The influence of the optical brighteners concentration on the degree of whiteness and UV protection of cotton fabric

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Chemically bleached cotton fabrics were optically brightened in a wide concentration range with optical brighteners (fluorescent brightening agents, FWAs) of different constitution, affinity and emission tone: stilbene derivatives Uvitex BHT and Uvitex RSB, and distyrylbiphenyl derivative Uvitex NFW with the purpose of process sustainability. The fluorescence of FWA solutions was investigated, and then cotton fabrics were optically brightened in these solutions. The influence of the FWA concentration on cotton fabric whiteness and the UV protection was researched after treatment and one cycle of washing in water. It has been shown that it is possible to achieve satisfactory whiteness and effective UV protection by applying a low concentration of FWA at a reduced temperature of 60°C, in a shorter treatment time of 30 min and at a neutral pH, which makes this treatment sustainable.
Keywords: *cotton, optical brightening, fluorescence, whiteness, UV protection*

1. Introduction

Protection against ultraviolet (UV) radiation is a very widespread and researched issue. The majority of the population is familiar with the fact that ultraviolet radiation is harmful and that adequate protection is required during long-term exposure to strong sunlight [1-8]. UV radiation represents a small part of the solar spectrum, only 5%, with wavelengths from 100 to 400 nm and is divided into: UV-A (320-400 nm), UV-B (290-320 nm) and UV-C (100- 290 nm) [1-3]. When it comes to the harmfulness of UV rays, rays of shorter wavelengths represent a greater danger, which would mean that UV-C rays are the most harmful. Fortunately, UV-C do not reach the Earth, it is completely absorbed by ozone in the stratosphere, as well as the part of UV-B radiation. Due to the damage to the ozone, rays with wavelengths of around 300 nm still pass through and pose a danger to the life of plants, animals and people.

Clothing provides the best protection of human skin against UV radiation, so clothing manufacturers should properly label clothing items that have the property of UV protection. When textile material comes into contact with UV rays, part of the radiation is reflected, part is absorbed, while part of the radiation is transmitted through the material. Optical brighteners (fluorescent brightening agents, FWAs) intensively absorb the energy of ultraviolet light (λ=300-400 nm), with the simultaneous emission of visible light of shorter wavelengths (blue light, λ_{max} =440 nm), which increases the overall

remission of visible light from the treated material, neutralizing the yellowness and achieving high brightness. The FWAs increase the material whiteness, and therefore it can be used in various branches. The largest application of optical brighteners is in the detergent industry, followed by the paper and textile industry. In addition to fabric brightening, FWAs are also used in dyeing for tinting and obtaining brilliant tones that are difficult to obtain in other ways [9-15]. Since they absorb UV-A rays and convert this radiation into blue light (fluorescence), their application leads to better UV protection [1-6].

Different FWAs can achieve maximum emission at different wavelengths, so depending on FWA applied, different shades of whiteness can be obtained. For example, if the maximum of fluorescence is at a wavelength of 435 nm, then the fluorescent light is violet-red; if it is at 440 nm, then the fluorescent light is blue; while in the case of maximum fluorescence at 500 nm, the greenish fluorescence is obtained [16]. Better tinting during optical brightening can also be achieved by adding blue or purple color to the bath, which reduces the total remission from the material, but increases the whiteness appearance because the remission of light moves more into the neutral white area [10].

The stilbene derivatives are mostly used FWAs, which are in various modifications widely used in the detergent and paper industry, while in the textile industry they are used exclusively as FWAs for almost all types of fibers. Stilbene is 1,2 diphenylethene and has a system of 7 conjugated double bonds, it has no affinity towards fibers. Therefore, stilbene derivatives are used, most often those derived from 4-4'-diaminostilbene-2-2'-disulfonic acid. One of the first such compounds was 4-4'-bis(phenylureido)-stilbene-2-2'-disulfonic acid, trade name Blankophor R. This compound gave a reddish shade of fluorescence, but it did not remain in use, because disintegrates at the boiling temperature [9].

Derivatives of 4-4'-bis(triazinylamino)-stilbene-2-2'-disulfonic acid have better properties. They are obtained by replacing two hydrogens in the amino groups of diamino-stilbene-disulfonic acid with cyanide chloride and subsequent replacement of the remaining chlorine from cyanide chloride with other radicals that determine the affinity to fibers, the exhaustion rate, solubility in water, etc. Such compounds are used in as optical brighteners for cellulose, polyamide and wool fibers.

Almost all optical brighte-ners used for cellulose fibers are made from bis-triazinyl-diamino-stilbene-disulfonic acid derivatives, but their disadvantage is poor light fastness, which is compensated for by subsequent washing with agents containing optical brighteners [9, 12]. Stilbene derivatives exist in cis and trans forms, but as optical brighteners they are used only in the trans form, because as such they have an affinity for fibers and show off fluorescence phenomenon. Compounds that have a high resistance to chlorine and light are derivatives of 4-4'-bis(azolyl)-stilbene-2-2' disulfonic acid, and they are used in the bleaching of cotton in a neutral and polyamide fibers in an acid bath [9].

To achieve high whiteness and brilliant tone, cotton should be chemically bleached prior to optical brightening. In scouring process cotton impurities are removed, i.e. pectin, waxes, organic acids, proteins and minerals, but colored substances - pigments remain. In chemical bleaching, natural pigments are degraded by oxidizing agents, usually hydrogen peroxide, into colorless products with low damage of the cotton cellulose [10, 17-22].

An increase of FWA concentration does not always mean an increase in the degree of whiteness. On the contrary, there is a limiting concentration up to which an increase occurs, and if exceeded, the whiteness decreases. When using higher FWA concentrations the absorption spectrum shifts to the visible part, so there is an increased absorption of blue and violet light, which results in an excess of yellow and green light in the remission spectrum. The limit concentration recommended for optical brightening is characteristic of each FWA, and it depends on the type of material applied, as well [11, 14].

The three main reasons for the reduced degree of whiteness when using excessive concentrations are: partial absorption of visible light, shift of the fluorescence spectrum towards longer wavelengths and concentration quenching of fluorescence.

Recently, there on the market new UV absorbers that have the property of fluorescence. So, as a special type of optical brighteners, in addition to absorbing UV-A, they also absorb UV-B rays and convert them into thermal energy. The latest research suggests that optical brighteners and such UV absorbers can be used in the washing process and in detergent formulations [4-6].

