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INFLUENCE OF THE FLUORESCENT BRIGHTENER PERIBLANC BA ON THE DEGREE OF WHITENESS OF KNITTED COTTON FABRIC

In this study, the influence of different fluorescent brightener Periblan BA concentrations on the degree of knitted cotton fabric whiteness was investigated. Two consecutive experimental runs were performed. The first was the bleaching of the knitted cotton fabric with hydrogen peroxide using the methods of two and single bath exhaustion, while the second was the optical bleaching with fluorescent brightener Periblan BA using the exhaustion method. CIE whiteness index and tint value were measured on the Color-Eye 3000 spectrophotometer at the standard illuminant D65 (Ice-Texicon, d/8, D65/10°) while K/S values were determined using the Kubelka Munk equation. The results show that cotton fabric bleached with fluorescent brightener Periblan BA after bleaching with hydrogen peroxide using two bath exhaustion method has a higher degree of whiteness (118.8) with a reddish tint in comparison to the one bleached with hydrogen peroxide using single bath method (106.1).

Cotton cellulose has excellent properties such as good water and moisture absorbability, being comfortable to wear and easy to dye. For these reasons, the apparel industry is predominantly cotton based, and the share of cotton in total fibre consumption is around 50% [1].

Cotton is composed almost entirely of cellulose, *i.e.*, 88.0–96% based on the fibre (owf) weight. The impurities in cotton fibre range from 4 to 12% and include protein (1.0–1.9%), wax (0.4–1.2%), ash (inorganic salts) (0.7–1.6%), pectin (0.4–1.2%) and other substances (resins, pigments, hemi-cellulose) (0.5–0.8%) [2,3]. The yellowish or brown coloration of the cotton fibre is related to the protoplasmic residues of the protein and flavones pigments of cotton flowers [4,5]. Apart from these, the loom-state fabric is also contaminated with processing lubricants, such as machine oils, tars, and greases from harvesting, ginning, spinning and weaving (or knitting) [1]. Waxy materials and pectins are responsible for the hydrophobic properties of the raw cotton [6]. Having all this in mind, purification of cotton in the fiber, yarn and fabric forms through removal of such impurities must be done before dyeing, finishing and utilization. With the exception of natural coloring matters that may be removed by bleaching using certain oxidants, other impurities are removed by alkali treatment in the scouring stage which usually involves boiling cotton in sodium hydroxide (2–5%) for 1 h [3,7]. However, the chemical bleaching method cannot completely remove a small quantity of yellowness.

The fluorescent brighteners (FBs) are essentially colorless fluorescent dyes used for whitening textiles and synthetic polymer materials [8]. Materials treated with FBs obtain a high degree of whiteness, which can-

not be achieved by the common bleaching methods. The whiteness is increased by the process of absorption of light in the ultraviolet region (330–380 nm) and the emission of a visible blue light (400–450 nm). An important class of fluorescent brighteners is based on triazine-stilbene, containing different amino and alkoxy derivatives in the triazine ring [9].

In solutions these FBs have low photo resistance and they are able to isomerize and exist in two isomeric forms [10]. This is because the double ethylene bond in the stilbene molecule favors *trans*–*cis* isomerization of FBs. The active component of this FBs is *trans* isomer ((*E*)-stilben), which is fluorescent, whereas *cis* isomer ((*Z*)-stilben) is not.

It is necessary that the fluorescent brightener has a planar molecular structure with conjugated double bonds and electron-donating groups in order to show the high fluorescence activity [11]. The fluorescent brightener currently used in the fiber industry holds higher stability for chemical bleaching since it possesses high quality whiteness and fastness [12]. Since 1886, when they were first used as dyes, disodium 4,4'-diaminostilbene-2,2'-disulfonate derivatives have been the most widely used as the fluorescent brighteners for whitening both cotton and wool [13–17].

