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Action of a finishing product in the improvement of the ultraviolet protection provided by cotton fabrics. Modelisation of the effect

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Abstract

The Ultraviolet Protection Factor of a fabric is a quantitative measurement of the effectiveness of the fabric to protect the human skin against ultraviolet radiation. The protection provided by uncoloured cellulosic fabrics is, in general, too low, but can be improved by the finishing treatment with UV-absorbers. In the present paper cotton fabrics with different compactness, and hence with different initial Ultraviolet Protection Factor values, are treated with several concentrations of an UV-absorber, according to a predefined experimental plan. The influence of each variable as well as their interaction on the response of Ultraviolet Protection Factor is analysed and a statistical model for predictions is proposed.

Introduction

The Ultraviolet Protection Factor (UPF) of a fabric is a quantitative measurement of the effectiveness of the fabric to protect the human skin against ultraviolet radiation. It can significantly vary depending on the manufacturing parameters of the fabrics: fibre type, structural characteristics of the fabric (weave construction, yarn number, thread count, cover factor, etc.), colour and dyeing intensity, presence of optical brightening agents, pigments or finishing products (especially UV-absorbers), washing conditions of the garments, etc. (Hilfiker et al. 1996; Pailthorpe 1996; Reinert et al. 1997; Zhou and Crews 1998; Crews et al. 1999; Haerri et al. 2000; Srinivasan and Gatewood 2000; Algaba et al. 2004).

Several products are used in the textile industry in order to protect the fibres from photo-degradation or to avoid the colour degradation in dyed articles or the deterioration of the whiteness degree in white fabrics, caused by the incidence of the ultraviolet radiation on the textile articles. The mechanism of action of these UV-absorbers consists in the selective absorption of the damaging radiation and its dissipation as thermal energy. They are non-coloured products with elevated extinction coefficients in the spectral range between 300 and 400 nm approximately (Zweifel 1998). Nowadays, some of these products and other new formulations have been proposed to improve as well the blocking of the ultraviolet radiation through the textiles, that is, to increase their UPF.

An UV-absorber would be considered as appropriate to improve the UPF of the fabrics if its absorption spectrum presents bands of elevated absorption preferentially in the wavelengths corresponding to the UVB zone. The UVB radiation is more damaging to the skin and it has a higher weight in the UPF formula. If the chemical added blocks the UVB radiation it will be very efficient to be used in garments labelled as UV protective.

The present paper analyses the action of a specific finishing product, based on oxalanilide, on the improvement of the UPF values of cotton fabrics. Previous experiences of the authors had shown that the improvement of the UPF obtained by application of chemicals depends on the compaction of the fabric. For this reason, cotton fabrics with different structures, and hence with different initial UPF (UPFi) values, were treated with different concentrations of the UV-absorber, according to a predefined experimental plan. The diffuse ultraviolet transmittance of the untreated and treated fabrics was measured and the UPF calculated. The response UPF has been modelised in function of the variables of the experimental plan: UPFi (that depends on the fabric compactness) and concentration of the finishing product.

Experimental

Material

Three different cotton fabrics have been used in the study in order to determine if the influence of the product depends on the structure of the original fabric. Their UPFi has been taken as the variable representing the structure the original fabrics, with three different levels, designated as low, medium and high UPFi. The authors in previous publications (Algaba et al. 2006; Riva and Algaba 2006) modelised the relationship between the fabric structure and UPF. The values of UPFi and the characteristics of each fabric are shown in Table 1.

Chemicals and treatments

The cotton fabrics have been treated with a commercial finishing product, an UV-absorber based on the oxalanilide, with anionic character. According to the technical information, it presents a weak absorption of radiation in the zone of high wavelengths of the UVA, strong absorption in the zone of short wavelengths of the UVA and maximum absorption in the UVB zone (Ciba Specialty Chemicals 2000).

Table 1. Characteristics of the original cotton fabrics.

Level of the variable UPFi	Original cotton fabrics		
	Low	Medium	High
Value of UPFi	4.06	4.78	6.57
Weight per surface unit (g/m^2)	94.93	122.09	177.99
Thickness (mm)	0.318	0.339	0.418
Cover factor image analysis (%)	89.42	93.96	97.72
Yarn number (tex)			
warp	14.3	14.3	25
weft	14.3	20	25
Thread count (yarns/cm)			
warp	40	40	40
weft	25	27	23

The product has been applied on every fabric sample at four different concentrations: 1, 2, 3 and 4% o.w.f. Sodium sulphate was added as auxiliary product of the treatment at different concentrations depending on the UV-absorber concentration: 9 g/l of sodium sulphate for the concentration of 1% and 2% o.w.f. of the product, 12 g/l for the concentration of 3% o.w.f. and 15 g/l for the concentration of 4% o.w.f. The bath ratio was 1/20 for all the treatments.

