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Discrepancy of Whiteness and UV Protection in Wet State

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A B S T R A C T B S T R A C

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 percent of all deaths associated with skin cancer. In Croatia only, more than 20.000 new cases of skin cancer has been diagnosed in 2008 of which melanoma 286 new cases and 118 yearly deaths in men, and 275 new cases and 79 deaths in women population. The back sides in men and women, as well as the lower limbs in women, are the most common site for melanomas. The primary cause of skin cancer is believed to be a long exposure to solar ultraviolet (UV) radiation crossed with the amount of skin pigmentation in the population. There are indications that other parts of solar spectrum (e.g. blue light) might also have effects on skin and eyes. Most people think all clothing will protect them, but that's not the case. UV clothing can show UV protection, but in the most cases it does not provide full sun screening properties. UV protection ability highly depends on large number of factors such are type of fiber, fabric surface and construction, type and concentration of dyestuff, fluorescent whitening agent *(FWA), UV-B protective agents, as well as nanoparticles, if applied. For that reason, jeans and tightly woven fabrics offer a very good level of protection. However, on a hot summer day, those aren't the kinds of clothing people usually reach for. More often, when they are on the beach, they wear T-shirt, as well during the swimming in the sea, thinking that it will protect them. Therefore, in this paper the discrepancy of UV protection in wet state was researched. For the purpose, FWA and UV absorber were applied in wide concentration range to white cotton knit fabrics commonly used for T-shirts. Afterwards, the discrepancy in whiteness and UV protection was research in distilled water as well as Adriatic Sea water.*

Key words: UV protection, melanoma, FWA, UV absorber, wet state

Introduction

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 melanoma¹, which accounts for 75 percent of all deaths associated with skin cancer. In Croatia only, more than 20.000 new cases of skin cancer has been diagnosed in 2008. With 286 new cases and 118 yearly deaths in men and 275 new cases and 79 deaths in women in Croatia in 2008 melanoma represents 2.6% of male cancer incidence and 1.1% of cancer deaths in men, and 2.9% and 1.4% in women respectively². The reason for that is most likely that in the most cases

melanoma was diagnosed in an advanced stage. The back sides in men and women, as well as the lower limbs in women, are the most common site for melanomas³.

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. 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. Dangerous UV-B $(\lambda=280-320 \text{ nm})$ 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^{6–22}. Experts estimate about 90% of

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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 exposure1 . 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 cancer³.

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, e.g. hats, shoes, shade structures such as umbrellas, awnings, and baby carrier covers etc, can be accomplished by chemical approach. Most people think all clothing will protect them, but that's not the case. UV clothing can show UV protection, but in the 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 11 . This is very important during summer months, when UV index is the highest. Fabric UV protection ability highly depends on large number of factors such are 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^{10–24}. For all these reasons, 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 aren't the kinds of clothing people usually reach for. Usually it is light fabric in pastel shades or white. More often, when they are on the beach, they wear T-shirt, as well during the swimming in the sea, thinking that it will protect them from harmful UV radiation.

When P. Krais in 1929 discovered fluorescent compound Esculin 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. This fluorescent compound and many others later synthesised add a new dimension to the white materials²⁵. Nowadays, it is relatively easy to accomplish great whiteness applying the fluorescent whitening agents (FWAs). On the other hand, he could never assume that this UV-A absorption of $FWA's$ would result in better UV protection as well^{14,17,20,22,23}. Recently, the new fluorescent compounds, UV absorbers, were developed for UV-B protection as well. Latest research declare that FWA's and UV absorbers can be applied in washing^{21,24}.

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 populations¹. On the other hand, European Union supported research of UV protective clothing in Eastern European and Mediterranean countries of high UV index. However, the influence of wetness was not included in that research²³. Therefore, in this paper the discrepancy of whiteness and UV protection in wet state by white cotton knit fabrics commonly used for T-shirts threated with fluorescent compounds was researched.

Materials and Methods

Knitted fabric for T-shirts, a circular weft single jersey of 100% cotton yarn, was used. Fabric had surface mass 130 g/m², 56 cm (22 inch) width in tubular form, having 11 whales/cm and 12 courses/cm. It was chemical bleached in peroxide baths in industrial conditions (B).