In this study, the influence of the different fluorescent brightener Periblan BA concentrations on the degree of knitted cotton fabric whiteness was investigated. Knitted cotton fabric was bleached with hydrogen peroxide by the methods of two and single bath exhaustion while the second was the optical bleaching with fluorescent brightener Periblan BA using the exhaustion method. CIE (International Commission on Illumination) whiteness index, CIE tint and *K/S* values of the fabric were monitored before and after the bleaching processes.

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EXPERIMENTAL PROCEDURE

Cotton fabric and chemicals

Raw 100% knitted cotton fabric with reddish tint, with protected code 10954/S was used (Interlock, No. 50/1, width 141 cm, horizontal thickness 13.5 cm^{-1} , vertical thickness 12 cm^{-1} , density 233 g m^{-2} , weight 328,53 g, vertical shrinking $-1,2\%$, horizontal shrinking $+1\%$; knitted cotton fabric was made by 72R- J machine, with fineness of E20).

Hydrogen peroxide (35 mass%), sodium hydroxide (1.162 g/cm^3), sodium carbonate and acetic acid (1 mol/dm^3) were of the technical grade purity.

Fluorescent brightener (stilbene-disulfonate derivative, anion) of the technical grade purity was kindly supplied under the commercial name Periblanc BA by Textilchemie dr. Petry GMBH. Alviron GBU (leveling agent, aqueous preparation of lipids, ester oils and natural emulsifiers), Alvirol NMB (sequestering agent, mixture of carboxylic acid derivatives and polyphosphates), Lavan OLKC (wetting agent, combination of selected anionic and non-ionic tensides with natural solvent components) and TC-Stabilizator OS (stabilizer, water micro-emulsion of lipids, ester oils and natural emulsifiers, liquid) were supplied from Textilcolor.

Scouring

The scouring of the raw knitted cotton fabric was carried out in the following order: 50 g of raw knitted cotton fabric was treated with aqueous solution containing Alviron NMB (1 g/dm^3), Lavan OLKC (2 g/dm^3) and Na_2CO_3 (2 g/dm^3) using material to liquor ratio (LR) of 1:20 at $50 \text{ }^\circ\text{C}$ for 10 min. The bath temperature was then gradually raised to $98 \text{ }^\circ\text{C}$ for 15 min and kept at this temperature for the next 45 min. The fabric was washed with Lavan OLKC, and then neutralized with $1 \text{ cm}^3/\text{dm}^3$ acetic acid, washed several times with hot ($40 \text{ }^\circ\text{C}$) and cold water ($20 \text{ }^\circ\text{C}$) and finally dried at ambient conditions.

Bleaching with hydrogen peroxide

Two techniques were performed to bleach the scoured cotton fabric with hydrogen peroxide: two and single bath exhaustion. The two bath exhaustion method comprised two steps. In the first step, 50 g of the scoured cotton fabric was treated with aqueous solution containing Alviron GBU (2 g/dm^3), stabilizator OS (1 g/dm^3), NaOH ($4 \text{ cm}^3/\text{dm}^3$) and H_2O_2 ($5 \text{ cm}^3/\text{dm}^3$) using material to liquor ratio (LR) of 1:20 at $50 \text{ }^\circ\text{C}$ for 10 min. The bath temperature was then gradually raised to $98 \text{ }^\circ\text{C}$ for 5 min and kept at this temperature for the next 30 min. The fabric was washed with Lavan OLKC, neutralized with $1 \text{ cm}^3/\text{dm}^3$ acetic acid, washed several times with hot ($40 \text{ }^\circ\text{C}$) and cold water ($20 \text{ }^\circ\text{C}$) and finally dried at the ambient conditions. In the second step, 50 g of cot-

ton fabric bleached as described above was treated with an aqueous solution containing Alviron GBU (2 g/dm^3), using material to liquor ratio (LR) of 1:20 at $40 \text{ }^\circ\text{C}$ for 10 min. Afterwards, NaOH ($7 \text{ cm}^3/\text{dm}^3$), stabilizer OS (1 g/dm^3), and H_2O_2 ($12 \text{ cm}^3/\text{dm}^3$) were added to the solution. The bath temperature was kept at $40 \text{ }^\circ\text{C}$ for 10 min. The fabric was neutralized with $0.5 \text{ cm}^3/\text{dm}^3$ acetic acid, washed several times with hot ($40 \text{ }^\circ\text{C}$) and cold water ($20 \text{ }^\circ\text{C}$) and finally dried at ambient conditions.

