table 1.

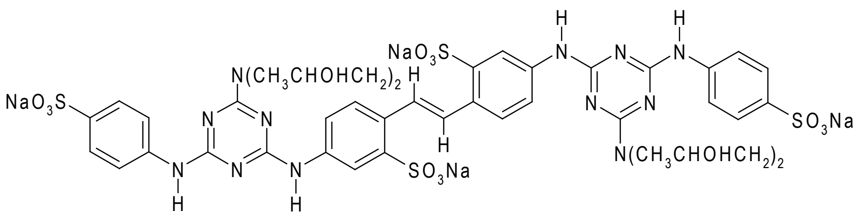


Figure 3 Structural formula of stilbene disulphonic acid triazine derivative (Uvitex RSB, Ciba).

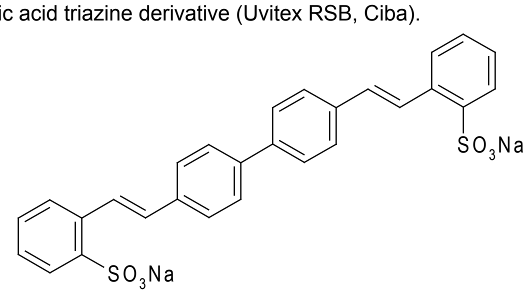


Figure 4 Structural formula of distyryl biphenyl derivative (Uvitex NFW, Ciba).

Table 1. The labels and treatments of cotton fabric.

Label	Treatment
B	Untreated chemically bleached cotton fabric
Z	Treatment with the 5 g/l zeolite (nanoparticles of activated natural zeolite clinoptilolite)
S	Treatment with the 10 g/l silicone – polydimethylsiloxane, PDMS (Softycon SRN)
RSB	Treatment with stilbene disulphonic acid triazine derivative (Uvitex RSB)
NFW	Treatment with stilbene distyryl biphenyl derivative (C.I. Fluorescent Brigthener 351, Uvitex NFW)
… 1, 5, 10, 50	… Concentration of applied FWA

2.2. Methods

The fabric UV protection was determined according to AS/NZS 4399:1996 *Sun Protective Clothing: evaluation and classification.* UVA and UVB transmission through fabric were measured on Varian Cary 50 Spectrophotometer, and UPF was calculated automatically. UPF indicates the ability of fabrics to protect the skin against sun burning saying how much longer a person can stay in the sun with the fabric covering the skin as compared with the uncovered skin to obtain same erythemal response [10-25]. According to the standards, excellent protection is if UPF is higher than 40. For countries with UV index 7–10 such as Mediterranean countries, Australia and USA, the UPF should be 15 times higher than UV index [17]. Therefore, it is recommended for people who spend 8 hours in the open to use UV clothing with UPF between 105 and 150 if they want excellent UV protection.

Remission spectrophotometer SF 600 PLUS CT (Datacolor) was used for measuring spectral characteristics of cotton fabrics. CIE whiteness degree (W_{CIE}) was calculated automatically according to ISO 105-J02:1997 *Textiles – Tests for colour fastness – Part J02: Instrumental assessment of relative whiteness* and Yellowing Index (YI) according to DIN 6167:1980 *Description of yellowing of practically white or practically colourless materials*. The relative intensity of fluorescence (Φ_{rel}) was calculated from measured fluorescence on adapted spectrophotometer Specol SV (Carl Zeiss). Illuminant is high voltage Hg bulb (λ_{max} = 366 nm). Fluorescent Reference Standard, Datacolor, was used for $\Phi_{rel.\ standard}$ = 40, with amplification of 200×.

Fabric hand was determined by subjective evaluation according to defined guidelines in *AATCC Evaluation Procedure 5 – Fabric Hand: Guidelines for the Subjective Evaluation of* (2007). Ten evaluators performed subjective hand evaluation and ranked fabrics according to the physical attributes of hand.

3. Results and discussion

The UV protective properties of cotton fabric achieved by light conversion and scattering were researched in this paper. For that purpose, the stilbene derivate FWA was applied on cotton fabric in wide concentration range without/with the addition of natural zeolite or silicone – polydimethylsiloxane (PDMS). UV protection was determined in vitro through UPF. Additionally, the influence to fabric whiteness and hand was researched.

UV protective ability is presented in Table 2 and Figure 5.

In every wet treatment, cotton swells leading to fabric shrinkage. For the purpose of this research, fabrics were treated by pad-dry procedure, which provides dimensional stability, and no shrinkage occurred. Therefore, the results of UV-R transmission are exclusively related to the agent applied.

The impact of fluorescent compounds – stilbene disulphonic acid triazine derivative and distyryl biphenyl derivative, zeolite and silicone on the UV protection of cotton fabrics – was monitored by the UV-A and UV-B (Table 3) transmission and UPF (Figures 5 and 6). It is evident that high effects in textile cleaning of genetic and added impurities such as waxes, protein substances, pectin and other during scouring and bleaching in peroxide baths, where pigments are removed [16], result in low UV protection. UPF of bleached cotton fabric is 11.8, which makes it non-rateable for UV protection.

