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SKIN CANCER AND UV PROTECTION

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Abstract:

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. The primary cause of skin cancer is long exposure to solar ultraviolet radiation (UV-R) crossed with the amount of skin pigmentation and family genetics. It is believed that in childhood and adolescence, 80% of UV-R gets absorbed while 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. Reducing the exposure time to sunlight, using sunscreens and protective textiles are the three ways of UV protection. Most people think that all the clothing will protect them, but it does not provide full sun screening properties. Literature sources claim that only 1/3 of the spring and summer collections tested give off proper UV protection. This is very important during the summer months, when UV index is the highest. Fabric UV protection ability highly depends on large number of factors such as type of fiber, fabric surface, construction, porosity, density, moisture content, type and concentration of dyestuff, fluorescent whitening agents, UV-B protective agents (UV absorbers), as well as nanoparticles, if applied. For all of these reasons, in the present paper, the results of UV protecting ability according to AS/NZS 4399:1996 will be discussed to show that standard clothing materials are not always adequate to prevent effect of UV-R to the human skin; and to suggest the possibilities for its improvement for this purpose enhancing light conversion and scattering. Additionally, the discrepancy in UV protection was investigated in distilled water as well as Adriatic Sea water.

Keywords:

UV protection, skin cancer, cotton, textiles, fluorescence, natural zeolite

1. Introduction

The incidence of skin cancer is increasing by epidemic proportions. One person dies of melanoma skin cancer every hour; between 2 and 3 million non-melanoma skin cancers and 132,000 melanoma skin cancers occur globally each year according to World Health Organization (WHO) [1]. Because of highly visible location, it is more easily diagnosed and treated than other types of cancer. Basal cell carcinoma (BCC) and squamous cell carcinoma (SCC), referred to as non-melanoma skin cancers (NMSC) [2]. These skin tumors are the most common tumors in human population, but due to very low mortality rate, until recently, there was no systematically collected data in the National Cancer Registries. On the other hand, most of the studies were focused on white populations in Australia, the U.S.A. and Europe; *while* limited data is available for other skin types as naturally brown and black people. The incidence and mortality are usually expressed as a rate per 100,000 persons per year. Worldwide, the incidence for NMSC varies widely; with the highest rates for BCC in Australia > 1000 and the lowest rates in parts of Africa < 1 person [2]. The average incidence rates for BCC in the U.K. were 76.21, what appears a greater rate when compared with the rest of Europe, for example, Italy and Switzerland 70, Slovakia 38, Croatia only 33.6 for BCC [2, 3]. In USA, south west states like Arizona and

New Mexico reported 935.9, *while* northern states reported only 170 incidence rate for BCC. SCC have much lower rates, for example, in Europe, for males in UK 22.65, in Switzerland 14.2, the highest rate is reported in Sweden 34.4 and the lowest in Croatia 8.9. In the USA, rate for SCC in southern states is 290, and in northern less than 60. In Australia, rates are significantly higher, > 500 [2–4]. BCC remains the most common skin neoplasm, and simple excision is generally curative. SCC detected at an early stage and removed promptly are almost always curable and cause minimal damage. However, in most cases, SCC recurs, especially in the same skin area or nearby within the first 2 years after surgery. If left untreated, it can penetrate the underlying tissues and even metastasize to local lymph nodes, distant tissues, and organs and can become fatal.

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 [5–9]. The reason for that is most likely that in most cases, melanoma was diagnosed in an advanced stage. The world's highest incidence of melanoma is in Australia and New Zealand, more than twice as high as in North America, or 5 times higher than Europe. For instance, in Australia, in 2012, ASR was 62.7 for men and 39.9 for women with mortality of 8.9 for men and 3.5 for female

[4]. In 2008, Croatia had an intermediate melanoma incidence, with the ASR of 8.7 for men and 7.0 for women. However, with the ASR of 3.5 for men and 1.8 for women, Croatia had the third highest male and fourth highest female mortality [5].