In the single bath method 50 g of the scoured cotton fabric was treated with aqueous solution containing Stabilizator OS (1 g/dm^3), Lavan OLKC (2 g/dm^3), NaOH ($4 \text{ cm}^3/\text{dm}^3$) and H_2O_2 ($5 \text{ cm}^3/\text{dm}^3$) using material to liquor ratio (LR) of 1:20 at $50 \text{ }^\circ\text{C}$ for 10 min. The bath temperature was then gradually raised to $98 \text{ }^\circ\text{C}$ for 5 min and kept at this temperature for the next 30 min. The fabric was washed using Lavan OLKC, washed several times with hot ($70 \text{ }^\circ\text{C}$) and cold water ($50 \text{ }^\circ\text{C}$), neutralized with $0.5 \text{ cm}^3/\text{dm}^3$ acetic acid, washed several times with hot ($40 \text{ }^\circ\text{C}$) and cold water ($20 \text{ }^\circ\text{C}$) and finally dried at ambient conditions.

Optical bleaching with fluorescent brightener

Periblanc BA

Three samples (per 5 g) were sliced from the cotton fabric bleached with hydrogen peroxide by the two bath exhaustion method and each sample was added in a separate aqueous solution using a material to liquor ratio (LR) of 1:20.

Freshly prepared solutions, containing fluorescent brightener Periblanc BA in different concentrations were added sequentially (5 cm^3 0.1%, 25 cm^3 0.5%, 50 cm^3 1%). The process was carried out at $40 \text{ }^\circ\text{C}$ for 30 min. Temperature was then raised to $98 \text{ }^\circ\text{C}$ and kept at this temperature for 60 min. Temperature was decreased to $60 \text{ }^\circ\text{C}$ after that and kept at this temperature for 15 min. The fabric was washed using Lavan OLKC, washed several times with hot water $70 \text{ }^\circ\text{C}$ /cold water $50 \text{ }^\circ\text{C}$, neutralized with $0.5 \text{ cm}^3/\text{dm}^3$ acetic acid, washed several times with hot ($40 \text{ }^\circ\text{C}$) and cold water ($20 \text{ }^\circ\text{C}$) and finally dried at ambient conditions.

Testing methods

CIE whiteness index (WT) and tint value (T) were measured on a Color-Eye 3000 spectrophotometer at the standard illuminant D65 (Ice-Texicon, d/8, D65/10°). The color strength value (K/S) was calculated using the Kubelka Munk Equation [18]:

$$K/S = (1 - R)^2/2R \quad (1)$$

where R is the reflectance of the dyed fabric at the wavelength of the maximum absorption, K/S is the ratio of the absorption coefficient, K (depending on the dye concentration) refers to the scattering coefficient, S , caused by the dyed substrate.

CIE whiteness index WI_{10} (for CIE 10° standard observer) formulates as shown below [19]:

$$WI_{10} = Y_{10} + 800(x_{n,10} - x_{10}) + 1700(y_{n,10} + y_{10}) \quad (2)$$

White samples may have the equal whiteness index, but they can be distinguished by tint (because they can have reddish, greenish or neutral tint). For this reason, a method that enables calculation of the tint was developed. CIE tint T_{10} (for 10° standard observer) formulates as shown below [18]:

$$T_{10} = 900(x_{n,10} - x_{10}) - 650(y_{n,10} - y_{10}) \quad (3)$$

Tint values are positive for probes with greenish tint and negative for probes with reddish tint. In this formula Y , x_{10} , y_{10} are the colorimetric values calculated by using 10° standard observers values under D65 illuminant while $x_{n,10}$ and $y_{n,10}$ are the chromaticity coordinates of D65 illuminant belonging to 10° standard observer.