The treatment process with the UV-absorber was a conventional exhaustion process with raise of temperature from 30 °C to 96 °C, addition of the sodium sulphate, treatment time of 60 min at the maximum temperature and cooling of the bath. The treatments were carried out in a Linitest apparatus.

Experimental plan

Table 2 shows the variables of the experimental design and their levels in each experience. Two variables compose the system: the UPFi of the fabrics (UPFi) with three different levels, and the concentration of the UV-absorber in % o.w.f. (C) with five different levels, including the untreated fabrics.

Table 2. Variables and their levels in each experience of the experimental plan.

Sample no.	UPFi	*C*
1	4.06	0
2	4.06	1
3	4.06	2
4	4.06	3
5	4.06	4
6	4.78	0
7	4.78	1
8	4.78	2
9	4.78	3
10	4.78	4
11	6.57	0
12	6.57	1
13	6.57	2
14	6.57	3
15	6.57	4

The combination of the variables and their levels results in 15 experiences. These experiences allow analysing the interactions between the concentration of the finishing product and the compactness of the fabrics (Pepió and Polo 1996).

Determined parameters

Absorbance spectra in UV region

The absorption spectrum in the UV region of a solution of 2 g/l of the UV-absorber has been determined, using a spectrophotometer Shimadzu 256 FS/FW.

Ultraviolet transmittance spectra – average transmittances UVR, UVA and UVB

The diffuse transmittance spectra of the untreated and treated fabrics were obtained using the Ultraviolet Transmittance Analyser UV1000F of Labsphere. The shown spectra are the average results of ten measurements.

According to the Standard AS/NZ 4399:1996 (Sun protective clothing – evaluation and classification), the UVR transmittance through the fabric is defined as the arithmetic mean of the transmittances in the ultraviolet range wavelengths, from 290 to 400 nm.

Due to the fact that there is a great difference in the effect that the UVA and UVB radiation have over the human skin, it is interesting to have a parameter that quantifies the amount of both UVA and UVB radiation that pass through the fabric. To this aim, the average UVA transmittance and the average UVB transmittance are defined as the arithmetic mean of the transmittance in the wavelengths of the UVA (from 315 to 400 nm) and UVB (from 290 to 315 nm) respectively. It is especially important that the UVB transmission is as low as possible, as the radiation in this wavelength interval is much more damaging for the human skin.

Ultraviolet Protection Factor

The UPF of the fabrics has been determined by the *in vitro* method, according to the indications of the standard AS/NZ 4399:1996.

The UPF of each specimen is calculated as follows:

$$\mathrm{UPF_i} = \frac{\sum\limits_{\lambda=290}^{400} E_\lambda \times S_\lambda \times \Delta\lambda}{\sum\limits_{\lambda=290}^{400} E_\lambda \times S_\lambda \times T_\lambda \times \Delta\lambda}$$

where E_λ: CIE relative erythemal spectral effectiveness; S_λ: solar spectral irradiance; T_λ: spectral transmittance of the fabric; $\Delta\lambda$: wavelength step in nm; and λ: wavelength in nm.

The Rated UPF of the sample is calculated introducing a statistical correction. Starting from the standard deviation of the mean UPF, the standard error in the mean UPF is calculated for a 99% confidence level. The Rated UPF will be the mean UPF minus the standard error, rounded down to the nearest multiple of five.

$$\mathrm{UPF} = \overline{\mathrm{UPF}} - t_{\alpha/2,N-1} \cdot \frac{\mathrm{SD}}{\sqrt{N}}$$

where $\overline{\mathrm{UPF}}$: mean UPF; $\mathrm{t}_{\alpha/2,\mathrm{N}-1}$: t variate for a confidence level $\alpha = 0.005$; and SD: Standard deviation of the mean UPF.

If the Rated UPF determined using the above formula is less than the lowest individual UPF measurement for that sample, then the Rated UPF shall be the lowest UPF measured for the specimens, rounded down to the nearest multiple of five. The rated UPF is always a multiple of five. For UPF ratings of 55 or greater, the term 50+ shall be used.