Fluorescent whitening agent (FWA) bis(4,4' triazinylamino)-stilbene-2,2'-disulfonic acid derivative (Uvitex BAM, Ciba-Geigy AG) and UV absorber stilbene disulphonic acid triazine derivative (Tinosorb FB, Ciba-Geigy AG) were applied in wide concentration range $(c_1 =$ 0.01% owf (over weight of fibre); $c_2=0.05\%$ owf; $c_3=0.25\%$ owf; $c_4 = 1\%$ owf; $c_5 = 5\%$ owf; $c_6 = 25\%$ owf) by exhaustion at 90°C for 30 minutes to achieve the best whiteness and UV protection. Afterwards, the discrepancy in whiteness and UV protection was research in distilled water as well as Adriatic Sea water.

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 discrepancy in wet state was determined through color differences of color coordinates according to:

$$
\Delta E^* = \left[\left(\Delta H^* \right)^2 + \left(\Delta L^* \right)^2 + \left(\Delta C^* \right)^2 \right]^{\frac{1}{2}} \tag{1}
$$

where ΔL^* is change in lightness, ΔC^* change in chroma and ΔH^* change in hue.

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 amplifying of 200x.

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 *ultraviolet protection factor* (*UPF*), which indicates the ability of body protection by textile materials to prevent erythema, was calculated¹⁰.

Results and Discussion

The discrepancy of whiteness and UV protection in wet state by white cotton knit fabrics commonly used for Tshirts was researched in this paper. The CIE whiteness

TABLE 1

CIE WHITENESS (W_{CIF}), YELLOWING INDEX (YI), RELATIVE INTENSITY OF FLUORESCENCE (Φ_m), MAXIMUM OF REMISSION (R_{max}) AND WAVELENGTH ($\lambda_{\rm max}$), AND THE DISCREPANCY OF WHITENESS IN WET STATE OF FWA TREATED COTTON FABRICS

degree, yellowing index, relative intensity of fluorescence (Φ_{rel}) , maximum of remission (R_{max}) and wavelength (λ_{max}) , as well as the discrepancy of whiteness in wet state are collected in Tables 1 and 2. UV protective ability in dry and wet state is presented in Table 3 and Figures 1 a and b.

From Table 1 it is evident that high effects in textile cleaning of genetic and added impurities such are waxes, protein substances, pectin and other during scouring and bleaching in peroxide baths, where pigments are removed 27 , leads to cotton whitening. As the whiteness increase, yellowness decreases. Optical brightening due to its fluorescence contributes to the fabric high whiteness and beauty in optimal range of concentration. That is the concentration of fluorescent compound at which the maximum of Φ_{rel} or W_{CHE} are observed^{14,26}. From the results of the whiteness and fluorescence of FWA treated cotton fabrics presented in Table 1 it can be seen that FWA concentration of 0.25% (up to 1%) in relation to mass of material is the optimum concentration for this optical brightener. Since this UV absorber is fluorescent as well, having similar chemical composition (stilbene disulphonic acid derivative) as FWA, optimum concentration for UV absorber could be determined and it is 0.25% owf as well (Table 2). At the low concentration of both fluorescent agents–FWA and UV absorber, blue fluorescence neutralizes the yellowness of bleached fabric giving the high luminosity and "most beautiful" white. Applied in the higher concentration than optimal one from results of remission and wavelength maximums, presented in Tables 1 and 2, it can be seen that change in emission spectrum occurred. It is a consequence of well-known bathochromic shift of the remission spectrum. It comes to a reduction of remission intensity with FWA and/or UV absorber's concentrations causing the extinction of fluorescence by quenching phenomenon, with a consequence of yellowness.

Considering the results of discrepancy of whiteness shown in Tables 1 and 2 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 what gives the sensation of seeing a certain level of brightness.

