Asian Journal of Chemistry; Vol. 23, No. 3 (2011), 1263-1268

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Ultrasonic Energy Utilization in Implementation UV Absorbers to Cotton Fabrics

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(*Received*: 3 May 2010; *Accepted*: 8 November 2010) AJC-9283

Clothing provides protection against the ultraviolet radiation emitted by the sun. However the protection provided is not sufficient in some cases. UV absorbers are used to reduce the fiber damage and to reduce fading away colours of dyestuffs fixed in the material caused by UV radiation, as well as those can also be applied especially to the textiles for protecting the people who are being or working in outdoor areas against UV radiation. In this study, the ultrasonic energy sources are utilized in the implementation of UV absorbers to cotton fabrics, based on the cavitation effect of ultrasonic energy it creates in liquid environment. In the study, 100 % cotton woven fabrics have been dyed with Remazol blue RR (DyStar) having 0.2 % colour intensity and after dyeing different concentrations [1, 2, 3 and 4 %] UV absorbers were applied to differently liquored fabrics by conventional ultrasonic probe and ultrasonic bath methodologies. The effects of ultrasonic energy, ultraviolet protection factor values, protection against UV radiation categories and ΔE*, ΔL*, ΔC* and ΔH* colour values and fastness properties were compared in terms of methods.

Key Words: Dyed fabric, UV absorber, UV protection factor values, UV radiation, Ultrasonic methods.

INTRODUCTION

Ultraviolet radiation (UVR) is part of the solar energy reaching to earth. The electromagnetic radiation having a wavelength of 290-400 nm is called ultraviolet (UV). UVA (320-400 nm) forms 95-98 % and UVB (290-320 nm) forms 2-5 % of the UVR. UVA is least harmful form of UV radiation. UVB radiation has the wavelength of 290-320 nm and it is known that it is much more harmful to the eyes, skin than UVA and it is responsible for skin cancer progression[1].

Although clothing protects from sun, adequate protection cannot be achieved against UV radiation since the light and thin clothing is being preferred especially in hot weather. The protection degree provided by a substance against the adverse effects of sunlight is known as the solar protection factor. Ultraviolet protection factor is a measure of protection provided by a fabric that against UV radiation. When the light falls directly on the fabric, a part of the radiation is reflected and the material absorbs a portion of it and another portion of it passes through the fabric. The amount of radiation passing through the material is expressed as spectral transmittance ($T\lambda$). The transmittance spectrum varies depending on the characteristics of the fabric[2].

UV absorbers can block the degradation of the polymer by absorbing UV rays and they convert UV energy to the heat form. These substances also have energy transfer functions at the same time. These types of materials capture the induced molecules and return them back to their base conditions and thus they prevent bond fragmentation. UV absorbers are derivatives of *o*-hydroxyl benzophenone, hydroxyphenyltriazine and hydroxyphenil benzotriazole[3].

Ultrasonic sound waves have frequencies outside of human hearing limits and the ultrasonic sound waves have frequencies between 20 kHz-20 MHz, while the human ear can only hear sound waves 16 Hz-16 kHz. The power of ultrasonic energy reveals its chemical effects through cavitation event. Like any sound wave, the ultrasonic energy is transmitted through the waves. These waves create compressions and relaxations of the molecular structure of the medium they pass through. When an adequate amount of negative pressure is applied in liquid, the fragments are observed and the cavitation bubbles are generated in the liquid. These balloons cause the release of a large amount of energy by colliding each other during consecutive compression periods[4].

The first requirement for studies in Sonochemistry is using the transducers to transform electrical energy into sound energy. Sound waves are usually applied in either ultrasonic bath or ultrasonic probe environment. In both cases, the changing electric field produces a mechanical vibration at 20-50 kHz[5].

The use of ultrasonic energy at the wet textile processing is beneficial in terms of process time, saving energy and chemicals and improving the product quality. As a result of cavitation formed on the solid/liquid interface the mass transfer from liquid to solid is increased[6]. In the wet textile processes large amounts of water, electricity and thermal energy are used. The chemicals helping to increase and decrease the processing speed are used in most of these transactions. High temperatures are required to ensure mass transfer from the liquid media, in which the transactions were made, to the surface of textile materials within the specified period of time. As with all chemical processes, these transfer processes are time and temperature dependent. Most of the radiofrequency, microwave and IR heating techniques are used to reduce energy consumption and processing time. Although the ultrasonic energy is an alternative considerable interest area in textile processing, it could not go beyond the laboratory conditions to reach to the industrial scale. For using the ultrasonic energy in industrial scale, the attention is drawn to issues such as the homogeneity in the bath and the distribution of ultrasonic pressures, the positions of transducers, passing form of fabric from the machine, bath temperature in designing of the machines[7].

