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A New Method of Determination of the UV-Radiation Permeability Through Cotton Cloth

Abstract

An investigation was carried out with the objective of imparting increased UV-absorbtivity to a cotton cloth. For experimental convenience, a Rayosan C UV-absorber was applied alone or in combination with Cibafast W and Uvinul DS 49. In the first case, a weaker effect was attained as compared to the combination; this fact was given a reasonable explanation. An original method was used for the estimation of UV-ray permeability by applying a highly photosensitive colorant as a standard. The degree of photo destruction of the colorant was determined by K/S and RCI. The research included the ability of evaluating the UV permeability of treated cotton cloth by the degree of photo-destruction of a highly photosensitive dye.

Key words: *cotton cloth, UV-absorbers, UV-permeability evaluation.*

Introduction

The specialists relate the sharp increase of dermal diseases (including carcinomas) to the increased permeability of UV-rays, caused by air pollution. In the last ten years of the twentieth century, a notable tendency was observed to use protective clothing as a barrier preventing these illnesses. In this connection, a thorough and systematic study into the protective properties of a large number of textile materials was undertaken. The initial results obtained were not very encouraging [1-4], as they revealed that almost all textiles are highly pervious to UV-rays. Reliable protection could only be achieved by dense and thick textiles, which unfortunately are unsuitable for hot summer days [5]. It was also found that a satisfactory protection level might be achieved by the additional treatment of textiles with substances known as UV-absorbers [1,6-8], causing an increased absorptivity of sunlight. We used the Cibafast W absorber recommended [1] for protein fibres as a benzotriazol representative applied not through exhaustion but through a pad-dry-cure.

The quantity of sunlight absorbed or permeated through the textile material is determined by its type. On one hand, each type is characterised by the chemical structure of the fibre-forming polymer and the ability of its functional groups to absorb UV-rays. On the other hand, structural features such as fibre thickness, braid type, presence of holes etc. should be taken into account. Of considerable importance is the presence of various compounds used as textile modifiers: dyes, optical bleaching agents, finishing additives etc.

Taking into account all the aspects mentioned above, the aim of this investigation was the preparation of cotton cloth with decreased UV-ray permeability by treating the initial specimens with UV-absorbers. The research would include evaluating the UV permeability of treated cotton cloth by the degree of photo-destruction of a highly photo-sensitive dye.

Experimental

Materials

UV-absorbers:
Rayosan C [Clariant] is a heterocyclic compound, which forms a covalent bond with the macromolecule of cellulose;
Cibafast W [Ciba] is based on benzotriazol;
Uvinul DS 49 [BASF] is based on benzophenone.
Methylene blue is a highly photosensitive colorant.
The textile cloth test specimen has a mass of 132 g/m^2.

Methods

The treatment with Rayosan C was carried out in accordance with the recommendations of the producer, and the conditions used are described in the corresponding table. The processing with the other two substances was carried out by the procedure of foulard soaking involving drying and subsequent thermal or vapour-fixation treatment. The particular conditions are also correspondingly described.

The irradiation was carried out under environmental summer conditions in the year 2001. For this reason, a 'zero filter' and a dyeing standard characterise each series of experiments. In the absence of suitable instrumentation for measuring the UV-permeability of the cloth, an original method based on the use of a highly photosensitive colorant as a standard was applied [9]. The degree of its photo-destruction is primarily determined by the intensity of the UV-rays, and is defined by the Kubelka-Munk function (*K/S*). The relative colour intensity (*RCI*) could be estimated from experimental data by the following expression:

$$RCI = \frac{(K/S)_t}{(K/S)_o} 100 \quad [\%] \qquad (1)$$

The numeric values acquired permit a relatively good description and comparison of the various types of cloth treatment, determining the variety of UV-absorption and permeability values. The standard (*S*) was prepared by using the methylene blue colorant, whose degree of bleaching allows the quantitative estimation of the experimental samples studied.