There are four basic types of melanoma (Figure 1). Superficial spreading melanoma (SSM) is the most common type, accounting 60–70% of all cases. This is the one most often seen in young people. It can be found almost anywhere on the body, but is most likely to occur on the trunk in men, the legs in women, and the upper back in both. Nodular melanoma (NM) is usually invasive at the time it is first diagnosed. The malignancy is recognized when it becomes a bump. The most frequent locations are the trunk, legs, and arms, mainly of elderly people, as well as the scalp in men. This is the most aggressive of the melanomas, and is found in 15–30% of all cases. Lentigo maligna melanoma (LMM) usually appears in the elderly, arising on chronically sun-exposed, damaged skin on the face, ears, arms, and upper trunk accounting 5–15% of all cases. Acral lentiginous melanoma (ALM) also spreads superficially before penetrating more deeply. It is quite different from the others, though, as it usually appears as a black or brown discoloration under the nails or on the soles of the feet or palms of the hands, accounting 2–8% of all cases. This type of melanoma is sometimes found on dark-skinned people, and can often advance more quickly than superficial spreading melanoma and lentigo maligna. It is the most common melanoma in African-Americans and Asians, and the least common among Caucasians. The rare types melanomas are: Salivary gland melanoma, which occurs in < 1% of all cases; Amelanotic melanoma, usually pink, red, purple, or of normal skin color; Desmoplastic (Neurotropic) melanoma, a rare cutaneous condition (< 4%) which is deeply infiltrating type with an abundance of fibrous matrix on the head and neck region; "Nevoid" or "spitzoid" melanoma, which is < 1% of all cases, usually in young people. The common treatment for localized (early stage) melanoma is surgery, and in the majority of cases, this is the only treatment required. If it spreads, it is usually fatal. Therefore, the most important is early melanoma diagnostics-ABCDEFG rule: A-asymmetry, B-border, C-color, D-diameter, E-elevation, evolution, F-feeling, G-growth [7].

In general, melanoma incidence rates in white populations increase with proximity to the Equator, and vary across Europe, with the highest rates for both sexes in Switzerland, Denmark, Norway, Sweden, and the Netherlands and the lowest rates in Central and Southeastern Europe. Recent trends in melanoma incidence and mortality have been less studied in both Mediterranean and Eastern European populations [6]. On the other hand, European Union supported research of UV protective textiles for the sunshade constructions, umbrella covers, hats, knitted and woven fabrics in Eastern European and Mediterranean countries of high UV index. The primary cause of skin cancer is long exposure to solar UV-R crossed with the amount of skin pigmentation and family genetics. 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 is known that, beside the UV-B radiation with biochemical reactions, the UV-A can also initiate deleterious biochemical reactions [5–11]. Dangerous UV-B (I = 280–320 nm) 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 [3–33]. 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. It is believed that in these periods of life, 80% of UV-R gets absorbed, while in the remaining, 20% gets absorbed later in the lifetime [7,10]. That is the main reason why the melanoma is the most common form of cancer for young adults 25–29 years old and the second most common form of cancer for young people 15–29 years old [34].

This suggests that proper and early photoprotection may reduce the risk of subsequent occurrence of skin cancer. Reducing the exposure time to sunlight, using sunscreens and protective textiles are the three ways of UV protection. Designing and engineering of UV protective fabrics, that are mostly clothing and accessories made of textiles, for example, hats, shoes, shade structures such as umbrellas, awnings, and baby carrier covers, etc, can be accomplished by chemical approach. UV clothing can show UV protection, but in most cases, it does not provide full sun screening properties. Literature sources claim that only 1/3 of the spring and summer collections tested give off proper UV protection [13]. This is very important during summer months when UV index is the highest. In contact with textile fabric, UV radiation can be reflected and/or scattered from fabric surface, or get absorbed or transmitted [18]. Most people think all clothing will protect them, but that is not the case. For instance, jeans offer a very good level of protection, as do garments made from other tightly woven, dark fabrics. However, on a hot summer day, those are not the kinds of clothing people usually reach for. More often, when they are

| SSM | NM | LMM | ALM |

Figure 1. The four basic types of melanoma [7]

on the beach, they wear T-shirt, as well during swimming in the sea, thinking that it will protect them from harmful UV-R.

The UV protection highly depends on large number of factors such as type of fiber, fabric surface, construction, porosity, density, moisture content, type and concentration of dyestuff, fluorescent whitening agents (FWA), UV-B protective agents (UV absorbers), as well as nanoparticles, if applied [11]. Since the back sides in men and women, as well as the lower limbs in women, are the most common site for melanomas, fabric UV protection in this paper was researched on the pretreated, finished and modified knitted fabrics for T-shirts, and ladies pantyhoses. The possibilities for its improvement enhancing light conversion and scattering are shown. Additionally, the discrepancy in whiteness and UV protection was investigated in distilled water as well as Adriatic Sea water.

2. Experimental

Knitted fabrics for T-shirts, a circular weft single jersey, of mass per surface area of 130 g/m^2 were made in 56 cm (22 inch) width in tubular form, having 11 whales/cm and 12 courses/cm. The yarn used was polyester (PES) of 25 tex, and of 100% cotton of 17 tex, 20 tex, and 25 tex. The cotton/PES blend was made as well. Ladies pantyhoses of 100% PA 6.6 of 40 den

in white, black, and skin color available in the market were selected for the research. Cotton knitted fabric was pretreated, modified, and finished-scoured with alkali, and with pectinase, bleached, mercerized, cationized and treated with FWA and UV absorber. It was dyed in black, navy blue, purple, and beige color in industrial conditions. The labels and treatments are listed in Table 1.