The Australian/New Zealand Standard establishes, in addition, a classification system of the fabrics according to their sun protective

Table 3. UPF classification system of sun protective clothing, for the purposes of labelling (Standard AS/NZ 4399:1996).

UPF range	UVR protection category	UVR transmission (%)	UPF rating
15–24	Good protection	6.7–4.2	15, 20
25–39	Very good protection	4.1–2.6	25, 30, 35
40–50, 50+	Excellent protection	≤ 2.5	40, 45, 50, 50+

properties. For the purpose of labelling, sun protective clothing shall be categorised according to its rated UPF, as shown in Table 3.

Modelisation of the UPF according to UPFi and concentration of the UV-absorber

Codification of the variables

The statistical analysis and modelisation of the UPF was carried out using codified variables. If the model, together with the effects of the factors, includes the quadratic effects and interactions, it is nearly sure that there will be problems during the matrix calculations. These problems are due to the higher or lower numerical value of one variable with regard to another and to the fact that the quadratic effects and interactions can reach numerical values much lower or higher than the simple effects. Hence, the use of original variables can lead to a model that, although perfectly valid to describe the response value, makes bigger the significance of quadratic effects and interactions and masks the significance of the simple effects. From the technical point of view this is not useful when looking for the optimisation of the system.

To avoid these problems and obtain reliable statistical models the data analysis should be always carried out with codified variables. When the variables are codified, the levels of all of them are converted into the values -1, 0 and $+1$, and hence all have the same weight in the analysis of their effects. In addition, the weight of every level of the variables with the codification is the same in the simple effects, quadratic effects and in the interactions, as multiplying -1, 0 or $+1$ between them will always give as a result -1, 0 or $+1$.

However, a requirement to codify the variables is that their levels are equidistant (Pepió and Polo 1996). In our system, the levels of the variable C (concentration of the finishing product) are equidistant and present no problems for their codification. But the levels of the variable UPFi (initial UPF) are not and thus a real codification of the variable is not possible. The adopted solution is to carry out a pseudo-codification of these variables, applying to each level the formulas shown in Table 4.

Table 4. Formulae for the pseudo-codification of the variables.

Original variables	Codified variables	Codification formulae
UPFi	*c*UPFi	$c\text{UPFi} = \frac{\text{UPFi}-5.2945}{1.2725}$
C	cC	$cC = \frac{C-2}{1}$

Initial model and estimation of the significant coefficients

The statistical data analysis was carried out by the lineal model method. The initial model includes the terms corresponding to the simple effects *c*UPFi and cC, as well as their interaction, quadratic terms and the interaction of the quadratic terms with the simple effects.

$$\begin{aligned}\text{UPF} =&\beta_0 + \beta_1 \cdot c\text{UPFi} + \beta_2 \cdot cC + \beta_3 \cdot c\text{UPFi} \cdot cC\\ &+ \beta_4 \cdot c\text{UPFi}^2 + \beta_5 \cdot cC^2 +\\ &+ \beta_6 \cdot c\text{UPFi}^2 \cdot cC + \beta_7 \cdot c\text{UPFi} \cdot cC^2\end{aligned}$$

The estimation of the significant coefficients of the model was carried out by the forward Stepwise Regression method. The significance of the coefficients and the complete model is checked for an α error prefixed in 5%.

Results and discussion

Absorbance spectra in the UV region

Figure 1 shows the absorbance spectra of a solution of 2 g/l of the UV-absorber in the ultraviolet region (190–400 nm) of the electromagnetic spectrum, as well as the wavelength of maximum absorption in the UVA and UVB regions.