But when the fabric gets wet, the water fills in 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. But as the water gradually evaporates, more and more light is reflected back to the eveball. and can be seen brighter again. 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. Therefore, for the highest concentration of applied FWA's, 0.25% owf, CIE whiteness falls from 115.4 to 107.2. This phenomenon is even more evident for UV absorber applied in concentrations higher than optimal one. The whiteness for applied 5% owf decreases from 84.9 to 77.9, and for 25% owf from 51.5 to low 13.9.

The impact of fluorescent compounds – FWA and UV absorber on the UV protection of cotton fabrics was monitored by the UV-A and UV-B (Tables 3) transmission and UPF (Figure 1). As it was said above, removing the impurities in scouring and bleaching leads to better whiteness. On the other hand, it leads to low UV protection as well. Therefore, chemically bleached cotton fabric (B) is nonrateable for UV protection since UPF is 5.24.

From the results shown in Table 3 and in Figure 1a it can be seen that fluorescent whitening agent applied even in small concentration leads to higher UPF (UPF $_{\text{FWA0.01\%}}$ = 10.77, $UPF_{\text{FWA0.05\%}}$ =20.13). 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 spectrum²⁵. By absorbing UV-A radiation optical brightened fabrics transform this radiation to blue fluorescence what leads to excellent UV protection in higher concentrations (UPF $_{\text{FWA5\%}}$ =47.68, UPF $_{\text{FWA25\%}}$ =

TABLE 3

UVA AND UVB TRANSMISSION, AND UV PROTECTION RATING ACCORDING TO AS/NZS 4399:1996 OF FWA AND UV ABSORBER TREATED COTTON FABRICS IN DRY AND WET STATE

Fabric	Dry			Sea water			Distilled Water		
	τ_{UVA}	τ_{UVB}	Rating*	$\tau_{\rm UVA}$	τ_{UVB}	Rating*	$\tau_{\rm UVA}$	τ_{UVB}	Rating*
B	50.233	17.533	5	5.069	6.422	15	4.362	5.409	15
FWA 0.01	8.907	8.021	10	3.945	4.036	20	3.909	3.861	20
FWA 0.05	4.402	3.206	20	2.904	2.352	25	2.298	1.794	30
FWA 0.25	3.534	2.634	20	2.314	1.968	35	1.527	1.208	50
FWA 1	2.278	1.702	35	0.695	0.577	$50+$	1.494	1.267	$50+$
FWA 5	1.633	1.189	45	0.668	0.548	$50+$	0.711	0.605	$50+$
FWA 25	0.788	0.728	$50+$	0.258	0.281	$50+$	0.553	0.574	$50+$
UV 0.01	7.182	7.368	10	2.962	3.307	25	3.855	4.224	20
UV 0.05	3.231	2.974	25	1.539	1.663	50	1.584	1.723	45
UV 0.25	1.763	1.589	40	0.851	0.869	$50+$	0.389	0.425	$50+$
UV ₁	1.606	1.477	50	0.651	0.668	$50+$	0.486	0.509	$50+$
UV ₅	1.246	1.093	$50+$	0.178	0.199	$50+$	0.273	0.296	$50+$
UV25	0.211	0.225	$50+$	0.394	0.419	$50+$	0.317	0.358	$50+$

*UPF rating according to AS/NZS 4399:1996 – 0, 5, 10: Non-rateable; 15, 20: Good; 25, 30, 35: Very good; 40, 45, 50, 50+: Excellent UV protection

Fig. 1. UV protection expressed via Ultraviolet protection factor (UPF) of cotton fabrics in dry and wet state treated with a) FWA, b) UV absorber.

93.89). Cotton fabrics of the highest FWAs concentration have the highest UPF in dry state. That confirms that FWA insures high protection of UV radiation. 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 UV protection in dry state (UPF_{UV0.01%}=12.53, UPF_{UV0.05%}=28.19). UV absorber offers excellent UV protection if applied in optimal concentration of 0.25% owf or higher. That is because UV absorbers absorb damaging UV-R range of 290 nm to 360 nm, and convert it into harmless heat energy17,21. For difference of FWA's 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 increase with fluorescent compound concentration, regardless of quenching phenomenon.