From the results shown in Table 3 and in Figure 5, it can be seen that both applied FWAs, stilbene disulphonic acid triazine derivative Uvitex RSB and distyryl biphenyl derivative Uvitex NFW, even at low concentration, lead to higher UPF ($UPF_{B\text{-}RSB\text{-}1}$ = 46.8, $UPF_{B\text{-}NFW\text{-}1}$ = 121.7), resulting in excellent UV protection. By absorbing UV-A radiation, optical brightened fabrics transform this radiation into blue fluorescence, which leads to maximum UV protection in higher concentrations ($UPF_{B\text{-}RSB\text{-}50}$ = 716.3, $UPF_{B\text{-}NFW\text{-}1}$ = 656.6). Since cotton fabrics of the highest FWAs concentrations have the highest UPF, it confirms that FWA insures high protection of UV radiation. When comparing applied FWAs, stilbene disulphonic acid triazine derivative Uvitex RSB and distyryl biphenyl derivative Uvitex NFW, it can be seen that in lower concentrations, distyryl biphenyl derivative (i.e. 1 and 5 g/l) gives off better UPF, whilst stilbene disulphonic acid triazine derivative gives off better UPF at higher FWA concentrations (10 and 50 g/l). It is assumed certain, but different, accumulation of FWAs.

From Table 3, it can be seen that zeolite nanoparticles increase fabric UV protection from non-rateable to good one $UPF_{B\text{-}Z}$ = 20.5. The reason for this is UV-R scattering resulted in lower UV-A and UV-B transmission. Additionally, zeolite increases fabric surface area resulting in higher adsorption of FWA. Therefore, UPF values

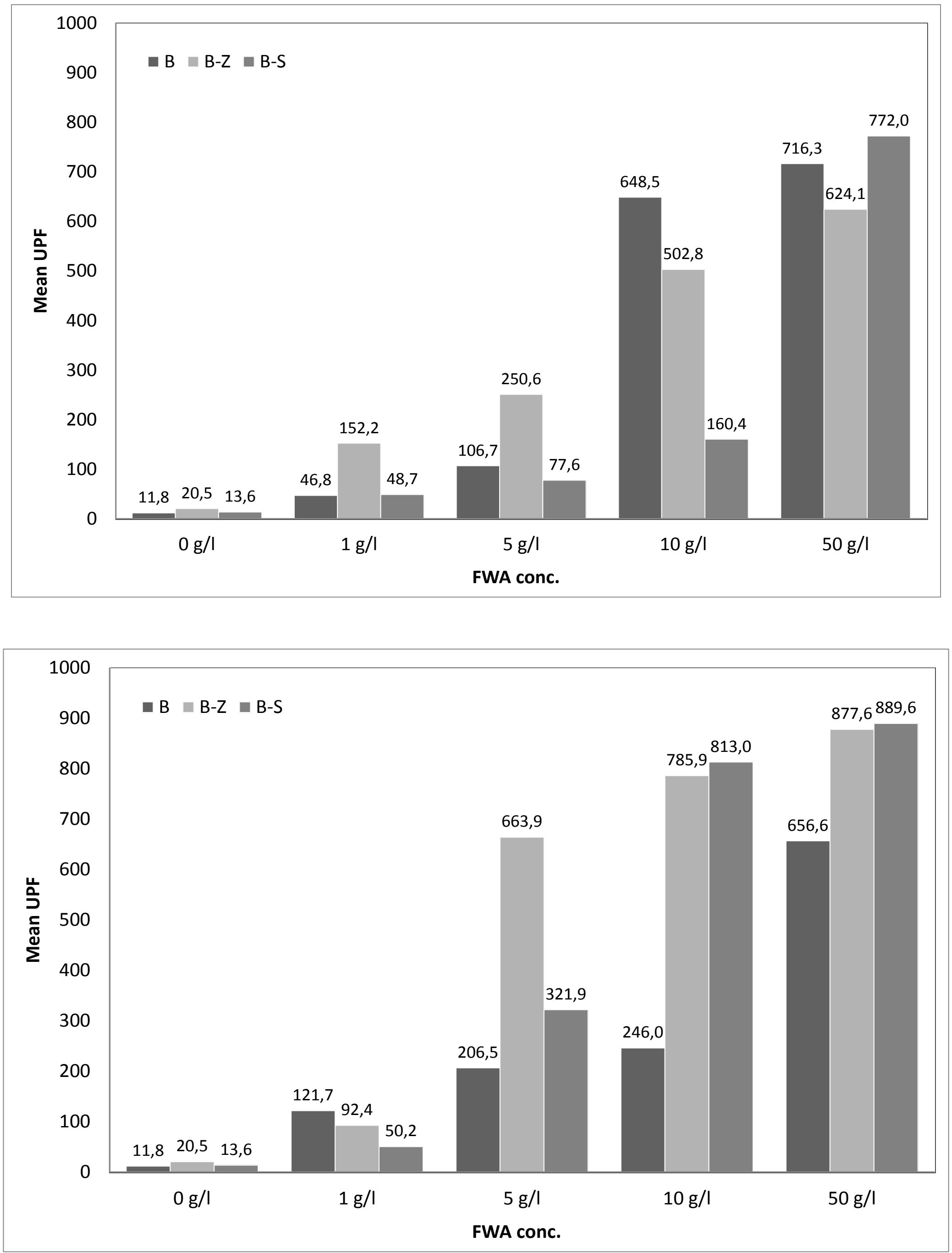
Table 2. Mean UPF, UV-A and UV-B transmission, calculated UPF and UV protection rating according to AS/NZS 4399:1996 of FWA, zeolite and silicone-treated cotton fabrics.