CIE LAB coordinates: L^* (lightness), a^* (red-green chromaticity index), b^* (yellow-blue chromaticity index), C^* (chroma) and H^* (hue) of the samples were also measured.

RESULTS AND DISCUSSION

The whiteness degree increases with the increase of the FBs concentration. When its maximum is reached, the whiteness degree drops regardless of the FBs content. The increase of the whiteness degree after the ma-

ximum concentration is the result of the fluorescence concentration quenching effect [20].

The data presented in Tables 1 and 2 enable us to observe how the K/S , WI and T values changed after each of the cotton fabric treatment. The biggest WI increase occurred after chemical bleaching of the scoured fabric with H_2O_2 . As it was expected, further increase in WI value occurred after bleaching with H_2O_2 in the second step of two bath exhaustion method (Table 2); this sample also had the lowest K/S value (Table 1) and the smallest reddish tint.

After bleaching with FBs, WI of the cotton fabric samples significantly increased, for both two and single bath exhaustion methods. The highest WI , the lowest K/S values and the smallest reddish tints are generally obtained for the cotton fabric bleached with FB after bleaching with the two bath exhaustion method (Tables 3 and 4). K/S , WI and T values depend on the concentration of the FB. For the samples bleached with FB after bleaching with two bath exhaustion method, WI slightly increased with the increase of FB concentration from 0.1 to 0.5% and there reached its maximum, while the K/S value was the lowest at 0.5% concentration. Further increase of concentration, from 0.5 to 1.0% resulted in a slight decrease of WI . The reason for this decrease could be the effect of fluorescence concentration quenching, which occurred after the optimal FB concentration was reached.

The K/S values of the cotton fabric samples bleached with FB after chemical bleaching with single bath me-

Table 1. Color strength value, K/S , of bleached cotton fabric with hydrogen peroxide as a function of wavelength, λ

Fabric		Values							
Untreated cotton fabric	λ / nm	400	420	440	460	480	500	520	540
	K/S	0.45	0.362	0.288	0.232	0.187	0.148	0.118	0.095
	λ / nm	560	580	600	620	640	660	680	700
	K/S	0.077	0.062	0.052	0.044	0.037	0.031	0.026	0.023
Scoured cotton fabric	λ / nm	400	420	440	460	480	500	520	540
	K/S	0.303	0.248	0.203	0.168	0.142	0.119	0.101	0.086
	λ / nm	560	580	600	620	640	660	680	700
	K/S	0.073	0.062	0.054	0.047	0.041	0.036	0.032	0.028
Bleached fabric with H_2O_2 (two bath exhaustion, I step)	λ / nm	400	420	440	460	480	500	520	540
	K/S	0.067	0.04	0.031	0.026	0.023	0.021	0.017	0.016
	λ / nm	560	580	600	620	640	660	680	700
	K/S	0.014	0.013	0.012	0.012	0.011	0.011	0.01	0.009
Bleached fabric with H_2O_2 (two bath exhaustion, II step)	λ / nm	400	420	440	460	480	500	520	540
	K/S	0.021	0.004	0.011	0.01	0.009	0.008	0.008	0.007
	λ / nm	560	580	600	620	640	660	680	700
	K/S	0.007	0.006	0.006	0.006	0.006	0.006	0.006	0.005
Bleached cotton fabric with H_2O_2 single bath exhaustion	λ / nm	400	420	440	460	480	500	520	540
	K/S	0.069	0.049	0.036	0.029	0.024	0.02	0.017	0.015
	λ / nm	560	580	600	620	640	660	680	700
	K/S	0.013	0.012	0.011	0.01	0.01	0.009	0.009	0.008

Table 2. Degree of whiteness (*WI*) and tint values (*T*) for 100% knitted cotton fabric treated with hydrogen peroxide in two bath exhaustion and single bath exhaustion method