Since research at the beginning of the 21st century showed that FWA are one of the effective agents for UV protection, this paper investigated the influence of the FWA concentration of different constitutions on cotton fabric whiteness and UV protection. For the purpose of sustainability, a reduced FWA concentration and processing at lowered temperature and neutral pH were investigated.

2. Experimental

2.1. Material and treatments

The research was carried out on a standard cotton fabric (WFK, Type 10000) that is chemically bleached, having mass per unit area of 170 g/m². For optical brightening, three FWAs of different constitutions, emissions, and affinities towards cellulose fibers, brand Uvitex® by Ciba-Geigy AG (tab. 1) were used in the following concentrations: c_1 = 0.2%; c_2 = 0.5%; c_3 = 2%; c_4 = 5%; c_5 = 20%; c_6 = 50% owf (over weight of fabric). High concentrations of 20 and 50% were used exclusively for the purpose of scientific research.

Optical brightening was performed by the exhaustion method on a Polycolor machine (Mathis). According to the manufacturer's recommendation, the addition of 5 g/l Na_2SO_4 as electrolyte is necessary, with bath ratio BR 1:20-1:30; and process parameters for Uvitex BHT – T=80-90°C, 60 min, pH 7-12; for Uvitex RSB – T=40-80°C, 30-60 min, pH 4-8; and for Uvitex NFW – T=40-60°C, 30-60 min, pH 4-7. Taking into account the manufacturer's recommendation and the sustainability of the process, optical brightening was carried out in reduced time - 30 min, in a neutral bath (pH 7), at 60°C having BR 1:25. After treatment fabrics were air-dried.

In order to investigate the FWA fastness, one washing cycle was carried out in distilled water at 60°C for 30 min.

2.2 . Methods

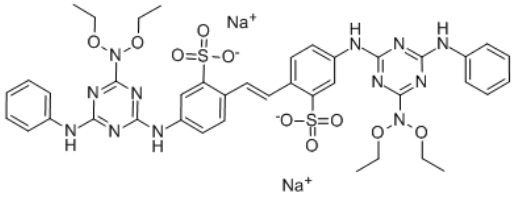
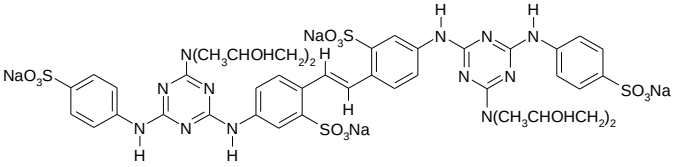
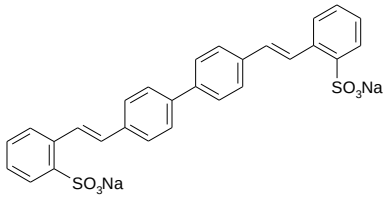
After processing the cotton fabrics, the following properties were tested: fluorescence of the FWA solution, whiteness, tint deviation and UV protection factor (UPF).

The fluorescence intensity of FWA solutions (FL int.) was measured on the fluorimeter F-7000 FL, Hitachi.

The spectral remission, R [%] was measured on a spectrophotometer Spectraflash SF 300, Datacolor. The degree of whiteness according to CIE was automatically calculated (W_{CIE}) in accordance with ISO 105-J02:1997 *Textiles - Tests for color fastness - Part J02: Instrumental assessment of relative whiteness*, as well as tint deviation from neutral white standard and its coloristic meanings according to [23].

On a transmission spectrophotometer Cary 50/Solascreen, Varian, the transmissions of UV-R were measured at 8 different places on sample. The results are expressed according to AS/NZS 4399:2017 *Sun protective Clothing – Evaluation and Classification* through the UV protection factor (UPF). UPF indicates the ability of the textile material to protect the body from unfavorable UV radiation so the erythema does not occur.

Table 1. Labels, names, structural formulas and properties of optical brighteners

Label	Name, structural formula and properties
BHT	 Uvitex BHT CI Fluorescent Brightener 113 Derivative of diaminostilbendisulfonic acid λ_{max} = 440 nm High affinity for cellulose fibers, PA, wool, silk and its blends
RSB	 Uvitex RSB Triazine derivative of stilbene disulfonic acid λ_{max} = 435-440 nm Medium affinity to cellulose fibers and its blends with polyester
NFW	 Uvitex NFW CI Fluorescent Brightener 351 Distyryl biphenyl derivative λ_{max} = 435-440 nm Low affinity for cellulose fibers; high for wool, silk, PA; medium to its blends

3. Results and Discussion

For the purposes of this research, cotton fabrics were optically brightened with three different FWAs in a wide concentration range. Before processing, fluorescence was measured on a fluorimeter, and the results of fluorescence intensity (FL int.) are shown in Fig. 1-3.

From the results shown in Fig. 1, it is evident that the emission of the Uvitex BHT at 440 nm is a pure blue emission. The highest fluorescence intensity is the FWA solution with a concentration of 0.2% (1600), followed by 0.5% (1400). The Uvitex BHT solution with a concentration of 2% indicates significantly lower fluorescence (100). At concentrations higher than 2%, fluorescence quenching is visible and the emission is close to 0. At the same time, a bathochromic shift of the emission can be observed.

From the results shown in Fig. 2, it is evident that the emission of the Uvitex RSB is at 440 nm. The solutions of 0.2 and 0.5% FWA have the same fluorescence intensity (2500). A solution of Uvitex RSB with a concentration of 2% indicates significantly lower fluorescence (400). At concentrations higher than 2%, fluorescence quenching is visible and the fluorescence emission approaches 0. A bathochromic shift towards higher wavelengths is visible as a consequence of fluorescence quenching.

Fig. 3 shows that the emission of Uvitex NFW is at 430 nm, blue-violet. FWA solution of concentration 0.2% shows a fluorescence intensity of 4900. As the concentration increases, the fluorescence increases, so the highest emission is a solution of optical bleach with a concentration of 0.5% per mm (6000). A solution with a concentration of 2% indicates a lower fluorescence than 2000.