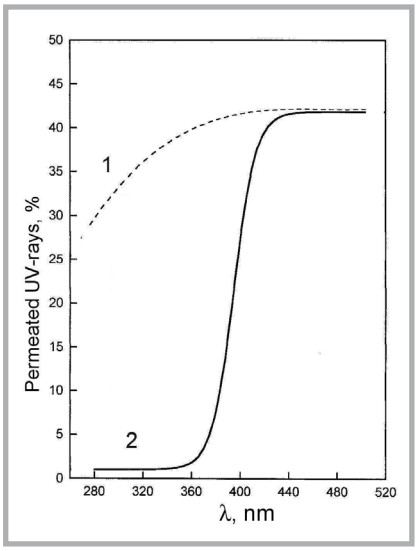

Figure 1. *UV-rays permeated through cotton cloth specimens with predefined characteristics: 1 - unprocessed; 2 - processed with a UV-absorber.*

These were processed under various treatment conditions, and are formally called *filters*. Each experimental series includes a sample called a 'zero filter' [ZF], which is essentially the unprocessed initial cotton cloth.

The preparation of the experimental specimens for irradiation was 'sandwich' type: the sample was placed over the standard, after which the sandwich was subjected to irradiation. The experimental results were processed by specialised and conventional graphic and statistical software.

Results and Discussion

UV-absorption increase by Rayosan C processing

As seen from Figure 1, the cotton fibres and the materials fabricated from them have a very high permeability throughout the whole UV-range [1]. The characteristics of the cloth are as follows: mercerised and bleached poplin with m=107 g/m^2; thickness 0.18 mm, number of warp in a weft: 52/25 and 0.4% holes. This data unambiguously demonstrates the necessity to process the samples by UV-absorbing substances. Figure 1 displays the satisfactory results attained after such treatment. The conditions of samples treatment are presented in Table 1.

The assessment of the degree of colorant bleaching for filters prepared as described in Tables 3, 4 and 5 was followed by irradiation at three different irradiation times as shown by the experimental data and RCI presented in Table 2.

The experiment was reproduced several times, and the results obtained support the initially observed tendencies. The presence of *Rayosan C* in cotton fibres resulted in a considerably increased absorption of UV-rays. However, due to the variation of concentration and localisation of the absorber, no stable tendency of the attained effect was outlined. This is probably related to the heterogeneous properties of the textile material, which requires the acquisition of more data for further analysis. The *Rayosan C* absorption band has a narrowly outlined maximum of λ=280 nm (see Figure 2). It falls in the UV-Vis region (280-320 nm), which is considered as highly hazardous for melanomas, or as harmful to DNA at high doses of irradiation [1].

Increase of UV-rays absorption by using a combination of absorbers

The inclusion of UV-A$_1$ absorbing substances expands the absorption range to 320-

Table 1. *Conditions for preparation of filters by treatment of specimens with Rayosan C.*

Treatment type no.	Rayosan C			
	4%		2%	
	Thermal fixation	Steam fixation	Thermal fixation	Steam fixation
	130 C; τ=3 min	102 C; τ=30 s	130 C;τ=3 min	102 C; τ=30 s
1	-	+	-	-
2	+	-	-	-
3	-	-	-	+
4	-	-	+	-

Table 2. *Degree of bleaching of methylene blue after irradiation through filters prepared by treatment of specimens with Rayosan C (RCI - relative colour intensity, K/S - Kubelka-Munk function); Irradiation conditions: June, T=26°C, $(K/S)_o$=2.64.*

Treatment type no.	Irradiation time, h					
	4	11	19	4	11	19
	K/S			RCI, %		
1	2.64	1.945	1.565	100	74	59
2	2.64	1.868	1.433	100	71	54
3	2.64	1.868	1.486	100	71	56
4	2.52	1.795	1.600	95	68	61
ZF	2.21	1.662	1.354	83	63	51
S	1.97	1.289	0.987	75	49	37