Sample	Mean UPF	τ_{UVA}	τ_{UVB}	Calculated UPF	UPF rating	
B	24.034	11.963	7.198	11.798	10	Non-rateable
B-Z	21.259	7.044	3.823	20.521	20	Good
B-S	14.111	19.412	5.376	13.634	10	Non-rateable
B-RSB-1	55.779	1.880	1.668	46.832	45	Excellent
B-RSB-5	120.219	1.204	0.761	106.698	50+	Excellent
B-RSB-10	683.360	0.721	0.100	648.460	50+	Excellent
B-RSB-50	768.730	0.683	0.100	716.340	50+	Excellent
B-Z-RSB-1	169.589	0.998	0.475	152.166	50+	Excellent
B-Z-RSB-5	280.844	0.889	0.305	250.648	50+	Excellent
B-Z-RSB-10	626.726	0.778	0.127	502.805	50+	Excellent
B-Z-RSB-50	683.360	0.739	0.100	624.128	50+	Excellent
B-S-RSB-1	51.974	1.881	1.690	48.671	45	Excellent
B-S-RSB-5	82.053	1.493	1.108	77.556	50+	Excellent
B-S-RSB-10	197.823	1.012	0.449	160.399	50+	Excellent
B-S-RSB-50	827.880	0.708	0.100	771.990	50+	Excellent
B-NFW-1	135.973	0.877	0.867	121.661	50+	Excellent
B-NFW-5	247.467	0.834	0.496	206.495	50+	Excellent
B-NFW-10	366.430	0.803	0.358	245.963	50+	Excellent
B-NFW-50	812.910	0.742	0.129	656.602	50+	Excellent
B-Z-NFW-1	114.531	1.035	0.981	92.439	50+	Excellent
B-Z-NFW-5	741.800	0.717	0.122	663.909	50+	Excellent
B-Z-NFW-10	902.170	0.705	0.100	785.938	50+	Excellent
B-Z-NFW-50	932.210	0.688	0.100	877.600	50+	Excellent
B-S-NFW-1	53.166	1.403	2.095	50.182	50	Excellent
B-S-NFW-5	392.274	0.763	0.329	321.905	50+	Excellent
B-S-NFW-10	866.040	0.690	0.100	813.010	50+	Excellent
B-S-NFW-50	928.410	0.688	0.100	889.620	50+	Excellent

of all fabrics treated with FWA and zeolite (B-Z-RSB-1 to B-Z-RSB-50, and B-Z-NFW-1 to B-Z-NFW-50) are higher than if only FWA applied. Since all fabrics achieved excellent UV protection when natural zeolite is applied with other UV absorbing agents, e.g. FWAs, it is to point out that synergistic effect occurred. This phenomenon is more evident when distyryl biphenyl derivative is applied with zeolite.

Treatment with silicone PDMS improves UPF value up to UPF_{B-S} = 13.6, but this cotton fabric is still non-rateable for UV protection. It assumes UV-R reflection from the fabric silicone-treated surface. This softening agent was chosen for this research since it results in highest soft handle properties and improves the sewability; it is resistant to yellowing and not steam-volatile; and the most important, combinable with high-grade finishing agents and optical brightening agents. It is interesting that when applied with stilbene disulphonic acid triazine derivative, it results in similar UPF values; whilst if distyryl biphenyl derivative applied UPF values are even higher. The reason for that is in the molecule structure of FWA. Since distyryl biphenyl derivative has smaller molecule, it is assumed that it can bind to available hydroxyl groups of cotton cellulose left after silicone was bonded. For the stilbene disulphonic acid triazine derivative, it is assumed that competition between the FWA and silicone occurred, and therefore the UPF is lower. However, all the UPF values indicate excellent UV protection.

a.



b.

Figure 5. UV protection expressed via ultraviolet protection factor (UPF) of cotton fabrics treated with (a) stilbene disulphonic acid triazine derivative Uvitex RSB and (b) distyryl biphenyl derivative Uvitex NFW.

Since this research was done on white cotton fabrics, it was interesting to research whiteness and yellowness, and the effect of fluorescence when FWAs were applied. The CIE whiteness degree, yellowing index, relative intensity of fluorescence, maximum of remission (R_{max}) and wavelength (λ_{max}), are presented in Table 3. Remission curves are presented in Figures 6 and 7.

(a) FWA, (b) FWA + zeolite and (c) FWA + silicone.