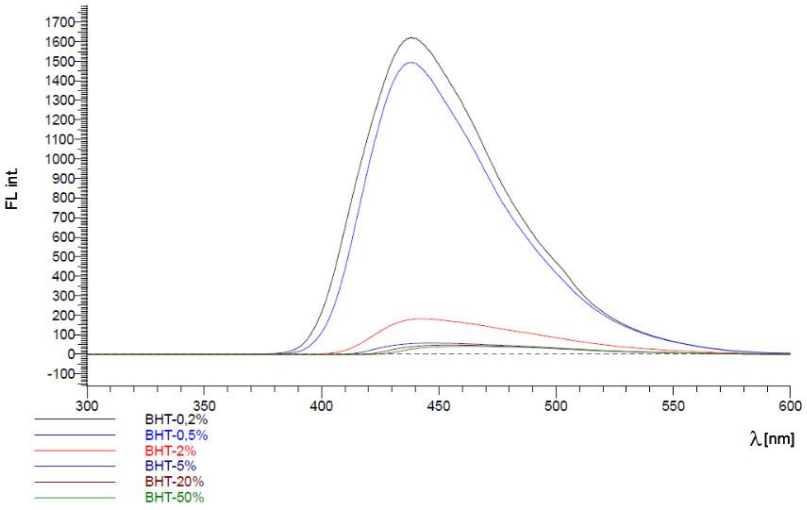


Figure 1. Fluorescence of Uvitex BHT solutions

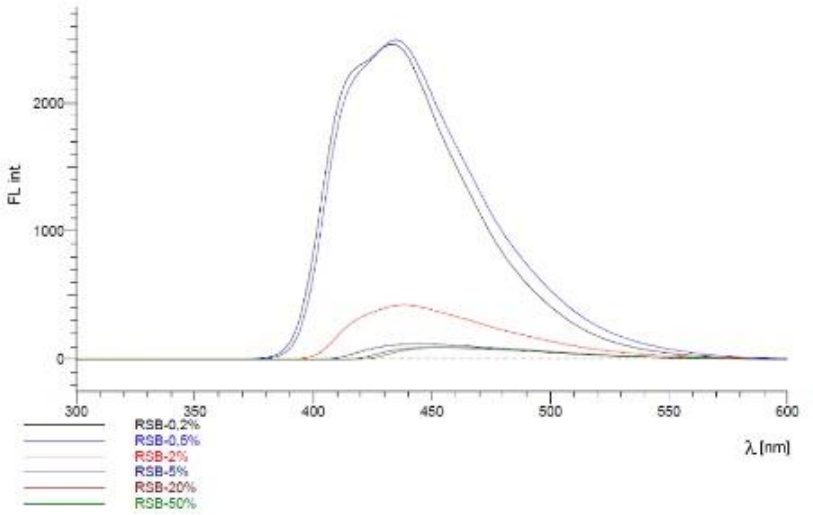


Figure 2. Fluorescence of Uvitex RSB solutions

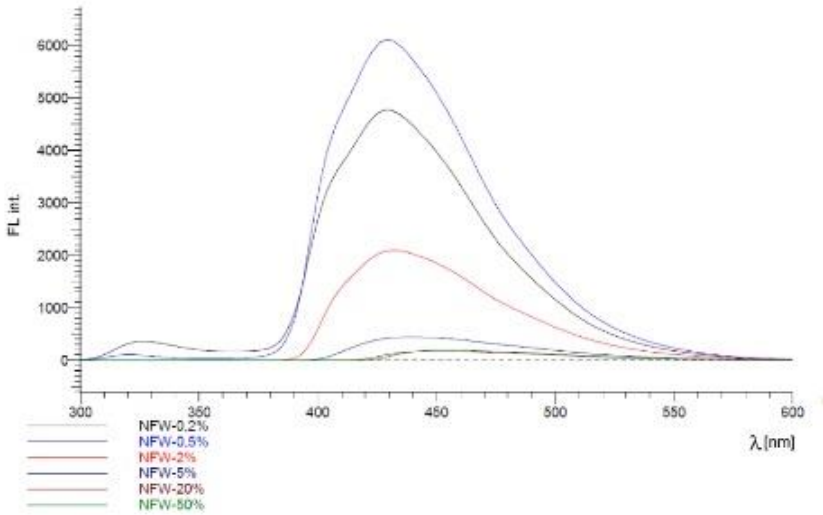


Figure 3. Fluorescence of Uvitex NFW solutions

With an increase in concentration, the quenching of fluorescence and the shift of the emission to 440 nm are clearly visible. At a concentration of 5%, the fluorescence is 300, and as the concentration increases, the emission is closer to 0. By comparing the intensity of fluorescence between the applied optical brighteners, it is evident that Uvitex NFW has twice the intensity of Uvitex BHT and RSB. Since it has a low affinity for cellulose fibers, the spectral characteristics were researched after optical brightening of the cotton fabric with the investigated solutions. Remission measurement was carried out and the degree of whiteness and tint deviation from the white standard were calculated automatically. The results are presented in figures 4-8 and tables 2-4.

Chemically bleached standard cotton fabric (CB) was used for this study. Since all impurities and pigments have been removed in its production, it has a degree of whiteness WCIE = 74.4. Higher degrees of whiteness of fabrics were achieved by optical brightening.

Even a very small concentration of Uvitex BHT of 0.2% greatly increases the degree of whiteness to 131.8. As the concentration of the optical brightener increases, the fabric spectral remission increases as well. The highest level of whiteness is achieved at a concentrations of 0.5 and 2%, therefore the optimal concentration is 0.5%. Exceeding the FWA concentration of 2%, the spectral remission decreases, and the shift of the remission spectrum towards longer wavelengths can be observed. This indicates that the fluorescence quenching has occurred. The tint deviation results confirm this. The true neutral whiteness, i.e. no appreciable deviation in tint from the white standard, has been achieved with a concentrations between 0.5 and