Table 3. *Conditions for filter* preparation by combined treatment of specimens with Rayosan C and Cibafast W or Uvinul DS 49 (*these filters were prepared after a preliminary treatment of specimens with Rayosan C as described in Table 1. The subscripts correspond to treatment types 1 or 2).*

Treatment type no.	Soaking solution		Heating/Vapour Treatment	
	Cibafast W 2%	Uvinul DS 49	Thermal fixation 150 C, 5 min	Vapour fixation 102 C, 2 min
5_1	+	-	-	+
6_2	+	-	+	-
7_1	-	+	-	+
8_2	-	+	+	-

Table 4. *Bleaching of methylene blue after irradiation through filters prepared by combined treatment of specimens. Irradiation conditions: August, T=28°C; $(K/S)_o$=2.64 (*filters used in the kinetic study).*

Treatment type no.	Irradiation time, h			
	4	12	4	12
	K/S		RCI, %	
1*	2.21	1.713	84	65
5_1*	2.32	1.929	88	73
6_2	2.32	1.929	88	73
7_1*	2.41	2.100	88	80
8_2	2.28	1.754	91	66
ZF*	2.06	1.498	78	57
S*	1.87	1.298	70	49

Table 5. *Bleaching of methylene blue after irradiation through filters* prepared by combined treatment of specimens. Irradiation conditions: August, T=38°C; $(K/S)_o$=2.64 (*filters used in the kinetic study).*

Treatment type no.	Irradiation time, h			
	4	12	4	12
	K/S		RCI, %	
1	1.809	1.262	68	48
5_1	2.030	1.403	77	53
7_1	2.040	1.433	77	54
ZF	1.781	1.140	67	43
S	1.501	0.981	56	37

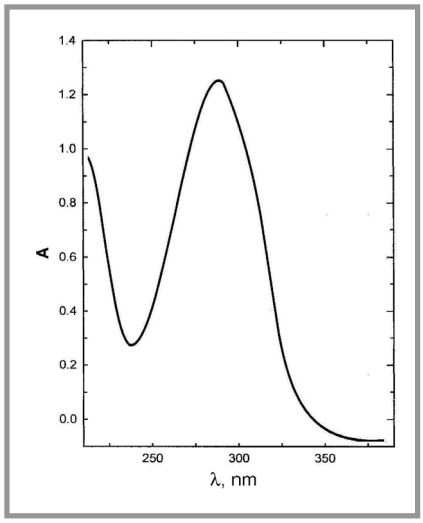

Figure 2. *UV-absorption spectrum of Rayosan C.*

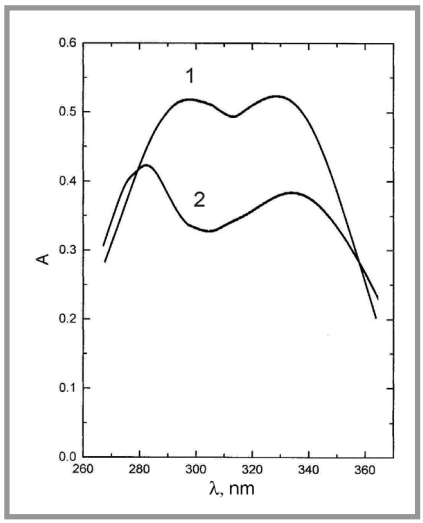

Figure 3. *UV-absorption spectra of Cibafast W (1) and Uvinul DS 49 (2).*

340 nm, in which the existence of carcinogenic potential is presumed [1]. It may be expected that this will cause higher absorption and protection effects. A suitable combination of absorbers is *Cibafast W* and *Uvinul DS 49*, whose absorption spectra are presented in Figure 3. It is seen that each of these substances has two maxima. One of the absorption bands is superimposed on that of Rayosan C, while the second is in the UV-A_1 range. The experimental conditions and the results acquired for the degree of bleaching of the colorant are presented in Tables 3, 4 and 5. The analysis of data shows that the combination of two additives causes considerably higher absorption compared to the single use of *Rayosan C,* as is evidenced by the higher RCI values.