From Table 3, it is evident that scouring and chemical bleaching resulted in white cotton fabric. High whiteness and outstanding brightness of cotton fabrics were achieved by FWA application regardless of their chemical composition. Based on electronically excited state by energy of ultraviolet radiation, the FWA molecules show the phenomenon of fluorescence, but only if applied in optimal range of concentration. Optimal concentration of fluorescent compound is the one at which the maximum of Φ_{rel} or W_{CIE} is observed [16, 35]. From the results of the whiteness and fluorescence of FWA-treated cotton fabrics, it can be seen that the concentration of 5 g/l is the optimum concentration for both FWAs – stilbene disulphonic acid triazine derivative (W = 132.7) and distyryl biphenyl derivative (W = 135.2). As the whiteness increases, the yellowness lowers to the negative values. At the low concentrations of both FWAs, blue fluorescence neutralizes the yellowness of a

b

c

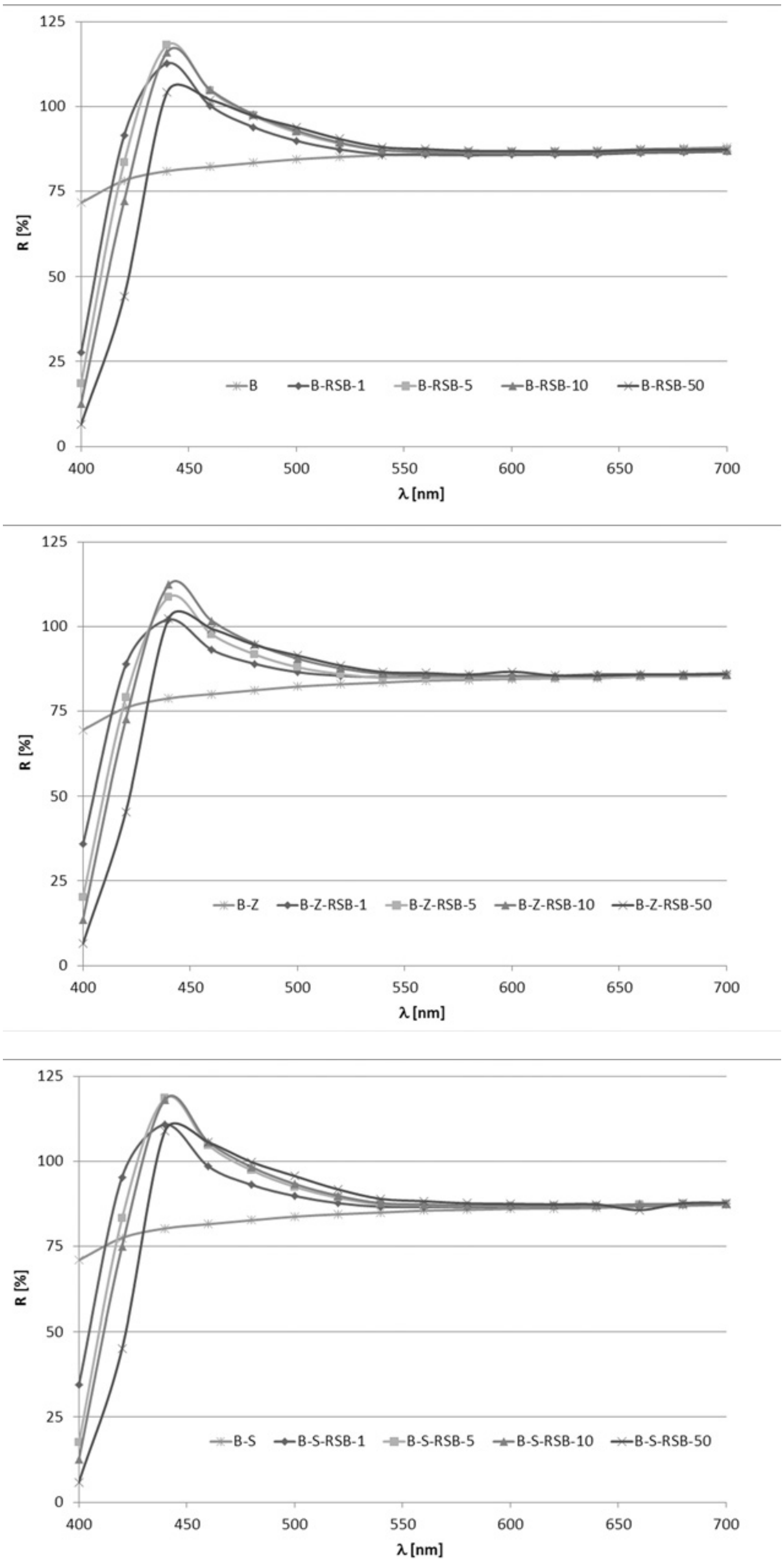


Figure 6. Remission curves of stilbene disulphonic acid triazine derivative treated cotton fabrics. (a) FWA, (b) FWA + zeolite and (c) FWA + silicone.