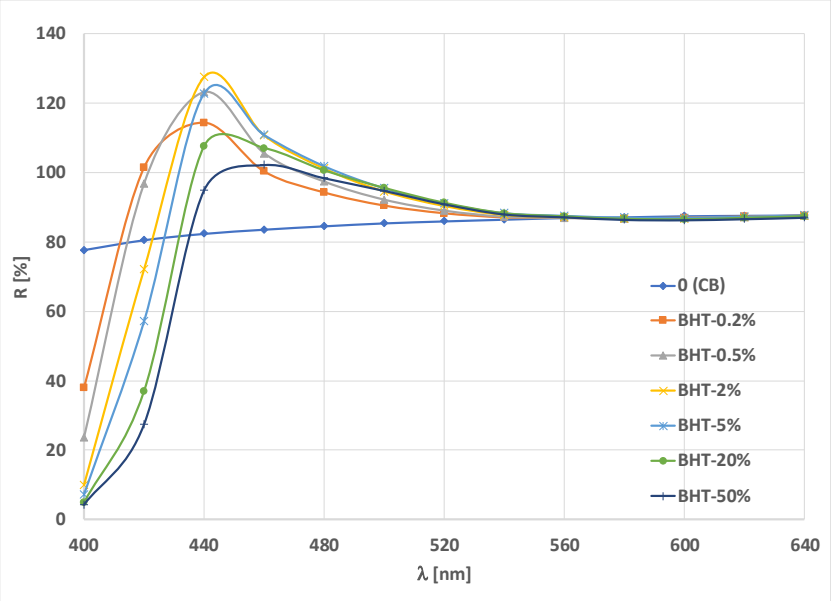


Figure 4. Remission curves of chemically bleached (CB) and optically brightened cotton fabrics with Uvitex BHT in a wide concentration range

Table 2. Degree of whiteness according to CIE (W_{CIE}) and tint deviation from the white standard of chemically bleached (CB) and optically brightened cotton fabrics with Uvitex BHT in a wide concentration range

Sample	**W_{CIE}**	**TV, TD [23]**	
0.0 (CB)	74.4	G1	Trace greener than the white standard
BHT-0.2%	131.8	R1	Trace redder than the white standard
BHT-0.5%	142.6	R1	Trace redder than the white standard
BHT-2%	142.0	G1	Trace greener than the white standard
BHT-5%	131.5	G3	Appreciably greener than the white standard
BHT-20%	105.1	GG	Tinted in green direction
BHT-50%	83.0	GG	Tinted in green direction

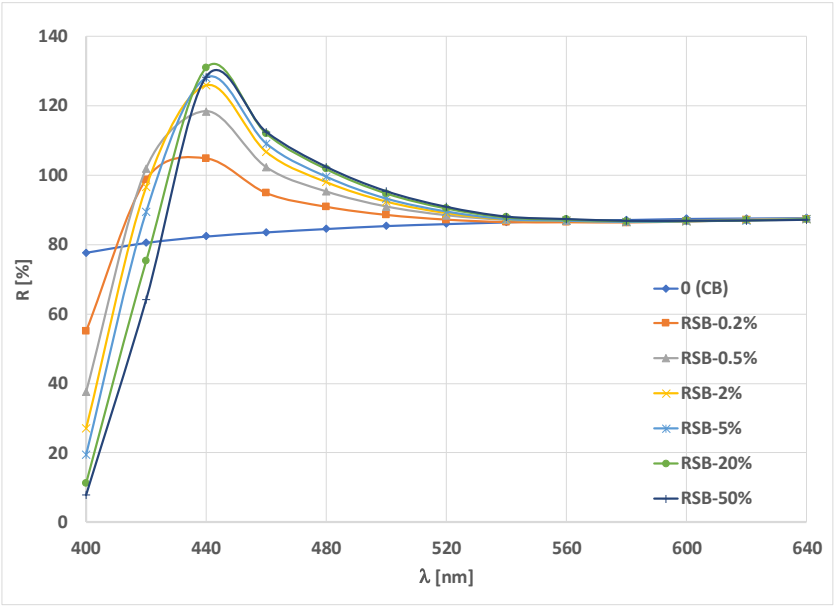


Figure 5. Remission curves of chemically bleached (CB) and optically brightened cotton fabrics with Uvitex RSB in a wide concentration range

2%. As the concentration increases, the layering of the FWA occurs and the fabric turns green.
Fabrics treated with a lower FWA concentration of 2% show a shift in tone from the neutral white towards the reddish-violet part of the spectrum, while samples bleached with a FWA concentration higher than 2% show a shift towards the blue-green part of the spectrum.
From the results of the spectral characteristics of cotton fabrics optically brightened with Uvitex RSB, it can be seen that the highest spectral remission was achieved at a FWA concentration of 20%, at a wavelength of 440 nm. It should be noted that a similar remission has been achieved at a concentration of 2% and it remains the same up to 50% (for 2% 146.6 to 20% 147.3).
Cotton fabrics brightened with Uvitex RSB in concentrations lower than 5% are trace redder, and higher than 20% trace greener than the neutral white standard. Taking into account that similar whiteness results are achieved at a concentration of 2%, this concentration is recommended as optimal for economic reasons.
From the presented results of spectral characteristics for cotton fabrics optically brightened with Uvitex NFW in the concentration range from 0.2 to 50%, it is evident that the spectral remission increases with increasing concentration, and then decreases. The limit concentration for this optical brightener is 2% at 440 nm.
However, using the smallest concentrations of 0.2 and 0.5%, a significant increase in whiteness is visible. The main reason for that is twice higher fluorescence intensity in this FWA solution than for the other FWAs. Fig.6 shows that the maximum remission for these concentrations is at 430 nm, which corresponds to the fluorescence intensity measured on the fluorimeter (Fig.3). At a concentration of 0.5%, a high level of whiteness of 145.8 is achieved, and the highest level is 148.5 at 2%. At concentrations higher than 2%, the maximum remission is at 440 nm, but the intensity of the remissions decreases. It is evident from the results that the cotton fabric optically brightened with a 2% FWA achieved the highest spectral remission and the highest whiteness. The optical brightening with more than 5% FWA results in a decrease of spectral remission and whiteness. The cotton fabric opti-

Table 3. Degree of whiteness according to CIE (W_{CIE}) and tint deviation from the white standard of chemically bleached (CB) and optically brightened cotton fabrics with Uvitex RSB in a wide concentration range

Sample	**W_{CIE}**	**TV, TD [23]**	
0.0 (CB)	74.4	G1	Trace greener than the white standard
RSB-0.2%	117.8	R1	Trace redder than the white standard
RSB-0.5%	137.7	R2	Slightly redder than the white standard
RSB-2%	146.6	R1	Trace redder than the white standard
RSB-5%	148.4	R1	Trace redder than the white standard
RSB-20%	147.3	G1	Trace greener than the white standard
RSB-50%	141.0	G2	Slightly greener than the white standard