Treatment	<i>WI</i>	<i>T</i>	CIE Coordinates				
			<i>L*</i>	<i>a*</i>	<i>b*</i>	<i>C*</i>	<i>H*</i>
Untreated fabric	-10.74	-10.97 reddish	84.88	2.34	15.44	15.62	81.40
Scoured cotton fabric	12.48	-8.01 reddish	85.51	1.82	11.05	11.20	80.67
Bleached cotton fabric with hydrogen peroxide using two bath exhaustion method, I step	66.08	-1.58 reddish	93.32	0.06	3.83	3.83	89.14
Bleached cotton fabric with hydrogen peroxide using two bath exhaustion method, II step	80.75	-0.62 reddish	95.39	0.03	1.73	1.73	91.07
Bleached cotton fabric with hydrogen peroxide using single-bath method	60.32	-1.75 reddish	93.48	-0.14	5.16	5.16	91.57

Table 3. Color strength value, *K/S*, of cotton fabric treated with three different concentrations (0.1, 0.5 and 1%) of Periblanç BA after bleaching with hydrogen peroxide using two bath exhaustion method as a function of wavelength, λ

Periblanç BA content, %		Value							
0.1	λ / nm	400	420	440	460	48	500	520	540
	<i>K/S</i>	1.573	0.050	0.004	0.000	0.003	0.007	0.010	0.012
	λ / nm	560	580	600	620	640	660	680	700
	<i>K/S</i>	0.012	0.012	0.011	0.011	0.011	0.010	0.009	0.009
0.5	λ / nm	400	420	440	460	48	500	520	540
	<i>K/S</i>	0.985	0.022	0.004	0.000	0.002	0.005	0.008	0.009
	λ / nm	560	580	600	620	640	660	680	700
	<i>K/S</i>	0.009	0.009	0.009	0.008	0.008	0.008	0.008	0.007
1.0	λ / nm	400	420	440	460	48	500	520	540
	<i>K/S</i>	0.693	0.015	0.001	0.001	0.005	0.009	0.011	0.012
	λ / nm	560	580	600	620	640	660	680	700
	<i>K/S</i>	0.012	0.012	0.01	0.011	0.011	0.010	0.010	0.009

Table 4. Degree of whiteness (*WI*) and color data (*T*) for cotton fabric treated with Periblanç BA after bleaching with hydrogen peroxide using two bath exhaustion method

Periblanç BA content, %	<i>WI</i>	<i>T</i>	CIE coordinates				
			<i>L*</i>	<i>a*</i>	<i>b*</i>	<i>C*</i>	<i>H*</i>
0.1	116.4	-0.16 reddish	94.69	1.62	-6.53	6.73	283.95
0.5	118.8	-0.59 reddish	95.31	1.96	-6.77	7.05	286.13
1.0	113.9	-1.06 reddish	94.49	2.08	-6.07	6.41	288.89

thod are given in Table 5 and their *WI* and *T* values are given in Table 6. The highest *WI* and the smallest reddish tint were achieved at the 0.1% concentration of FB. Further increase of the FB concentration caused the decrease of *WI* and it decreased almost linearly in the investigated concentration range. It can be noted that the influence of FB concentration on *WI* is not exactly the same for the samples bleached with two bath and those bleached with single bath method; in the second case, *WI* maximum is reached at the lower FB concentration (0.1%). The reason is not completely clear, but beside the effect of fluorescent quenching, some other effect could occur; perhaps the substances that cause the reddish tint of the fabric affected in some way on the absorption of the FB and their influence were higher for the samples bleached with single bath method, since

they are present here in higher amount in comparison to the samples bleached with two bath exhaustion method.

CONCLUSION

The duration of the applied bleaching treatment with fluorescent brightener Periblanç BA is longer than conventional bleaching with hydrogen peroxide using the two bath exhaustion and single bath exhaustion method, and it has been revealed that generally almost twice the whiteness was obtained after bleaching with fluorescent brightener Periblanç BA. Higher CIE whiteness index for bleaching with fluorescent brightener Periblanç BA was obtained for chemical bleached knitted cotton fabric with H₂O₂ using the two bath exhaustion method. Variations on the concentration of fluorescent

Table 5. Color strength value, *K/S*, of cotton fabric treated with three different concentrations (0.1, 0.5 and 1%) of Periblan BA after bleaching with hydrogen peroxide using single bath exhaustion method as a function of wavelength, λ