bleached fabric giving the high luminosity and "most beautiful" white. Applied in the higher concentration than the optimal one from results of remission and wavelength maximums, presented in Table 3 and Figures 5 and 6, it can be seen that the change in emission spectrum occurred. It is a consequence of well-known bathochromic shift of the remission spectrum, for these FWAs applied, from 440 to 450 nm. It comes to a reduction of remission intensity with FWAs concentration (for stilbene disulphonic acid triazine derivative from 117 to 104, and for distyryl biphenyl derivative from 122 to 118), causing a

b

c

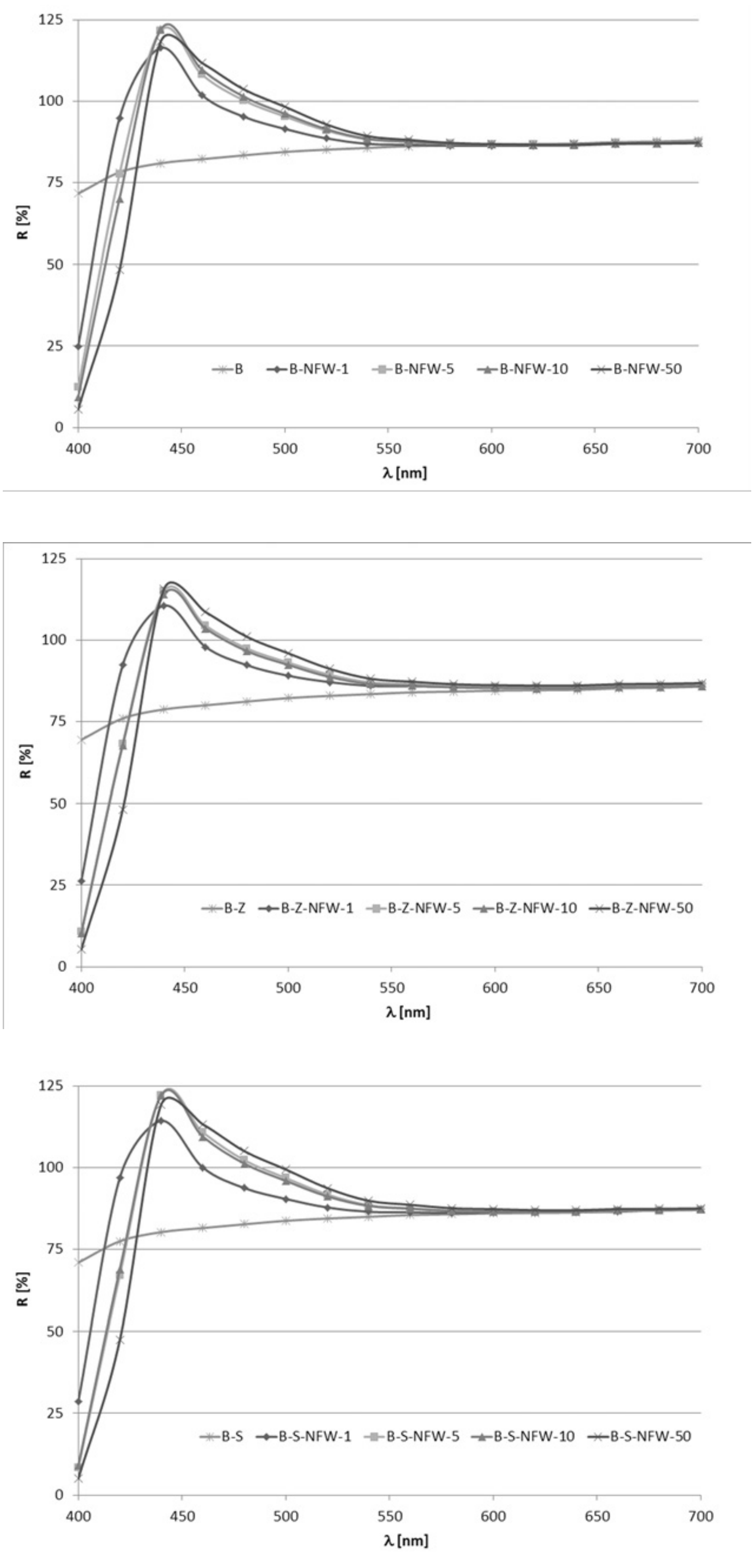


Figure 7. Remission curves of distyryl biphenyl derivative treated cotton fabrics.

the extinction of fluorescence by quenching phenomenon, with a consequence of yellowness, e.g. from 18.2 (B-RSB-5) to 6.2 (B-RSB-50). Considering the chemical construction of FWA, the quenching phenomenon is significantly lower for distyryl biphenyl derivative.

Natural zeolites are yellowish. Its application lowers fabric whiteness, from 71.1 to 68.5, and a small yellowing occurs, from 5.9 to 7.7. However, the surface area increases, such treated fabric absorbs high amounts of FWA, resulting in the change of optimal concentration, which arises to 10 g/l. Additionally,

Table 3 CIE whiteness (W_{CIE}), yellowing index (YI), relative intensity of fluorescence (Φ_{rel}), maximum of remission (R_{max}) and wavelength (λ_{max}),of FWA, zeolite- and silicone-treated cotton fabrics.