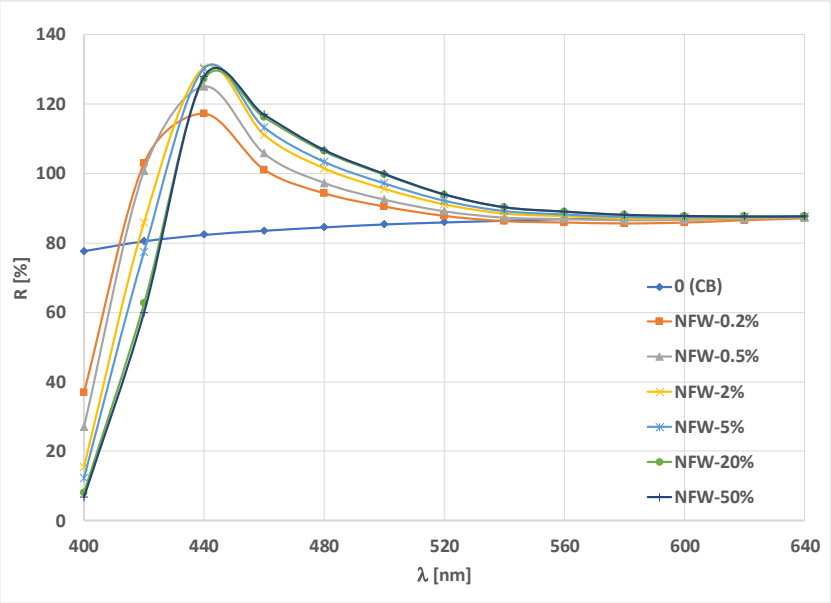


Figure 6. Remission curves of chemically bleached (CB) and optically brightened cotton fabrics with Uvitex NFW in a wide concentration range

Table 4. Degree of whiteness according to CIE (W_{CIE}) and tint deviation from the white standard of chemically bleached (CB) and optically brightened cotton fabrics with Uvitex NFW in a wide concentration range

Sample	**W_{CIE}**	**TV, TD [23]**	
0.0 (CB)	74.4	G1	Trace greener than the white standard
NFW-0.2%	137.0	R1	Trace redder than the white standard
NFW-0.5%	145.8	R1	Trace redder than the white standard
NFW-2%	148.5	G1	Trace greener than the white standard
NFW-5%	146.0	G2	Slightly greener than the white standard
NFW-20%	139.3	G5	Very markedly greener than the white standard
NFW-50%	139.7	G5	Very markedly greener than the white standard

cally brightened with 2% Uvitex NFW shows a tint deviation from the white standard towards the blue part of the spectrum. Cotton fabrics optically brightened with a lower concentration show a slight tint deviation towards the red-violet part of the spectrum.

In the case of the Uvitex NFW, based on the measurement of the spectral characteristics, it can be recommended the concentration of 0.5% as an optimal one, even though it does not give the highest remission, it shows approximately the same degree of whiteness. It should be noted that this brightener shows the highest fluorescence intensity (FL int.) and excellent whiteness was achieved even though it is has low affinity for cellulose fibers.

In this work, three optical brighteners of different constitutions, affinities and emission tones were used: Uvitex BHT, Uvitex RSB and Uvitex NFW. According to their chemical composition, they are derivatives of stilbene: Uvitex BHT, which has a high affinity towards cotton (2 sulfonate groups) and Uvitex RSB, which has a medium affinity (4 sulfonate groups), and Uvitex NFW, which is distyrylbiphenyl derivative of a low-affinity for cellulose fibers. By comparing the degrees of whiteness, it is evident that the high whiteness of the cotton fabric is achieved with concentration of 2% FWA, regardless of the chemical composition. At the same time, a concentration of 0.5% is sufficient to achieve excellent whiteness for all FWAs. Considering the achieved maximum remission using 0.5 and 2%, for Uvitex BHT is at 440 nm and for Uvitex NFW is at 430-440 nm, it is in a blue. This is confirmed by the results shown in the CIE chromaticity diagram (Fig. 7).

The remission of fabrics treated with Uvitex RSB corresponds to a red-violet tone, and at higher concentrations they shift to blue,

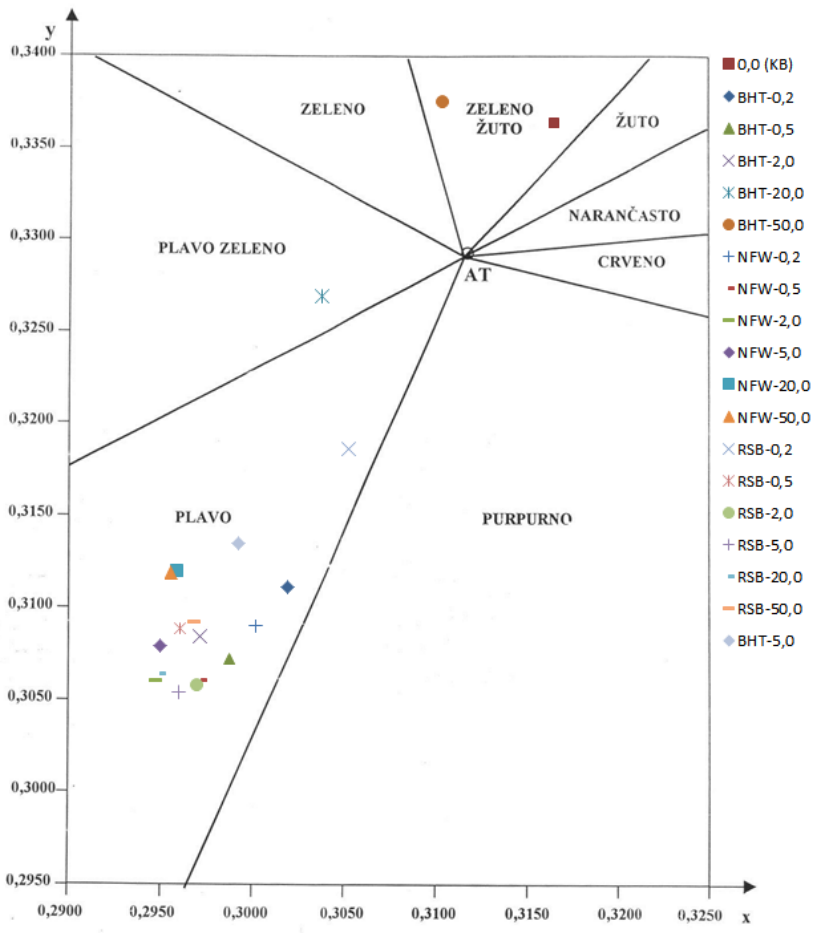


Figure 7. Part of the CIE chromaticity diagram

i.e. to neutral at 20%. In the case of FWAs with a blue tone, Uvitex BHT and Uvitex NFW, quenching of fluorescence is observed (decrease in whiteness and remission and shift to blue-green). This can be explained by the excessive concentration of optical brightener molecules on the fabric. By layering FWA molecules, not all layers can be excited, and therefore there is no fluorescence that directly affects the reduction of whiteness. In addition, FWA molecules at high concentrations build dimers that do not show fluorescence phenomenon.