Periblan BA content, %		Value							
0.1	λ / nm	400	420	440	460	48	500	520	540
	<i>K/S</i>	1.600	0.062	0.001	0.001	0.005	0.009	0.012	0.012
	λ / nm	560	580	600	620	640	660	680	700
	<i>K/S</i>	0.012	0.011	0.010	0.009	0.008	0.008	0.007	0.007
0.5	λ / nm	400	420	440	460	48	500	520	540
	<i>K/S</i>	0.995	0.038	0.000	0.003	0.009	0.012	0.014	0.014
	λ / nm	560	580	600	620	640	660	680	700
	<i>K/S</i>	0.013	0.012	0.011	0.010	0.009	0.009	0.008	0.008
1.0	λ / nm	400	420	440	460	48	500	520	540
	<i>K/S</i>	0.618	0.028	0.000	0.006	0.012	0.014	0.015	0.015
	λ / nm	560	580	600	620	640	660	680	700
	<i>K/S</i>	0.015	0.013	0.012	0.011	0.010	0.009	0.008	0.007

Table 6. Degree of whiteness (*WI*) and tint values (*T*) for cotton fabric treated with Periblan BA after bleaching with hydrogen peroxide using single bath exhaustion method

Periblan BA content, %	<i>WI</i>	<i>T</i>	CIE coordinates				
			<i>L*</i>	<i>a*</i>	<i>b*</i>	<i>C*</i>	<i>H*</i>
0.1	106.1	-1.23 reddish	94.58	1.75	-4.30	4.64	292.14
0.5	101.8	-2.02 reddish	94.10	2.06	-3.58	4.13	299.97
1.0	95.76	-2.50 reddish	93.98	2.04	-2.30	3.08	311.63

brightener Periblan BA have a different effect on the Whiteness Index of bleached cotton fabric, and it depends on applied chemical bleaching treatment. The highest whiteness index for bleached cotton fabric with hydrogen peroxide using the two bath exhaustion method was obtained for the 0.5% concentration of the fluorescent brightener Periblan BA. The highest Whiteness Index for bleached cotton fabric with hydrogen peroxide using the single bath exhaustion method was obtained for the 0.1% concentration of the fluorescent brightener Periblan BA.

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IZVOD

UTICAJ FLUORESCENTNOG SREDSTVA ZA BELJENJE PERIBLANC BA NA STEPEN BELINE PLETENINE OD PAMUKA

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U ovom radu ispitivan je uticaj različitih koncentracija fluorescentnog sredstva za beljenje Periblanc BA na stepen beline pletenine od pamuka. U vezi sa tim su izvršena dva uzastopna ispitivanja. U prvom, izbeljivanje pamučne pletenine vodonik peroksidom je vršeno sa dve različite metode, i to metodom dvobanjskog i jednobanjskog izbeljivanja. U drugom, izbeljivanje je vršeno fluorescentnim sredstvom za beljenje Periblanc BA metodom iscrpljenja. CIE indeks beline i vrednost tona boje, kao i Kubelka Munkove (K/S) vrednosti su određene na spektrofotometru Color-Eye 3000 sa standardnim izvorom osvetljenja D65 (Ice-Texicon, d/8, D65/10°). Dobijeni rezultati pokazuju da pamučna pletenina beljena fluorescentnim sredstvom za beljenje Periblanc BA nakon izbeljivanja vodonik peroksidom metodom iscrpljenja poseduje viši stepen beline (118.8) sa crvenim tonom u odnosu na pamučnu pleteninu beljenu fluorescentnim sredstvom za beljenje Periblanc BA nakon izbeljivanja vodonik peroksidom jednobanjskom metodom (106.1).

Ključne reči: Fluorescentno sredstvo za beljenje • Periblanc BA • Stepens beline • Pamučna pletenina • Izbeljivanje • Standardni izvor osvetljenja D65

Key words: Fluorescent brightener • Periblanc BA • Whiteness • Knitted cotton fabric • Bleaching • Standard illuminant D65