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. This instrument measures sunlight transmission in the range from 280 to 400 nm. The irradiation applied is a simulation of a part of sunlight spectrum, as measured at noon on January 17th 1990 in Melbourne, Australia, while the results obtained indicate the degree of protection offered by the fabric when worn directly on the skin. The *ultraviolet protection factor* (*UPF*), which indicate 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, was calculated automatically. According to the standards, excellent protection is when UPF is higher than 40 (Table 2). However, for the countries with UV index 7–10 as Mediterranean countries, Australia, and USA, the UPF should be 15 times higher than UV index [18].

Table 1. Labels and treatments of cotton knitted fabrics

Label	Treatment
R	Raw-untreated
S	*Traditional scouring* with NaOH-3% NaOH and 2 g/l nonionic surfactant Kemonecer NI (Kemo), t = 2h, T = 100°C in autoclave (Scholl) *Enzymatic scouring* with neutral pectinase-3 g/l Beisol PRO (Bezema), 1 g/l Felosan NOG (Bezema); pH 7, t = 50 min, T = 80°C, LR 1:10
B	Chemical bleaching (HP)-in industrial conditions in peroxide baths
BM	Mercerization in 24% NaOH, 8 g/l Subitol MLF
BMC	Cationization with 3-chloro-2-hydroxypropyl-trimetyl ammonium chloride (CHPTAC) (Fluka), during the mercerization process [35,36]
FWA	FWA treatment by exhaustion method in Turbomat (Mathis), t = 30 min, T = 90°C, LR 1:30 *Uvitex BHT* (Ciba-Geigy AG)-derivative of stilbene disulphonic acid in optimal conc. of 0.6% (owf) *Uvitex BAM* (Ciba-Geigy AG)-bis (4,4'-triazinylamino)-stilbene-2,2'-disulfonic acid derivative in wide concentration range
UV	UV absorber treatment by exhaustion method in Turbomat (Mathis), t = 30 min, T = 90°C, LR 1:30 *Tinofast CEL* (Ciba) on the base of oxalanilide *Tinosorb FD* (Ciba-Geigy AG) -stilbene disulphonic acid triazine derivative in wide concentration range by exhaustion method
Z	Natural zeolite treatment by impregnation or during the mercerization process [37]

Table 2. UV protection rating according to AS/NZS 4399:1996

UPF range	UPF rating	UV-R protection category	UV-R blocking [%]
< 14	0, 5, 10	non-rateable	< 93.3
15–24	15, 20	good	93.3–95.8
25–39	25, 30, 35	very good	95.9–97.4
> 40	40, 45, 50, 50+	excellent	> 97.5

Remission spectrophotometer SF 600 PLUS CT (Datacolor) was used for measuring spectral characteristics of cotton and PES/cotton blend fabrics. CIE whiteness degree (W_{CIE}) was calculated automatically according to ISO 105-J02:1997 *Textiles - Tests for color fastness - Part J02: Instrumental assessment of relative whiteness.* The discrepancy of color, *dE*,* in wet state was determined through color differences of color coordinates automatically.

3. Results and discussion

The obtained results according to AS/NZS 4399:1996 are summarized in Figures 2–4 showing mean UPF value of differently pretreated, modified, and finished knitted fabrics cotton and PES for T-shirts, and polyamide pantyhoses.

Considering the results of mean UPF value of T-shirts and pantyhoses shown in Figure 1, it can be seen that PES fabric gives off better UV protection than cotton one, due to the PES benzene rings [18, 26]. White PES T-shirt offers good UV protection (UPF = 33.92), but on the other hand, it is not comfortable due to its low water adsorption. Bleached cotton fabrics is non-rateable for UV protection (UPF = 5.24). Blending with PES increases UPF to 11.35, resulting in UV rating 10, but still it is non-rateable for this purpose.

Dyeing in darker shades significantly improves UV protection as dyes are selective absorbers. All dyes absorb visible light, but some of them also absorb light in the near UV region. On textiles, dyes often provide tangible UV blocking with the structure of dye molecules playing an important role. Other important factors are including type of dye or pigment, present absorptive groups, depth of dyeing, and the uniformity [11, 13]. According to the color physic principles, results of dyed cotton T-shirts confirm that darker colors (e.g. black, navy blue, and dark red) absorb UV-R much more strongly than light pastel colors resulting in excellent UV protection, while beige one gives off only good. For the polyamide ladies pantyhoses dyed in lighter shades, for example, white and skin color, it can be seen that there is no UV protection, while black one gives good protection.

The evaluation of the cotton fabric protection against UV-R regarding the fabric surface construction, porosity, and yarn density is shown in Figure 3b, while the results of UV protection and whiteness of pretreated cotton knitted fabrics, additionally modified by mercerization, cationization and/or zeolite addition, and optically brightened with Uvitex BHT and UV reactive absorber on the base of oxalanilide Tinofast CEL (Ciba) are shown in Figure 3a and in Table 3.