Considering the different refractive index in water and in the air it is differently reflected from the surface as explained before. Because of higher and scattered reflection, transmission is lower for both water applied, distilled and sea water, resulting in higher UPF values. It can be said that in wet state cotton knit fabrics treated with fluorescent compounds give off better UV protection than in dry state regardless of the concentration and type of fluorescent compound applied. This phenomenon is more enhanced for Sea water, since the refractive index increases with salinity increment and decrease of 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 compound applied, better UV protection was achieved in wet state. The only exception is the highest concentration of UV absorber. From Figure 1b 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, it can be assumed that this drop of UPF in wet state can be result of quenching of fluorescence as well. However, achieved UV protection is excellent regardless of the drop 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>UV index*15.

Conclusion onclusion

Primary prevention and early detection are essential regarding deduction of melanoma incidence. Considering prevention, especially in childhood and adolescence, it is necessary to apply sunscreening lotions and wear adequate clothing. Chemically bleached cotton fabrics are non-rateable for UV protection. Therefore, for summer

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clothing additional fabric protection is necessary. Treatment with fluorescent compounds, FWA and UV absorber in wide concentration range, leads to multifunctionality – high whiteness, neutralizing of yellowness, giving to the fabric the high luminosity and protection against UV radiation. The fluorescence contributes to the high whiteness and beauty in optimal concentration. In the range of higher concentration quenching of fluorescence occurs, resulting in fabric yellowness. The harmonic change from bleached cotton knitted fabric, through its brilliant whiteness, to its yellowness has been more outlined for UV absorber than FWA. 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 contained in the pores of the knitted fabric. On the other hand, because of reflection from water, better UV protection is achieved in wet state. 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 compounds are present in laundry detergents, and it accumulation during washing process leads to even better UV protection^{19,20}, it is to suggest application of these compounds to protective cloth-

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ing for prevention of skin cancer incidence.

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ODSTUPANJE BJELINE I UV ZAŠTITE U MOKROM STANJU DSTUPANJE

SAŽETAK

Učestalost raka kože poprima razmjere epidemije. Bazaliom je najčešći karcinom kože, no jednostavnim kirurškim zahvatom u principu je izlječiv. S druge strane, agresivan lokalni rast i metastaze glavne su osobine malignog melanoma, koji čini 75 posto svih smrtnih slučajeva povezanih s rakom kože. Samo u Hrvatskoj je u 2008. dijagnosticirano više od 20.000 novih slučajeva raka kože od kojih 286 novih slučajeva melanoma u muškaraca od koji 118 sa smrtnim ishodom, i 275 novih slučajeva u žena od kojih 79 sa smrtnim ishodom. Najčešća mjesta pojave melanoma su leđa u muškaraca i žena, te potkoljenice u žena. Vjeruje se da je dugo izlaganje sunčevom ultraljubičastom (UV) zračenju primarni uzrok raka kože, uzevši u obzir i pigmentaciju kože. Postoje indicije da i drugi dijelovi sunčeva spektra (npr. plavo svjetlo) mogu imati učinak na kožu i oči. Većina ljudi smatra da će im sva odjeća pružiti zaštitu, ali to nije slučaj. Odjeća može pružiti određenu UV zaštitu, ali u većini slučajeva ne potpunu. Sposobnost UV zaštite ovisi o velikom broju čimbenika kao što su vrsta vlakana, površine i konstrukcija tekstilije, vrsta i koncentracija bojila, fluorescentnih spojeva – optičkih bjelila (FWA) i UV apsorbera, kao i nanočestica, ukoliko su primijenjeni. Iz tog razloga, traperice i debele, guste tkanine pružaju izvrsnu zaštite. Međutim, za vrućih ljetnih dana, to nije odjeća za kojom ljudi najčešće posežu. Češće, kada su na plaži, nose majicu, čak i za vrijeme kupanja u moru, misleći da će ih zaštititi. Upravo iz tog razloga, u ovom radu su istražena odstupanja UV zaštite u mokrom stanju. U tu svrhu pamučno pletivo koje se koristi za majice obrađeno je optičkim bjelilom i UV apsorber u širokom koncentracijskom rasponu. Potom je istraženo odstupanje bjeline i UV zaštite u mokrom stanju primjenom destilirane i vode iz Jadranskog mora.