Sample	W_{CIE}	YI	Φ_{rel}	R_{max}	λ_{max}
B	71.02	5.89	0	87.93	700
B-Z	68.45	7.66	0	85.73	700
B-S	70.80	6.01	0	87.23	700
B-RSB-1	128.52	16.54	44.2	112.69	440
B-RSB-5	132.72	18.19	70.6	117.99	440
B-RSB-10	126.37	16.16	65.9	115.96	440
B-RSB-50	99.47	6.18	55.5	104.19	450
B-Z-RSB-1	110.96	9.40	31.0	102.06	440
B-Z-RSB-5	118.65	13.02	59.9	108.64	440
B-Z-RSB-10	121.99	14.44	68.7	112.30	440
B-Z-RSB-50	97.33	5.66	50.8	102.36	450
B-S-RSB-1	124.80	14.51	40.3	110.78	440
B-S-RSB-5	132.54	18.02	72.3	118.48	440
B-S-RSB-10	129.66	17.03	67.1	118.16	440
B-S-RSB-50	107.21	8.96	52.4	109.00	450
B-NFW-1	132.41	17.94	58.7	116.38	440
B-NFW-5	135.17	19.53	73.3	121.61	450
B-NFW-10	124.00	19.35	70.1	122.00	450
B-NFW-50	123.51	15.77	67.2	118.35	450
B-Z-NFW-1	110.95	9.40	49.7	110.58	440
B-Z-NFW-5	118.67	13.02	53.2	114.95	450
B-Z-NFW-10	121.92	14.44	61.1	113.98	450
B-Z-NFW-50	97.39	5.66	55.3	115.70	450
B-S-NFW-1	130.20	16.90	56.4	114.29	440
B-S-NFW-5	135.33	20.10	74.2	122.14	450
B-S-NFW-10	133.87	19.31	73.8	122.06	450
B-S-NFW-50	124.89	16.26	59.2	119.32	450

such high adsorption of FWA leads to synergistic effect on UV protection. As said above, zeolite-treated cotton fabrics give off excellent UV protection after FWA treatment, regardless if stilbene disulphonic acid triazine derivative or distyryl biphenyl derivative applied.

Considering silicone treatment, the results in Table 3 confirm that applied PDMS with amino-alkyl groups (Softycon SRN, Textilcolor) is combinable with both FWAs – stilbene disulphonic acid triazine derivative and distyryl biphenyl derivative optical brightening agents. Not only it is resistant to yellowing but also it improves fabric whiteness at higher FWA concentrations as well. Structurally, amino functional silicone consists of an inorganic siloxane backbone with pendant methyl groups – PDMS with additional amino-alkyl groups (Figure 8). It is to assume that hydrogen bonding and Coulombic forces of interaction between the partly protonated amino-alkyl groups of the silicone and hydroxy groups at the cellulose surface are reinforced by additional interaction between the dimethyl siloxane units and the FWAs.

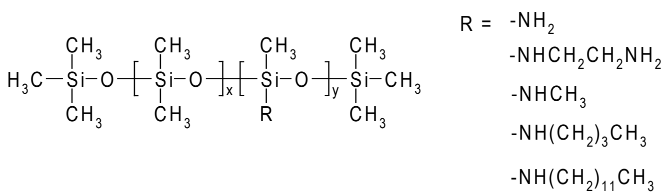


Figure 8. Polydimethylsiloxane (PDMS) with amino-alkyl groups.

Since the fabric hand is an important aesthetic and comfort characteristic, usually defined according to Vigo [36] as “the subjective assessment of a textile material obtained from the sense of touch” or according to AATCC EP 5 as “the tactile sensation or impressions which arise when fabrics are touched, squeezed, rubbed or otherwise handled”, it was evaluated by subjective assessment, respectively. Results are presented in Table 4.

Cotton fabrics generally have soft handle and good drape. If absorptivity is taken in account as well, it is the one of the most comfortable wear. From Table 4, the zeolite treatment effects fabric hand is quite evident. All the evaluators have described these fabrics little bit stiff and rough. Zeolites, as micro- and nano-particles, penetrate into the cotton fabric, but most of those particles remain on the fabric surface. Application of zeolites with FWAs results in similar evaluation. These results clearly indicate a worse fabric hand, but it significantly contributes to a better UV protection. Silicone application significantly improves fabric hand. All evaluators described these fabrics much softer and smoother. The mobility of the silicone polymer segments is favoured by electrostatic repulsion between cationic groups, which results in the optimum degree of softness.

4. Conclusions

Primary prevention and early detection are essential regarding deduction of melanoma incidence. Since chemically bleached cotton fabrics are non-rateable for UV protection, additional treatments are necessary. In this paper, the UV protective properties of cotton fabric were achieved by light conversion and scattering. Treatment with FWAs in wide concentration range without/with the addition of natural zeolite or silicone – PDMS

Table 4. Fabric hand subjective evaluation for FWA, zeolite- and silicone-treated cotton fabrics.

Sample	Attribute and rank			
	Compression	Bending	Shearing	Surface
B	Soft	Limp	Firm	Smooth
B-Z	Little bit hard	Little bit stiff	Firm	Rough
B-S	Softer	Limp	Firm	Smoother
B-RSB-1	Soft	Limp	Firm	Smooth
B-RSB-5				
B-RSB-10				
B-RSB-50				
B-Z-RSB-1	Little bit hard	Little bit stiff	Firm	Rough
B-Z-RSB-5				
B-Z-RSB-10				
B-Z-RSB-50				
B-S-RSB-1	Softer	Limp	Firm	Smoother
B-S-RSB-5				
B-S-RSB-10				
B-S-RSB-50				
B-NFW-1	Soft	Limp	Firm	Smooth
B-NFW-5				
B-NFW-10				
B-NFW-50				
B-Z-NFW-1	Little bit hard	Little bit stiff	Firm	Rough
B-Z-NFW-5				
B-Z-NFW-10				
B-Z-NFW-50				
B-S-NFW-1	Softer	Limp	Firm	Smoother
B-S-NFW-5				
B-S-NFW-10				
B-S-NFW-50				

leads to multifunctionality – high whiteness, neutralization of yellowness, giving to the fabric high luminosity, soft hand and protection against UV radiation.