UPF directly depends upon transmission of UV-A and UV-B radiation through fabric. On the other hand, these transmissions
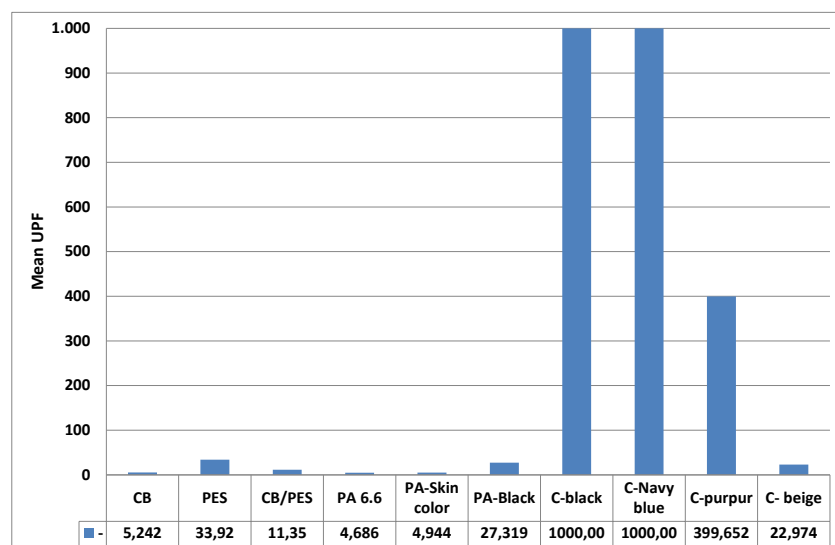

Figure 2. Mean UPF of knitted fabrics for T-shirts— C = cotton, PES = polyester (25 tex); and PA 6.6 (40 den) for pantyhoses

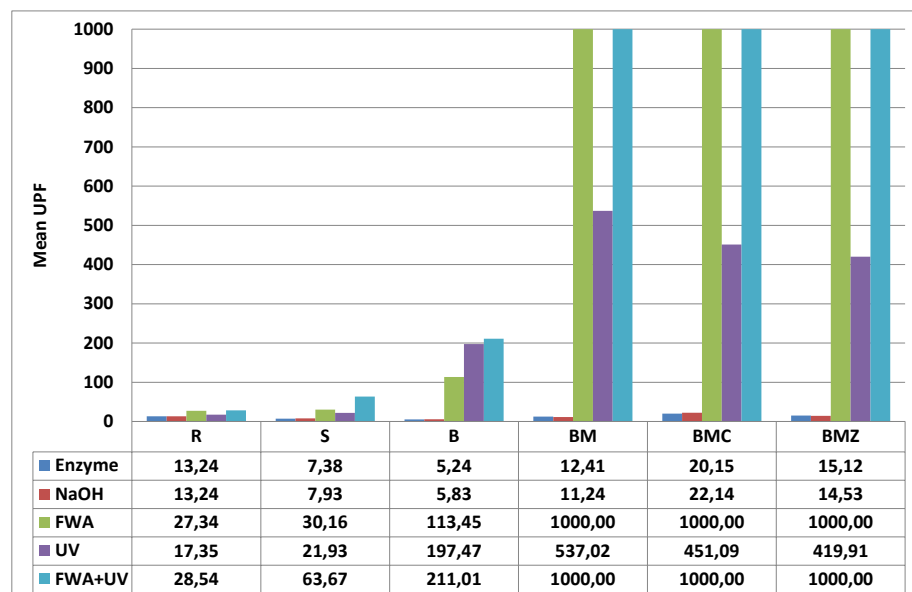|	CB	PES	CB/PES	PA 6.6	PA-Skin color	PA-Black	C-black	C-Navy blue	C-purpur	C- beige
-	5,242	33,92	11,35	4,686	4,944	27,319	1000,00	1000,00	399,652	22,974

Table 3. CIE whiteness (W_{CIE}) of knitted cotton fabrics after pretreatment, modification and treatment with FWA (Uvitex BHT) and UV absorber Tinofast CEL

Fabric	NaOH	Enzyme	FWA (0.9 % Uvitex BHT)	UV (Tinofast CEL)	FWA+UV
R	9.88	9.88	90.23	30.56	80.32
S	37.71	17.51	85.55	33.11	83.60
B	69.87	69.42	125.36	88.61	117.26
BM	51.38	51.48	129.08	94.05	118.54
BMC	47.32	48.15	122.13	92.37	116.93
BMZ	60.22	59.78	120.27	87.82	110.13

depend upon fabric cover factor [20, 21]. It is well known that in every wet treatment, cotton swells, which leads to shrinkage of fabric, lowering the UV-R transmission, resulting in higher UV protection [21, 38]. Shrinkage of knitted fabric in wet condition is affected by stresses accumulated during the production so that relaxation in wet conditions is inevitable. Yarn linear mass density has the same influence on UV protection. The increment of yarn linear mass density lowers fabric porosity and transmission of UV-R, resulting in higher UPF values. Results of UPF in Figure 3b for cotton of 17 tex, 20 tex and 25 tex yarns, regardless of pretreatment, confirm that. For example, for HP bleached fabrics, $UPF_{B\ 17\ tex} = 3.48$ is increasing to $UPF_{B\ 25\ tex} = 5.24$.