The influence of the concentration of optical brighteners on UV protection was monitored through UV-A and UV-B transmission and the mean value of the UV protection factor (UPF). The results of measurement according to AS/NZS 4399:2017 are shown in tab. 5-7. It can be seen that chemically bleached fabric (CB) provides only good UV protection (UPF =20,998). Even the application of a small concentration of FWA leads to an increase in the degree of whiteness and thus UV protection. Regardless of the applied optical brightener, excellent UV protection is achieved by applying the lowest concentration of 0.2%. Applying a concentration of 0.5% achieves the maximum possible UV protection (UPF=1000) regardless of applied the optical brightener. As for the countries of high UV index (7-10+), is recommended UPF>105, or UPF=15*UV index, for the protection of people who spend eight hours a day outdoors, it can be seen that achieved UV protection obey the highest standard [1-3].

Table 5. UV-A and UV-B transmission, standard deviation, standard error, and UV protection of chemically bleached (CB) and optically brightened cotton fabrics with Uvitex BHT in a wide concentration range

Sample	medium UPF	τ_{UVA}	τ_{UVB}	standard deviation	standard error	UV protection	
0.0 (CB)	20.998	3.406	7.376	2.335	2.895	15	good protection
BHT-0.2%	734.958	0.149	0.111	226.559	280.933	50+	excellent protection
BHT-0.5%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
BHT-2%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
BHT-5%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
BHT-20%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
BHT-50%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection

Table 6. UV-A and UV-B transmission, standard deviation, standard error, and UV protection of chemically bleached (CB) and optically brightened cotton fabrics with Uvitex RSB in a wide concentration range

Sample	medium UPF	τ_{UVA}	τ_{UVB}	standard deviation	standard error	UV protection	
0.0 (CB)	20.998	3.406	7.376	2.335	2.895	15	good protection
RSB-0.2%	144.281	0.770	0.724	103.690	128.576	50+	excellent protection
RSB-0.5%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
RSB-2%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
RSB-5%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
RSB-20%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
RSB-50%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection

Table 7. UV-A and UV-B transmission, standard deviation, standard error, and UV protection of chemically bleached (CB) and optically brightened cotton fabrics with Uvitex NFW in a wide concentration range

Sample	medium UPF	τ_{UVA}	τ_{UVB}	standard deviation	standard error	UV protection	
0.0 (CB)	20.998	3.406	7.376	2.335	2.895	15	good protection
NFW-0.2%	614.747	0.212	0.103	363.942	451.288	50+	excellent protection
NFW-0.5 %	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
NFW-2%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
NFW-5%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
NFW-20%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
NFW-50%	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection

Comparing the applied FWAs, it is evident that the blue-toned Uvitex BHT and NFW at the lowest concentration give a higher UPF than the red-toned Uvitex RSB.

It should be noted that the maximum UV protection does not decrease with the quenching of fluorescence, that is, with a decrease of whiteness and remission at higher FWA concentrations.

Since the applied FWAs have different affinity for cotton, the change in remission, whiteness and UV protection after one cycle of washing in distilled water at 60°C for 30 min was investigated. The results of remission and whiteness are shown in Figs.8-10 and in tabs.8-10, and of UV protection in tabs.11-13.

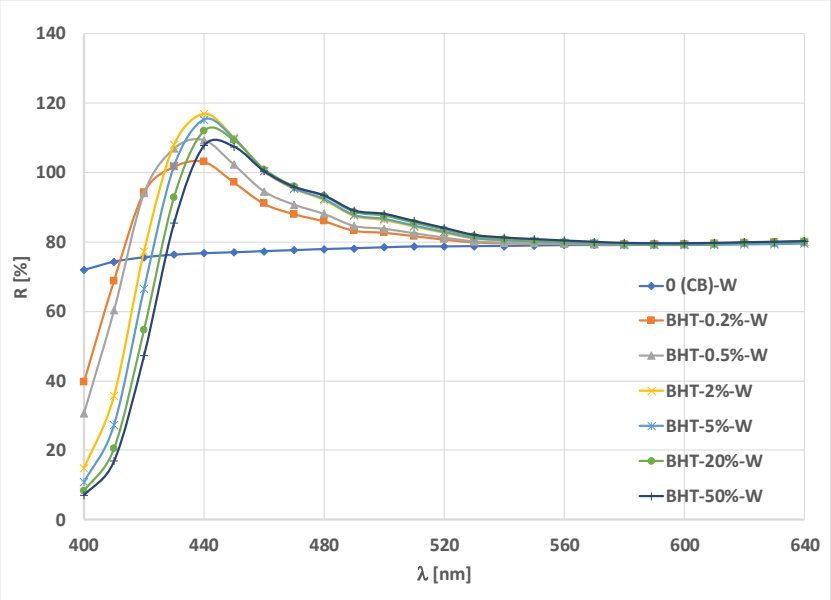


Figure 8. Remission curves of washed chemically bleached (CB) and optically brightened cotton fabrics with Uvitex BHT in a wide concentration range

From the results, it is evident that the layers of FWA are removed from all fabrics during washing, which reduces the remission and whiteness. It can be assumed that an equal amount of optical whitener is removed for each optical brightener, because the change in whiteness and remission is more pronounced at lower concentrations. However, significant differences in the change of remission and whiteness are visible depending on the type and affinity of the optical brightener.

From the results after the washing in water for cotton fabrics optically brightened with Uvitex BHT, there is a visible decrease in the maximum remission and degree of whiteness by ten units, for example, for BHT-0.5% remission decreased from 127 to 116 and whiteness from 142 to 132. It is interesting that after one washing cycle the fabrics have a higher degree of whiteness and a smaller tint deviation from the white standard indicating that removal of the layers of the optical brightener led to a reduction in the fluorescence quenching effect.