By absorbing UV-A radiation and transforming it into blue fluorescence, optical brightened fabrics give off excellent UV protection. As higher concentration of FWAs was applied, better UV protection was achieved. On the other hand, FWAs show the phenomenon of fluorescence only if applied in optimal range of concentration. In the range of higher concentration quenching of fluorescence occurs, resulting in fabric yellowness. The harmonic change from bleached cotton fabric, through brilliant whiteness, to yellowness has been more outlined for distyryl biphenyl derivative.

Applying the natural zeolite to the cotton fabric surface, micro and nanoparticles scatter UV-R, lowering UV-A and UV-B transmission, leading to good UV protection. Zeolite increases fabric surface area resulting in higher adsorption of FWA. Zeolite and FWAs showed synergism and yield excellent UV protection. This phenomenon is more evident if distyryl biphenyl derivative is applied with zeolite.

Reflection of UV light from the silicone PDMS on the fabric surface improved UV protection, whilst fabric whiteness is unchanged. FWA, distyryl biphenyl derivative additionally improved UV protection when synergistic effect with PDMS occurred.

Cotton fabrics showed soft hand. Zeolite improved UV protection; however, comfort and aesthetics were clearly deteriorated. On the other hand, these properties have been improved to a significant extent by the application of polydimethylsiloxane.

It is to point out that achieved UV protection is excellent and can even obey that request regarding UV index during the summer time in Mediterranean countries, as well as Australia and USA, which acquire UPF >150.

ACKNOWLEDGEMENTS

Authors thank Ministry of Science, Education and Sports of Republic of Croatia for funding this research.

References

[1] *Robins, P., Perez, M. (1996). Understanding melanoma; The Skin Cancer Foundation (New York).*

[2] *Barbarić, J., Znaor, A. (2012). Incidence and mortality trends of melanoma in Croatia. Croatian medical journal, 53 (2), 135-140.*

[3] *Šitum M. (2012) Melanoma. Chapter 57 in Giddiness in common dermatoses and skin cancers diagnostics and treatments (in Croatian: Smjernice u dijagnostici i liječenju najčešćih dermatoza i tumora kože). Naklada Slap (Jastrebarsko).*

[4] *Armstrong, B. K., Kricker, A. (1993). How much melanoma is caused by sun exposure? Melanoma Res 3 (6), 395-401.*

[5] *Berwick, M., Armstrong, B. K., Ben-Porat, L., Fine, J., Kricker, A., Eberle, C., Barnhill, R. (2005) Sun exposure and mortality from melanoma. J Natl Cancer Inst 97(3), 195-199.*

[6] *Tarbuk, A., Grancarić, A. M., Šitum, M. (2014) Discrepancy of Whiteness and UV Protection in Wet State, Collegium Antropologicum 38(3), (in press).*

[7] *Lugović Mihić, L.; Bulat, V.; Šitum, M.; Čavka, V.; Krolo, I. (2008). Allergic hypersensitivity skin reactions following sun exposure. Collegium antropologicum 32 (suppl 2); 153-157.*

[8] *Šitum, M.; Buljan, M.; Čavka, V.; Bulat, V.; Krolo, I.; Lugović Mihić, L. (2008). Skin changes in the elderly people--how strong is the influence of the UV radiation on skin aging? Collegium antropologicum 32 (suppl 2); 9-13.*

[9] *Diffey, B. L. (1991). Solar ultraviolet radiation effects on biological systems. Physics in Medicine and Biology 36(3), 299-328.*

[10] *Eckhardt, C., H. Rohwer (2000). UV protector for cotton fabrics. Textile Chemist and Colorist, 32(4), 21-23.*

[11] *Hoffmann, K., Laperre, J., Avermaete, A., Altmeyer, P., Gambichler, T. (2001). Defined UV protection by apparel textiles, Arch Dermatol. 137(8),1089-1094.*

[12] *Gambichler, T., Rotterdam, S., Altmeyer, P., Hoffmann, K. (2001). Protection against ultraviolet radiation by commercial summer clothing: need for standardised testing and labelling, BMC Dermatology 1 (6).*

[13] *Reinert, G., Fuso, F., Hilfiker, R., Schmidt, E. (1997). UV-protecting properties of textile fabrics and their improvement. Textile Chemist and Colorist 29(12), 36-43.*

[14] *Gies, P. H., Roy, C. R., Toomey, S., Mclennan, A. (1998). Protection against solar ultraviolet radiation, Mutation Research 422, 15-22.*

[15] *Tarbuk, A., Grancarić, A.M., Šitum, M., Martinis, M. (2010). UV Clothing and Skin Cancer, Collegium Antropologicum. 34 (Suppl.2); 179-183.*