Raw cotton fibers contain around 95% of pure cellulose balanced by the non-cellulosic impurities of proteins, oils, waxes, proteins, pectins, carbohydrates, and inorganic materials [36, 38]. Pectin and waxes absorb small quantities of UV-R; therefore, raw fabric has small sun screening properties, but for UV protection, it is still non-rateable (UPF rating 10). Removing impurities like pectin and waxes, etc., during scouring and pigments in chemical bleaching results in lower UV protection even though fabric shrunk. On the other hand, textile cleaning of genetic and added impurities leads to cotton whitening (Table 3). Conventional alkali scouring, which is performed at high temperatures, removes non-cellulosic genetic and added impurities from the cuticles of the cotton fibers, while pectinase scouring degrades only pectin [38]. Therefore, whiteness of
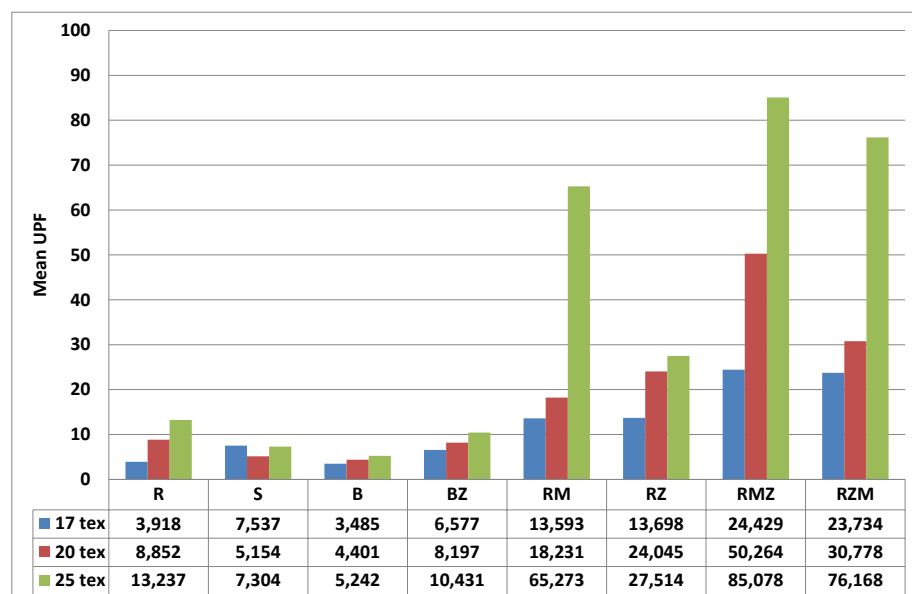
a.

	R	S	B	BM	BMC	BMZ
Enzyme	13,24	7,38	5,24	12,41	20,15	15,12
NaOH	13,24	7,93	5,83	11,24	22,14	14,53
FWA	27,34	30,16	113,45	1000,00	1000,00	1000,00
UV	17,35	21,93	197,47	537,02	451,09	419,91
FWA+UV	28,54	63,67	211,01	1000,00	1000,00	1000,00

b)

	R	S	B	BZ	RM	RZ	RMZ	RZM
17 tex	3,918	7,537	3,485	6,577	13,593	13,698	24,429	23,734
20 tex	8,852	5,154	4,401	8,197	18,231	24,045	50,264	30,778
25 tex	13,237	7,304	5,242	10,431	65,273	27,514	85,078	76,168

Figure 3. UV protection expressed via Ultraviolet protection factor (UPF) of pre-treated and modified knitted cotton fabrics after a. treatment with FWA (Uvitex BHT) and UV absorber Tinofast CEL; b. different yarn density

pectinase-scoured cotton is a little bit lower than alkali-scoured ones (Figure 3a). Bleaching in peroxide baths removes pigments [36, 38] resulting in white cotton, but the UPF values are low, and non-rateable for UV protection. Therefore, it is necessary to modify and/or treat knitted fabric for better UV protection. In mercerization, fabrics highly shrink, resulting in lower transmission of UV-R through a more tightly knitted fabric. Therefore, UV protection of mercerized cotton is good (UPF > 15). Cationization during mercerization results in good UV protection while treatment with UV absorber leads to very good UV protection. Mercerization and cationization leeds to small lost of fabric whiteness and small yellowing occurs.