In the wavelength interval from 290 to 400 nm, which is the one that is considered in the

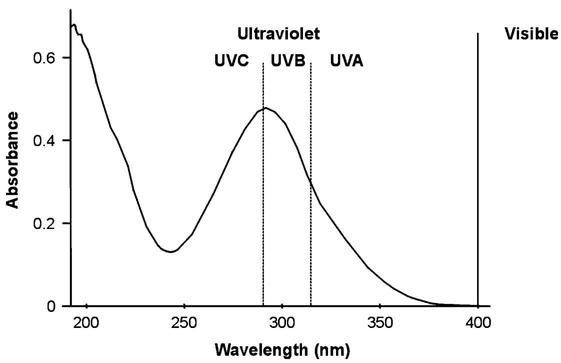

Figure 1. Absorbance spectrum in the UV region.

calculation formula of the UPF, the maximum absorption of radiation by the product is located at 290 nm, in the shortest wavelength of the UVB. From this point, when the wavelength increases, the absorption decreases and it is null in the border of the ultraviolet and visible regions, at 400 nm. Although the absorption in the UVA zone is low, the finishing product absorbs a great amount of radiation in the UVB zone. This fact makes the UV-absorber very appropriated in order to improve the protection factor, as it preferentially absorbs the radiation of the most damaging wavelengths that has a higher weight in the calculation of the UPF of the fabrics.

Transmission spectra in the UV region

Figure 2 shows the transmission spectra in the UV region of the untreated cotton fabrics (fabrics with low, medium and high UPFi), as well as the spectra of these fabrics after being treated with the UV-absorber at the different concentrations. Table 5 shows the calculated average transmittances in the UVR as well as in the UVA and UVB regions.

The addition of the UV-absorber decreases the transmittance values at all the wavelengths of the ultraviolet range and varies the characteristic shape of the cotton fibre. Particularly, in the UVB zone, the decrease of the transmission is very noticeable, the curves present a nearly horizontal shape along the UVB and up to 350–360 nm in the UVA zone. From this wavelength to the beginning of the visible range the transmission increases progressively. In other words, the higher decrease of the transmission of UV radiation is produced in the wavelengths where a higher light absorption by the UV-absorber was found.

The numerical results corroborate the general decrease of the average transmittances when the UV-absorber is applied on the fabrics. The average transmittances decrease when the concentration of the finishing product increases. A synergetic effect

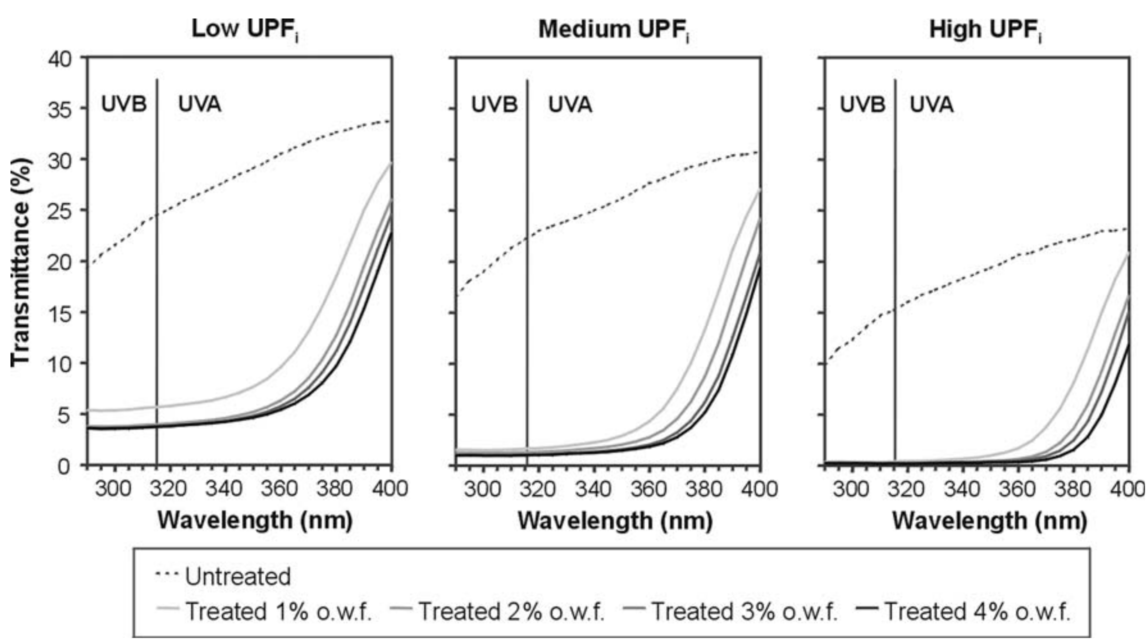

Figure 2. Transmission spectra in the UV of the cotton fabrics untreated and treated with the UV-absorber.

Table 5. Average transmittances of the cotton fabrics, untreated and treated with the UV-absorber (T_{UVA}: 315–400 nm; T_{UVB}: 290 –315 nm; T_{UVR}: 290–400 nm).