[16] *Grancarić, A. M., Tarbuk, A., Dumitrescu, I., Bišćan J. (2006). UV Protection of Pretreated Cotton – Influence of FWA's Fluorescence, AATCC Review 6(4), 44-48.*

[17] *Tarbuk, A., Grancarić, A.M., Jančijev, I., Sharma, S. (2006). Protection against UV radiation using a modified polyester fabric, Tekstil 55 (8), 383-394.*

[18] *Hilfiker, R., Kaufmann, W., Reinert, G., Schmidt, E. (1996). Improving sun protection factors of fabrics by applying UV-absorbers. Text. Res. J. 66(2), 61-70.*

[19] *Algaba, I., Riva, A., Crews, P. C. (2004). Influence of Fiber Type and Fabric Porosity on the UPF of Summer Fabrics, AATCC Review, 4(2), 26-31.*

[20] *Dobnik Dubrovski P., Dumitrescu J., Zabetakis A. (2004). Special Finishing Treatments and UPF improvement; in Book of Proceedings, 2nd International Textile, Clothing & Design conference – Magic World of Textiles, (Ed. Z. Dragčević), Dubrovnik, 3-6 October 2004, 340-346.*

[21] *Grancarić, A.M., Penava, Ž., Tarbuk, A. (2005) UV Protection of Cotton – the Influence of Weawing Structure, Hemijska industrija (Serbian Society of Chemical Industry Journal) 59(9-10), 230-234.*

[22] *Grancarić, A. M.; Tarbuk, A.; Marković, L. (2007). UV Protection with Zeolite Treated Cotton Knitted Fabric - The Influence of Yarn Linear Density; Buletinul Institutului Politehnic din Iasi. LIII (LVII) (5); 441-446.*

[23] *Grancarić, A. M., Tarbuk, A. (2009). EDA Modified PET Fabric Treated with Activated Natural Zeolite Nanoparticles, Materials Technology: Advan. Performance Materials, 24 (1); 58-63.*

[24] *Grancarić, A. M., Tarbuk, A., Kovaček, I. (2009). Nanoparticles of Activated Natural Zeolite on Textiles for Protection and Therapy, Chem. Ind. & Chem. Engineering Quarterly. 15(4), 203-210.*

[25] *Cox Crews P., Zhou Y. (2004). The effect of wetness on the UVR transmission of woven fabrics. AATCC. Review, 4(8), 41-43.*

[26] *Riva, A., Algaba, I., Prieto, R. (2007). Optical Brightening Agents Based on Stilbene and Distyryl Biphenyl for the Improvement of Ultraviolet Protection of Cotton Fabrics, Tekstil 56 (1), 1-6*

[27] *Zhou Y., Cox Crews P., (1998). Effect of OBAs and repeated launderings on UVR transmission through fabrics. Textile Chemist and Colorist 30 (11), 19-24.*

[28] *Dekanić, T., Pušić, T., Soljačić I. Impact of artificial light on optical and protective effects of cotton after washing with detergent containing fluorescent compounds, Tenside Surf. Det. 51 (2014) 5, doi: TS110329 – 16.7.14 dk/stm köthen*

[29] *Tang, E., Cheng, G., Pang, X., Ma, X., Xing, F. (2006). Synthesis of nano-ZnO/poly(methyl methacrylate) composite microsphere through emulsion polymerization and its UV-shielding property, Colloid and Polymer Science 284 (4), 422-428.*

[30] *Farouk, A., Textor, T. Schollmeyer, E. Tarbuk, A. Grancarić, A. M. (2010). Sol-gel Derived Inorganic-organic Hybrid Polymers Filled with ZnO Nanoparticles as Ultraviolet Protection Finish for Textiles, AUTEX research journal 10 (8); 58-63.*

[31] *Sundaresan, K., Sivakumar A., Vigneswaran, C., Ramachandran, T. (2012). Influence of nano titanium dioxide finish, prepared by sol-gel technique, on the ultraviolet protection, antimicrobial, and self-cleaning characteristics of cotton fabrics, Journal of Industrial Textiles 41 (3), 259-277.*

[32] *Xin, J. H., Daoud, W. A., Kong, Y. Y. (2004). A new approach to UV-blocking treatment for cotton fabrics. Text Res J 74:97–10.*

[33] *Ranby, B., Rabek, J. F. (1975). Photodegradation, Photo-oxidation and Photostabilization of Polymers, John Wiley, (London, New York, Sydney and Toronto), 6-27.*

[34] *Grancarić, A. M.; Prlić, I., Tarbuk, A., Marović, G. (2011). Activated Natural Zeolites on Textiles: Protection from Radioactive Contamination in Intelligent Textiles and Clothing for Ballistic and NBC Protection; NATO Science for Peace and Security Series B: Physics and Biophysics (eds. Kiekens, P.; Jayaraman, S.) Springer, (Heidelberg), 157-176.*

[35] *Grancarić A. M., Soljačić, I. (1980). Einflus der Konzentration optischer Aufheller auf Fluorescenz und Weissgrad von Baumwollgeweben, Melliand Textilberichte 61, 242-245.*

[36] *Vigo, T.L., (1994). Textile Processing and Properties, Elsevier, (Amsterdam).*