Textile finishing agents for UV protection can be incorporated into the fiber matrix, or it can be applied to the surface of the fabric [28–31]. The presence of inorganic pigments in the fibers also allows better scattering of light from the substrate, thus providing better protection. 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 to 400 nm reflecting visible and infrared rays. Incorporation of TiO_2 in fiber matrix improves the UV blocking capacity of the fiber. 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 nanoparticles of TiO_2 titanium, and zinc oxide [28–30], and nowadays, of natural zeolite clinoptilolite [22, 32, 33].

Natural zeolites are rock-forming, micro porous 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 ground by a certain tribomechanical processing in a patented machine (Patent: PCT/1B99/00757) yielding 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 [32, 37]. Applied as nanoparticles to textile surface (Figure 3), it scatters the UV-R, resulting in lower UV-A and UV-B transmission. Addition of micronized and nanoparticles of natural zeolite to the bath increases significantly UV protection, regardless of the applying method (BZ, RZ). If applied during the mercerization process (RZM), synergistic effect occurs. Application after mercerization (BMZ, RMZ) results in excellent UV protection because more nanoparticles remain on fabric surface and UV-R scattering is higher. Considering the yarn linear density (Fig. 3b) fabrics of higher yarn linear density, 20 and 25 tex, give off excellent UV protection. If applied with other UV absorbing agents, for example, FWAs, synergistic effect occurs.

Usually, sun protection effect is achieved through the use of UV absorbers [10,15–19]. Molecules of UV absorbers such as benzotriazole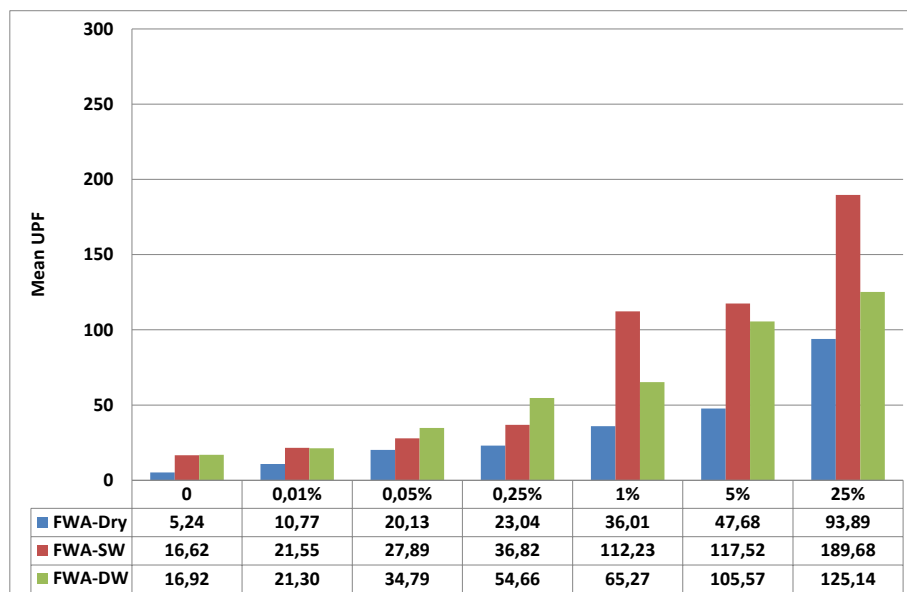 and phenyl benzotriazole, are able to absorb the damaging UV-R range of 290 to 360 nm, and convert it into harmless heat energy. Latest research declares that FWAs and UV absorbers can be applied in washing process and in detergent formulations [26, 27]. After treatment with UV reactive absorber on the base of oxalanilide fabric, whiteness increased a little bit due to its chemical constitution.

Based on electronically excited state by energy of UV-R (usually 340– 370 nm), the molecules of FWAs or optical brightening agents (OBAs) show the phenomenon of fluorescence giving to white textiles the high whiteness of outstanding brightness by re-emitting the energy at the blue region (typically 420– 470 nm) of the spectrum. By absorbing UV-A radiation optical brightened fabrics transform this radiation to blue fluorescence, which leads to the better UV protection [10, 11, 17, 18, 24–27]. From Table 1, it is evident that FWAs increase UPF values from $UPF_{EB} = 4.24$ to $UPF_{EB-FWA} = 113.81$ for bleached cotton; and from $UPF_{EBM} = 12.41$ to $UPF_{EBM-FWA} = 1000$ for mercerized cotton knitted fabrics. It can be seen that maximum UV protection can be accomplished without UV absorber.