A comparative kinetic study

The experimental results obtained were partially used in the kinetic investigation we carried out. This study permits us to specify the character of the photo-discolouration reaction, and to evaluate the rate constants as a prerequisite for further analysis.

According to Giles, [10-12] the aggregation of colorants is decisive for their light stability. The type of aggregation affects the colorants' photo destruction as evidenced by the corresponding kinetic curves.

By analogy with the kinetic regularities established by Giles, two series of kinetic data were obtained in this investigation, corresponding to a first-order reaction and characterised by the monomolecular state of the colorant or by small size aggregates (Figures 4a and 5a). In general, such data may be presented by the following equations:

$$\ln \frac{C_o}{C} = kt \qquad (2)$$

$$\ln C = \ln C_o - kt \qquad (3)$$

where:

C_o - the initial intensity of the standard $(K/S)_o$,

C - the intensity of the standard after a definite irradiation time $(K/S)_t$.

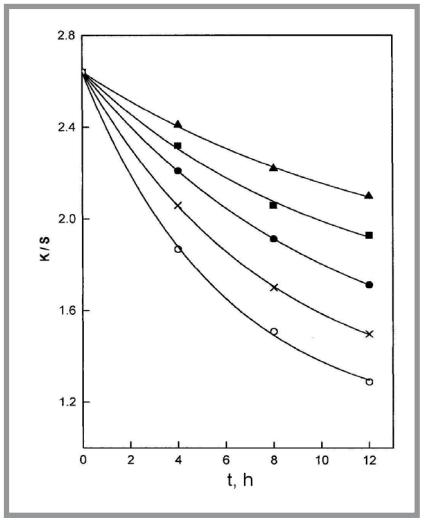

Figure 4a. *Kinetic curves for photo bleaching of the methylene blue standard through various filters: o - without a filter; x - 'zero filter'; ● - samples processed with Rayosan C; ■ - a combination of Rayosan C and Cibafast W; ▲ - a combination of Rayosan C and Uvinil DS 49; Irradiation conditions: T= 28°C, and natural environment.*

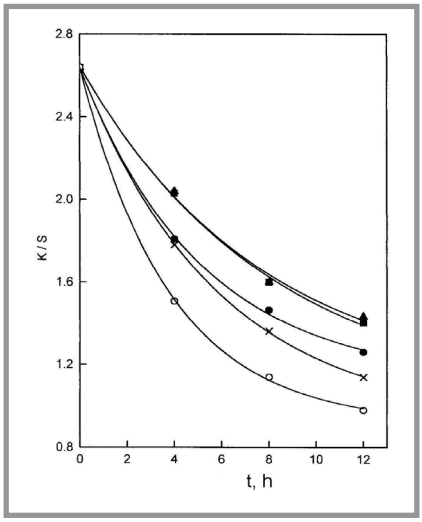

Figure 5a. *Kinetic curves for the methylene blue standard photo bleaching through various filters: o - without a filter; x - with a 'zero filter';● - samples processed with Rayosan C; ■ - a combination of Rayosan C and Cibafast W; ▲ - a combination of Rayosan C and Uvinil DS 49; Irradiation conditions: T= 38°C, and natural summer environment.*

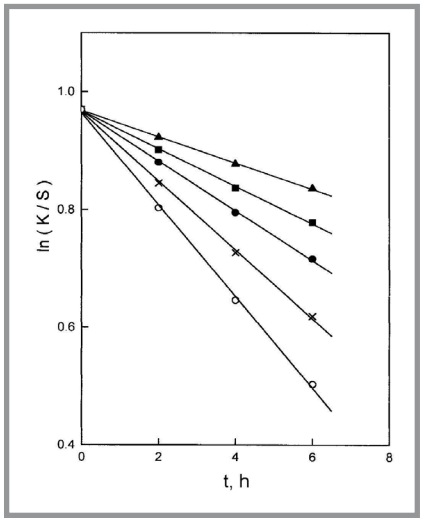

Figure 4b. *Kinetic curves for the photo bleaching of methylene blue standard through filters presented in semi-logarithmic co-ordinate system.*