Sample			Average transmittance (%)		
No.	UPFi	*C*	T_{UVA}	T_{UVB}	T_{UVR}
1	Low	0	29.76	22.01	27.97
2	Low	1	13.13	5.63	11.49
3	Low	2	9.67	4.01	8.44
4	Low	3	8.98	3.87	7.87
5	Low	4	8.07	3.71	7.12
6	Medium	0	25.22	19.03	23.79
7	Medium	1	8.39	1.59	6.91
8	Medium	2	6.29	1.25	5.19
9	Medium	3	5.03	1.06	4.16
10	Medium	4	4.48	1.03	3.73
11	High	0	19.91	12.87	18.27
12	High	1	5.19	0.38	4.14
13	High	2	3.13	0.24	2.50
14	High	3	2.53	0.24	2.04
15	High	4	1.92	0.22	1.55

of the two variables (concentration of the UV-absorber and UPFi of the fabric) is observed, thus the blocking of the UV radiation is accelerated when the product concentration and UPFi are increased simultaneously.

In a great number of treated fabrics it is achieved a decrease of the average transmission below the values of 6.7%, 4.1% and 2.5%, which are the guide values given by the standard AS/NZ 4399:1996, needed to reach good, very good and excellent protection, respectively.

UPF of the fabrics

The results obtained in the measurement of the UPF of the untreated and treated fabrics are shown in Table 6.

The table shows that the application of the UV-absorber at any of the studied concentrations produces an improvement of the UPF of the fabrics.

When the lightest fabric is treated, a high concentration of the finishing product is needed to achieve a good protection (UPF ≥ 15). The treatment with the highest concentration of the product does not promote a level of very good protection on the fabrics (UPF ≥ 25). But if the fabric has a sufficient compactness a level of excellent protection (UPF ≥ 40) is reached even with the treatment at the lowest concentration of the UV-absorber.

Table 6. UPF and Rated UPF of the untreated and treated cotton fabrics (UPF < 15: no protection; 15 ≤ UPF < 25: good protection; 25 ≤ UPF < 40: very good protection; UPF ≥ 40: excellent protection).

Sample			Ultraviolet Protection Factor	
No.	UPFi	*C*	UPF	Rated UPF
1	Low	0	4.06	1
2	Low	1	14.86	10
3	Low	2	21.13	20
4	Low	3	21.04	20
5	Low	4	23.42	20
6	Medium	0	4.78	1
7	Medium	1	48.82	45
8	Medium	2	64.38	50+
9	Medium	3	75.80	50+
10	Medium	4	77.11	50+
11	High	0	6.57	5
12	High	1	159.49	50+
13	High	2	267.86	50+
14	High	3	297.13	50+
15	High	4	344.02	50+

Modelisation of the response UPF of the fabrics

The model that estimates the response UPF regarding the UPFi of the fabrics and the concentration of the UV-absorber is the following, in codified variables, with $R^2 = 99.95\%$:

$$\begin{aligned} \text{UPF} =\, & 114.3044 + 123.9658 \cdot c\text{UPFi} \\ & + 31.0565 \cdot cC + 39.9391 \cdot c\text{UPFi} \cdot cC + \\ & + 28.4156 \cdot c\text{UPFi}^2 - 11.8227 \cdot cC^2 \\ & + 13.3796 \cdot c\text{UPFi}^2 \cdot cC \\ & - 10.8925 \cdot c\text{UPFi} \cdot cC^2 \end{aligned}$$

Figure 3 shows the response surfaces according to the estimated model for the cotton fabrics against the variables: UPFi (initial UPF) and *C* (concentration). The curves show the combination of the variables that provide UPF values multiple of 5 until reaching a UPF value of 50 and multiple of 25 for higher values. According to the UPF intervals for classification and labelling indicated by the standard AS/NZ 4339:1996, the different grey intensities distinguish the zones with UPF