Recently, the new fluorescent agents on the base of stilbene derivative were developed for UV-B protection as well. Therefore, FWA and such UV absorber were applied in wide concentration range and the discrepancy in whiteness and UV protection was research in distilled water as well as Adriatic Sea water. Results are presented in Figure 4 and Table 4. It can be seen that FWA applied even in small concentration leads to higher UPF and whiteness. From Table 4, it can be seen that FWA concentration of 0.25% (up to 1%) over weight of fabric is the optimal concentration for this optical brightener. That is the concentration of fluorescent agent at which the maximum of Φ_{rel} or W_{CIE} are observed [17]. Since this UV absorber has similar chemical composition (stilbene disulphonic acid derivative) as FWA, its optimum concentration is 0.25% owf. Applied in the higher concentration then optimal one, as a consequence of bathochromic shift of the remission spectrum, comes to a reduction of remission intensity with FWA and/or UV absorber's concentrations causing the extinction of fluorescence by quenching phenomenon what leads to fabric yellowing. On the other hand, absorption of UV-A radiation leads to excellent UV protection in the higher concentration ($UPF_{FWA5\%} = 47.68$, $UPF_{FWA25\%} = 93.89$). Therefore, cotton fabrics of the highest FWAs concentration have the highest UPF in dry state. By treating cotton fabric with an UV absorber in the wide concentration range, protective effect is more enhanced. Application of small amount of UV absorber results in good, while in optimal concentration or higher, it offers excellent UV protection in dry state. For difference of FWAs, UV absorbers offer UV-B protection as well. However, the fabrics with the highest intensity of fluorescence do not show the highest UPF values. In dry state, UV protection increases with fluorescent agent concentration, regardless of quenching phenomenon.

Considering the results of discrepancy of whiteness, it can be observed that all fabrics get darker when wet and in general, bluer and redder. The reason for that is lower reflection of light from the fabric. In dry fabric, some of the photons of light are absorbed, but some are reflected and land on the eye's retina, which gives the sensation of seeing a certain level of
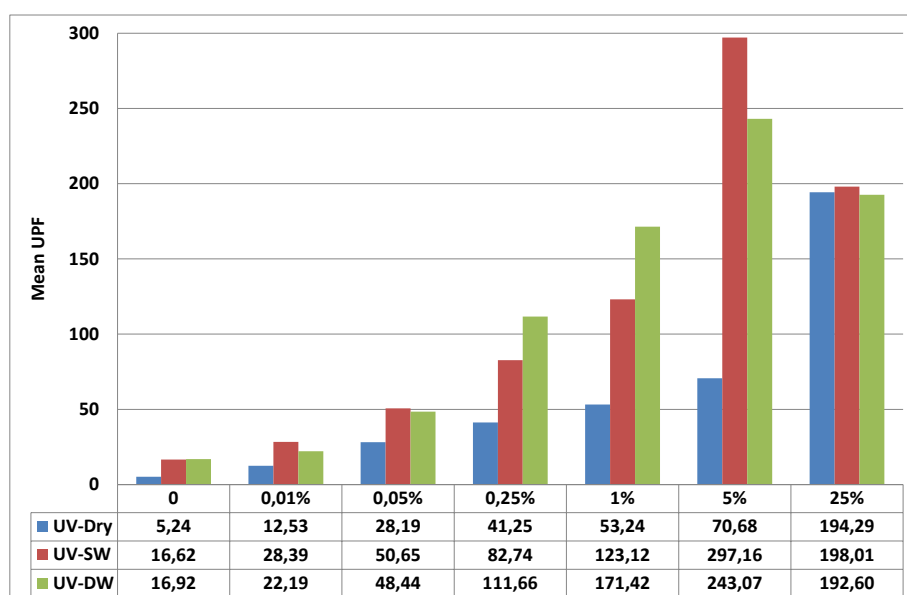
a.

	0	0,01%	0,05%	0,25%	1%	5%	25%
FWA-Dry	5,24	10,77	20,13	23,04	36,01	47,68	93,89
FWA-SW	16,62	21,55	27,89	36,82	112,23	117,52	189,68
FWA-DW	16,92	21,30	34,79	54,66	65,27	105,57	125,14

b.

	0	0,01%	0,05%	0,25%	1%	5%	25%
UV-Dry	5,24	12,53	28,19	41,25	53,24	70,68	194,29
UV-SW	16,62	28,39	50,65	82,74	123,12	297,16	198,01
UV-DW	16,92	22,19	48,44	111,66	171,42	243,07	192,60

Figure 4. UV protection expressed via Ultraviolet protection factor (UPF) of cotton fabrics in dry and wet state treated with stilbene type-a. FWAUvitex BAM, b. UV absorber Tinosorb FD

brightness. But when the fabric gets wet, the water fills the interyarn spacing. When the light falls on the wet fabric, some of it enters the water at one angle and refracts at other because the light waves travel at a slower speed in water than it does in air. Fewer photons of light get back to the eyeball, and therefore the wet fabric "appears" darker than the dry one. The amount of refraction, referred to as the refractive index, is affected by both the salinity and temperature of the water, and therefore there is a difference between fabrics treated with sea and distilled water. It is to point out that the salts in sea water act as quenchers of fluorescence as well, resulting in decreased whiteness. As for the UV protection, it can be said that in wet state, cotton knit fabrics treated with fluorescent agents give off better UV protection than in dry state regardless of the concentration and type of fluorescent agent applied. This phenomenon is more