From the results after the washing in water for cotton fabrics optically brightened with Uvitex RSB, there is a visible decrease in the maximum remission and degree of whiteness by as twenty units, for example, for RSB-2% remission decreased from 125 to 103 and whiteness degree from 146 to 122. The highest whiteness that was achieved at all concentrations higher than 2% and did not changed with increasing concentration, shows significantly different behavior after washing than if other two FWAs were applied. With the removal of layers in the washing, it is clearly visible that the degree of whiteness increases with the increase in concentration. Taking into account the tint deviation, it is clearly visible that the neutral white was not achieved

Table 8. Degree of whiteness according to CIE (W_{CIE}) and tint deviation from the white standard of washed chemically bleached (CB) and optically brightened cotton fabrics with Uvitex BHT in a wide concentration range

Sample	**W_{CIE}**	**TV, TD [23]**	
0.0 (CB)-W	71.7	R1	Trace redder than the white standard
BHT-0.2%-W	122.9	R1	Trace redder than the white standard
BHT-0.5%-W	132.2	R1	Trace redder than the white standard
BHT-2%-W	138.2		
BHT-5%-W	132.5	G2	Slightly greener than the white standard
BHT-20%-W	124.0	G3	Appreciably greener than the white standard
BHT-50%-W	115.2	G4	Markedly green than the white standard

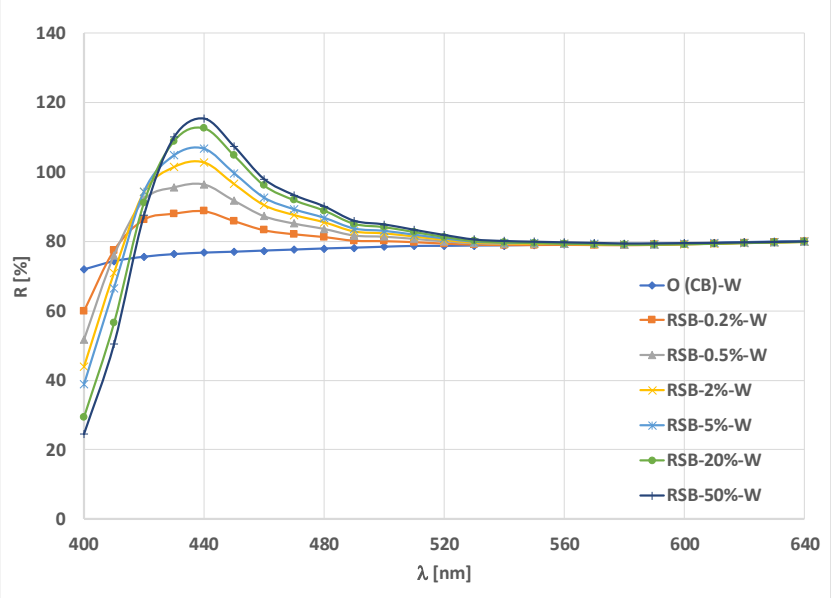


Figure 9. Remission curves of washed chemically bleached (CB) and optically brightened cotton fabrics with Uvitex RSB in a wide concentration range

Table 9. Degree of whiteness according to CIE (W_{CIE}) and tint deviation from the white standard of washed chemically bleached (CB) and optically brightened cotton fabrics with Uvitex RSB in a wide concentration range

Sample	**W_{CIE}**	**TV, TD [23]**	
0.0 (CB)-W	71.7	R1	Trace redder than the white standard
RSB-0.2%-W	97.3	R1	Trace redder than the white standard
RSB-0.5%-W	111.9	R1	Trace redder than the white standard
RSB-2%-W	122.4	R1	Trace redder than the white standard
RSB-5%-W	128.2	R1	Trace redder than the white standard
RSB-20%-W	136.3	R1	Trace redder than the white standard
RSB-50%-W	138.8	R1	Trace redder than the white standard

Table 10. Degree of whiteness according to CIE (W_{CIE}) and tint deviation from the white standard of washed chemically bleached (CB) and optically brightened cotton fabrics with Uvitex NFW in a wide concentration range

Sample	**W_{CIE}**	**TV, TD [23]**	
0.0 (CB)-W	71.7	R1	Trace redder than the white standard
NFW-0.2%-W	109.1	R1	Trace redder than the white standard
NFW-0.5%-W	115,1	R1	Trace redder than the white standard
NFW-2%-W	127.4	R1	Trace redder than the white standard
NFW-5%-W	135.6		
NFW-20%-W	130.8	G1	Trace greener than the white standard
NFW-50%-W	137.2	G1	Trace greener than the white standard

with this FWA, but that all the fabrics show traces of a red tone. From the results after the washing in water for cotton fabrics optically brightened with Uvitex NFW, a reduction of the maximum remission and degree of whiteness by more than twenty units is visible. For example, for NFW-0.5% remission decreased from 125 to 98 and whiteness from 146 to 115, while for NFW-2% remission decreased from 130 to 106 and whiteness from 148 to 127. Samples treated with this optical brightener at concentrations greater than 2% showed a decrease in whiteness and pronounced tint deviation, i.e., very markedly greener than the white standard.

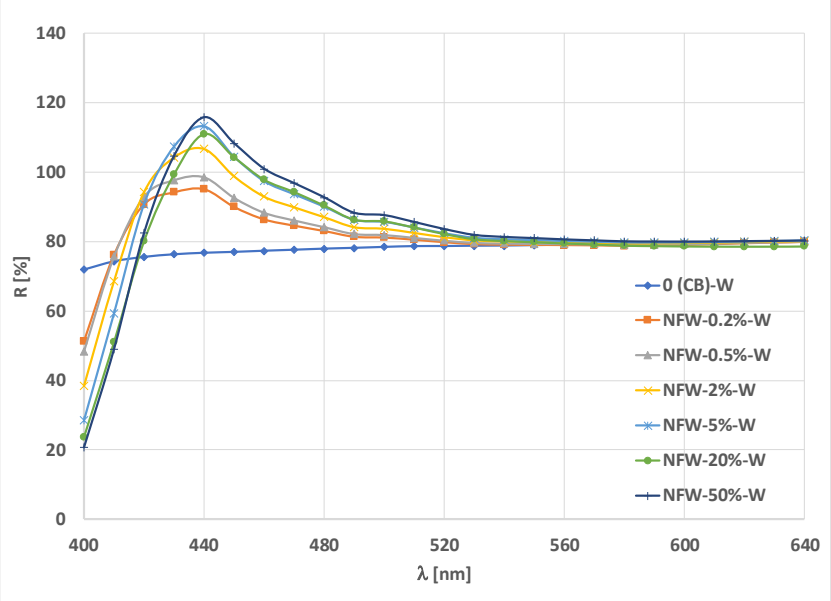


Figure 10. Remission curves of washed chemically bleached (CB) and optically brightened cotton fabrics with Uvitex NFW in a wide concentration range for the wavelength range 400-640 nm