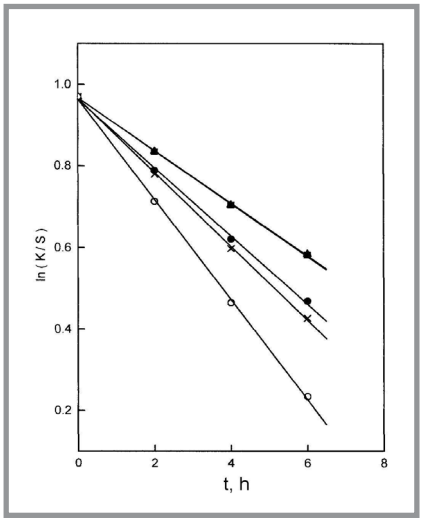

Figure 5b. *Kinetic curves for the photo bleaching of methylene blue standard through filters, as presented in a semi-logarithmic co-ordinate system.*

Table 6. *Rate constants of the photo-destruction reaction of the methylene blue for various treatment types and conditions.*

Treatment type	T=28 C	T=38 C
k_1	0.042	0.084
k_{51}	0.032	0.065
k_{71}	0.022	0.064
k_{ZF}	0.059	0.091
k_S	0.078	0.123

The presentation of data in a semi-logarithmic co-ordinate system confirms the linear character of the kinetic expressions (Figures 4b and 5b). The slope of equation (3) is the rate constant whose values for the various treatment types are presented in Table 6.

The rate of photo destruction of methylene blue depends on the permeability of the filters, which is variable for the different combinations. The rate constant *k* is highest for the irradiated standard, i.e. without a filter. The 'zero filter' slightly retards the photo destruction. In the presence of absorbers, the lowest permeability of UV-rays is attained. The best results are obtained when absorbers combinations are used.

The experimental impact of temperature is easily observed and its effect corresponds to the basic laws of theory (Tables 4 and 5). The destruction of the tiazine colorant is essentially a photo oxidative reaction, proceeding in the presence of sunlight. This type of colorant is characterised by the proceeding of reduction as a reverse reaction in the dark. Due to this fact, it must be understood that for the acquisition of reliable and reproducible data the standard colorant must be evaluated every 24 hours.

It should be stated that the kinetic studies we did were incomplete, and were only aimed at illustrating the sensitivity of the standard as well as its abilities to define the type of absorbers upon the permeability of the treated filters. This was why no statistical analysis was made, but it should be stressed that each version was reproduced several times. The analogy in the way the photo-destruction kinetic curves of methylene blue run is also an indirect proof of the repeatability of our test results. The irradiation conditions were one and the same, as were the mechanisms of photo-fading. The various different chemical constituents of the filters was the reason for their different permeabilities, as manifested by the different photo-fading rates of the standard.

The dye's concentration upon the standard was chosen so that the photo-destruction rates would be constant, i.e. would not depend upon the concentration of dye. An analogy with the data obtained by Giles was made, while the partial kinetic tests confirmed that the reaction was actually of the first order indeed.

Conclusion

An investigation was carried out aimed at preparing cotton cloth specimens with an increased absorptivity of UV-radiation, which is initially absent. Using UV-absorbers attains this objective.

The combination of Rayosan C with other absorbers resulted in a higher filtration effect of the harmful UV-rays.

The possibility of estimating and quantifying permeability was studied by using numerical values, which enabled their comparative analysis. A highly photosensitive standard colorant was used for this purpose. This original study was successful, as the experimental specimens were satisfactorily described by both K/S and the calculated RCI values.

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Received 21.01.2002 Reviewed 10.01.2003