enhanced for sea water, since the refractive index increases with salinity increment and decrease in temperature. That can be explained by that some of the Sun's radiant energy is reflected from the water surface; it is not absorbed, but additionally scattered by molecules suspended in the water, whilst the other part penetrates the water's surface, absorb and converse to other forms of energy such as heat that warms or evaporates water, or is used by plants to fuel photosynthesis. Considering the applied concentrations, in general, it can be said that higher concentration of fluorescent agent applied, better UV protection was achieved in wet state. The only exception is the highest concentration of UV absorber. From Figure 3b, it can be seen that the UV protection in wet state is lower if applied 25% owf than 5% owf of UV absorber. As it was observed for the CIE whiteness, which significantly decreased,

Table 4. CIE whiteness (W_{CIE}), and the discrepancy of whiteness in wet state of cotton fabrics treated with stilbene type FWA (Uvitex BAM) and UV absorber (Tinosorb FD)

Fabric	FWA			UV		
	WCIE	dE*	Discrepancy	WCIE	dE*	Discrepancy
B	69.4	-	-	69.4	-	-
B-DW	65.6	1.989	Darker greener less yellow	65.6	1.989	Darker greener less yellow
B-SW	67.3	1.528	Darker greener	67.3	1.528	Darker greener less yellow
B-0.01	100.5	-	-	116.3	-	-
B-0.01-SW	97.7	1.610	Darker redder bluer	110.0	2.727	Darker redder less blue
B-0.01-DW	102.9	1.227	Darker redder bluer	110.1	2.181	Darker less blue
B-0.05	138.6	-	-	139.4	-	-
B-0.05-SW	134.8	1.981	Darker redder less blue	137.1	1.699	Darker bluer
B-0.05-DW	136.4	1.639	Darker redder bluer	139.5	1.481	Darker redder bluer
B-0.25	144.8	-	-	145.1	-	-
B-0.25-SW	145.5	1.987	Darker redder bluer	144.2	1.084	Darker less red bluer
B-0.25-DW	147.1	2.160	Darker redder bluer	143.6	1.127	Darker less red
B-1	143.2	-	-	132.7	-	-
B-1-SW	144.8	2.145	Darker redder bluer	133.0	1.356	Darker bluer
B-1-DW	146.6	2.374	Darker redder bluer	130.1	1.136	Darker less red less blue
B-5	133.4	-	-	84.9	-	-
B-5-SW	137.8	2.272	Darker redder bluer	77.9	1.715	Darker greener less blue
B-5-DW	138.0	2.038	Darker redder bluer	83.8	0.928	Darker greener bluer
B-25	115.4	-	-	51.5	-	-
B-25-SW	107.2	1.913	Darker greener less blue	13.9	7.014	Darker greener yellow
B-25-DW	104.1	2.419	Darker greener less blue	28.9	4.448	Darker greener yellow

it can be assumed that this drop of UPF in wet state can be the result of quenching of fluorescence as well. However, achieved UV protection is excellent regardless of its decrease and can even obey that request regarding UV index during the summer time in Mediterranean countries, as well as Australia and USA.

4. Conclusions

Primary prevention and early detection are essential for decreasing melanoma incidence. Considering prevention, especially in childhood and adolescence, it is necessary to apply sun screening lotions and wear adequate clothing, not forgetting that UV-A does not lead to vitamin D synthesis. Blocking all UV-R can lead to vitamin D deficiency, which is estimated to affect 1/3 of Australians. Skin needs to be exposed for around half the time it takes to get erythema. How much vitamin D is produced from sunlight depends on the time of day, location on Earth, phototype, and the size of exposed area.

Raw cotton fabric contains pectin and waxes that give it some sun screening properties, but it still is non-rateable. Pre-treatments,

as scouring and chemically bleaching, lower the UV protection. Therefore, for summer clothing, additional fabric protection is necessary. Yarn linear density increment results in higher UV protection regardless of fabric treatment. Mercerization and cationization lower UV-A and UV-B transmission, which leads to good UV protection. Natural zeolite treatment increases significantly UV protection, regardless of the applying method. It scatters the UV-R resulting in lower UV-A and UV-B transmission. If applied after or during the mercerization process, synergistic effect occurs. Treatment with fluorescent agents, FWA and UV absorber leads to multifunctionality, which is high whiteness, neutralizing yellowness, giving the fabric high luminosity and protection against UV-R. In wet state, regardless of applied water—sea or distilled, fabrics get darker, lowering its whiteness. UV light is not absorbed, but reflected from the water, resulting in better UV protection. This phenomenon is more evident for sea water because of additional light scattering since it contains about 40% of inorganic salts. Having in mind that fluorescent agents are present in laundry detergents and their accumulation during washing process leads to even better UV protection [27], application of these agents to protective clothing for prevention of skin cancer incidence is suggested.

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