Table 11. UV-A and UV-B transmission, standard deviation, standard error, and UV protection of washed chemically bleached (CB) and optically brightened cotton fabrics with Uvitex BHT in a wide concentration range

Sample	**medium UPF**	**τ UVA**	**τ UVB**	**standard deviation**	**standard error**	**UV protection**	
0.0 (CB)-W	37.048	1.451	5.403	2.697	7.876	30	good protection
BHT-0.2%-W	976.115	0.100	0.102	27.719	80.940	50+	excellent protection
BHT-0.5%-W	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
BHT-2%-W	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
BHT-5%-W	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
BHT-20%-W	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
BHT-50%-W	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection

Table 12. UV-A and UV-B transmission, standard deviation, standard error, and UV protection of washed chemically bleached (CB) and optically brightened cotton fabrics with Uvitex RSB in a wide concentration range

Sample	**medium UPF**	**τ UVA**	**τ UVB**	**Stand. deviation**	**Stand. error**	**UV protection**	
0.0 (CB)-W	37.048	1.451	5.403	2.697	7.876	30	good protection
RSB-0.2%-W	80.185	0.782	1.565	9.035	26.381	50+	excellent protection
RSB-0.5%-W	245.123	0.300	0.311	14.641	42.751	50+	excellent protection
RSB-2%-W	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
RSB-5%-W	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
RSB-20%-W	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
RSB-50%-W	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection

Table 13. UV-A and UV-B transmission, standard deviation, standard error, and UV protection of washed chemically bleached (CB) and optically brightened cotton fabrics with Uvitex NFW in a wide concentration range

Sample	**medium UPF**	**τ UVA**	**τ UVB**	**Stand. deviation**	**Stand. error**	**UV protection**	
0.0 (CB)	37.048	1.451	5.403	2.697	7.876	30	good protection
NFW-0.2%-W	103.495	0.716	0.539	29.599	86.430	50+	excellent protection
NFW-0.5%-W	329.730	0.241	0.159	91.222	266.367	50+	excellent protection
NFW-2%-W	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
NFW-5%-W	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
NFW-20%-W	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection
NFW-50%-W	1000.000	0.100	0.100	0.000	0.000	50+	excellent protection

The removal of the layers of FWA in washing resulted in an improvement of the whiteness of the samples treated with FWA in concentrations higher than 2%, i.e. led the to neutral whiteness at higher concentrations instead of quenching. These differences in the maximum remission and the degree of white-ness of the applied FWAs, from a dozen for Uvitex BHT to about twenty units for Uvitex RSB and NFW, can be interpreted as a different affinity for cellulose fibers. Uvitex BHT, which has a high affinity for cellulose fibers, is less washed off than medium to low affinity FWAs.

From the results of the level of protection against UV radiation, it is evident that for chemically bleached standard fabric, the level of protection increases in washing. The mean UPF of the chemical bleached fabric was 21 and after washing it increased to 37. The reason for this is the well-known shrinkage of the cotton fabric during the washing process due to swelling and drying (become fabric of more denser structure). By washing off the optical brightener, the UV protection is lower, but still excellent (50+). Since the optical brightener Uvitex BHT shows the least washing, there is no significant change in the UPF values. However, for the optical brighteners that have a low affinity for cellulose fibers and whose degree of whiteness and remission has decreased by more than 20 units, a decrease in the mean UPF value is also visible. By applying a concentration of 0.5% optical brightener, the maximum possible values of UPF 1000 were achieved, but after washing in water for one cycle they are reduced to 245 for Uvitex RSB and 329 for Uvitex NFW. At higher concentrations, regardless of the reduced values, they are still at the maximum of UPF 1000.

4. Conclusion

The paper investigated the fluorescence of optical brighteners of different constitutions, affinity and emission tones: stilbene derivatives Uvitex BHT and Uvitex RSB, and distyrylbiphenyl derivative Uvitex NFW, in a wide concentration range from 0.2 to 50% owf. The influence of the FWAs concentration on the whiteness and UV protection of cotton fabric after optical brightening and after one cycle of washing in water was researched.

It was shown that the optical brighteners Uvitex NFW and Uvitex BHT emit in blue, while Uvitex RSB emits in red-violet, whereby Uvitex NFW has twice the fluorescence intensity. For the FWAs of blue tone, the optimal concentration is 0.5%, although the highest whiteness is achieved at 2%. At higher concentrations, the fluorescence is getting quenched. Unlike Uvitex BHT and Uvitex NFW, the whiteness of Uvitex RSB increases with the concentration increment and shows the highest whiteness at a concentration of 20%. However, a concentration of 2% gives similar whiteness and UV protection and therefore can be considered as optimal one.

All optical brighteners contribute to increased UV protection of cotton fabrics even at the lowest concentration, and when FWA concentration of 0.5% or more were applied the maximum possible UV protection (UPF=1000) was achieved. Blue-toned optical brighteners at a concentration of 0.2% provide slightly higher protection than red-toned one. It is to point out that the maximum UV protection achieved at higher concentrations does not decrease with the occurrence of fluorescence quenching, i.e. a decrease in whiteness and remission at higher concentrations of optical brighteners.

It has been shown that the difference in the affinity affects the washing of optical brightener - Uvitex BHT, which has a strong affinity for cellulose fibers, is removed less than FWAs with medium to low affinity. By removing the optical brightener, the UV protection is reduced, however, it is still excellent.

It can be concluded that it is possible to achieve satisfactory whiteness and effective UV protection by applying a low concentration of optical brighteners of 0.5% and at a reduced temperature of 60°C, in a shorter processing time of 30 min and at a neutral pH, which makes the process sustainable.

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