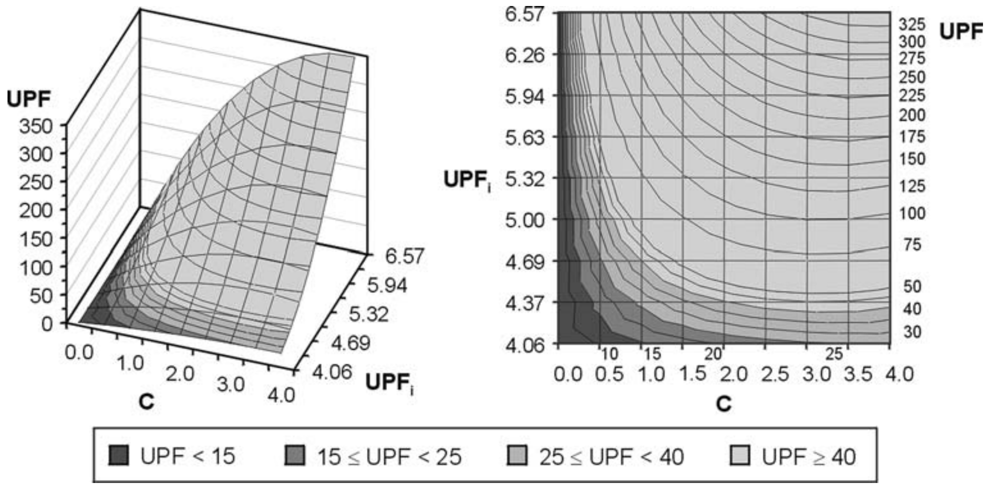

Figure 3. Response surfaces estimated according to the model that correlates the response UPF of the fabric in function of the UPFi of the fabric and the concentration of the UV-absorber.

that do not provide protection (UPF < 15), that provide good protection (15 ≤ UPF < 25), very good protection (25 ≤ UPF < 40) and excellent protection (UPF ≥ 40).

The model proves that the treatment of the fabric with the UV-absorber has a significant influence on the UPF of the fabrics, producing an increase in the value of the UPF. The variables of the system, concentration of the product and the initial compactness of the fabric (represented by its UPFi), have both a significant influence on the response UPF.

The increase of the variable concentration of the finishing product has a positive effect on the protection factor. In addition, the tendency of the curves shows that there is a very important contribution on the increase of the UPF due to the effect of the interaction of this variable with the UPFi. For the fabrics with a low UPFi (less compacted structure) the concentration of the finishing product produces very small increments on the final UPF while for the fabrics with a high UPFi small increases of the concentration produce very high improvements on the UPF. Hence the higher the UPFi the more noticeable is the effect of the concentration on the protection provided by the fabrics against ultraviolet radiation.

The negative coefficients of the quadratic terms of the concentration are as well remarkable and produce a noticeable curvature of the response surface, a deceleration in the speed with which the UPF increases with the concentration. For a fabric with a fixed UPFi, the same increment in the concentration produces lower and lower increments of the UPF when the concentration is higher and higher. The tendency is to reach the saturation approximately with a concentration of 3–3.5% o.w.f. of the product and higher concentrations will not produce an improvement on the UPF.

When the objective is the optimisation of the treatment conditions in order to reach a fixed level of protection, an adjustment of both the product concentration and the fabric compactness is needed. The treatment of any fabric with a sufficient concentration of the UV-absorber may be not enough to reach a high protection; hence the appropriate amount of the product must also be applied on a fabric with a minimum compactness.

Conclusions

The finishing treatment with an UV absorber is an efficient mean to improve the protection provided by the fabrics against the damaging effect of the ultraviolet radiation.

The statistical model proves that the application of the finishing product increases significantly the UPF of the fabrics and allows the obtention of light fabrics that can provide level of good protection (15 ≤ UPF < 25), very good protection (25 ≤ UPF < 40) and excellent protection (UPF ≥ 40). The reached level of protection depends, nevertheless, on both the variables considered in this study: the concentration of the UV absorber and the UPFi of the fabric, that is, the structure of the original untreated fabric.

The increase of the concentration of the UV-absorber produces an increase on the final UPF. The influence of this variable has a clear negative parabolic tendency, that is, a deceleration in the speed with which the UPF increases with the concentration. There is a tendency to reach saturation, a point from which an increase in the concentration will not produce a significant variation of the UPF.

The increase on the UPF produced by the concentration of the UV-absorber is strongly influenced by the fabric compactness. There is a noticeable interaction between the UPFi of the fabric and the concentration of the finishing product. In the treatment of the fabric with low UPFi, the increase of the UV-absorber concentration provides very small increments of the response UPF. But the higher the UPFi the more noticeable is the effect of the concentration of the product, and a small increment of the concentration produces a very significant improvement on the UPF.

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