The researches are ongoing on using ultrasonic energy in preparation of dressing baths and emulsion paths, removing dressing, alkaline media processes and bleaching processes, dyeing and final washing, enzymatic processes. In the ultrasonic method, it is indicated that the processing time decreased in the hydrogen peroxide bleaching and the whiteness degree increased in spite of continued operation at low-temperatures[8], that in the bio-cleaning of raw cotton with pectinase the sonication had positive effects on tensile strength, wettability and whiteness degree of materials above[9], that combination of conventional and ultrasonic methods decreased enzyme consumption, processing time and fiber damage, that ultrasonic energy greatly developed the enzyme effect without decreasing the fabric strength in enzymatic pretreatment of cotton[10,11]. In the reduction cleaning of PLA fibers dyed with disperse dyestuff the chemical material consumption, fiber damage, waste liquor burden could be reduced when ECE detergent used instead of reducing agent in ultrasonic method[12]. In the method in which ultrasonic probe was used in final washings of reactive dyeing process, it is indicated that the fastnesses cleaning was better[13], that sonication had positive effects for dyeing cellulosic fibers with reactive dyes in terms of dyeing and fastness propertie[14,15], that sonication had no effect on Tg value and dyeing rate and dye shrinkage of fiber PES dyeing with disperse dyes[16], that more dye adsorption was happening in dyeing of PA/lycra mixed materials with reactive dyestuffs. However the dyeing processes were not effective on the fastness properties in ultrasonic method[17], that the colour strength of dyeing processes were better in dyeing nylon 6 with reactive dyestuffs, that the diffusion was better because of de-aggregation in dyestuff molecules and that from the ultrasonic energy could be effective on dyestuff-fiber covalent bond fixation[18].

EXPERIMENTAL

Textile: 155 g/m^2 weighted knitted fabrics produced by using number Ne30 100 % cotton yarn that do not contain bleached optical whiteners.

Dyestuff: Bi-functional reactive dyestuff (Remazol Blue RR- C.I. No. has not been referred to-DyStar).

UV absorbent: ((Rayocan C- is a heterocyclic compound, which forms a covalent bond with the macromolecule of cellulose-Clariant).

Used set-up: Polimat HT Sample Dyeing Machine-(Type A11612N-Emsey) was used in the dyeing process of test samples, the percentage transmittance values of fabrics were measured by Lambda 9 Perkin Elmer UV-visible spectrophotometer and the spectral reflectance values were measured by Datacolor Spectra Flash 600 plus reflectance spectrophotometer. Branson 2200-E4 ultrasonic bath and Branson Sonifier 250 ultrasonic probe were used as ultrasonic energy resources.

Dyeing process of test samples: The dyeing process of fabrics was performed at 60 °C for 80 min through the isothermal dyeing method by adding salt and alkali in portions according to shrinking method according to the recipe indicated in Table-1 and then the washing procedure in Table-2 was implemented.

TABLE-1
DYEING RECIPE

Material amount	5 g
Bath ratio	1:10
Remazol Blue RR	0.2 % o.w.f.
NaCl	180 g/L
Na_2CO_3	20 g/L

TABLE-2
WASHING PROCESSES APPLIED AFTER DYEING

Cool rinsing with overflow	3 L water
Neutralization with acetic acid	pH = 7
Hot rinsing	2 min at 80 ºC with 500 mL water
Soaping at the boil	10 min with 400 mL water
Cold rinsing	10 times with 1000 mL water

UV absorbent application to the test samples: UV-absorbent was applied to dyed fabric as UV absorbent material at 1, 2, 3 and 4 % according to in the recipe given in Table-3 and using the process shown in Fig. 1. Three methods were applied as conventional, ultrasonic probe and ultrasonic bath. In the method in which ultrasonic probe was used in UV-absorbent substance applications, 1/4 probe tip was used and the output control setting was set to 4. The ultrasonic energy was applied continuously during the operation by 1 cm dipping probe tip into the bath. The ultrasonic bath used in the study was at 220 V and 205 watts of power with a wave range of 50-60 Hz and a wave sensitivity of 47 Hz ± 6 %. The methods for applications were repeated three times.

TABLE-3
UV ABSORBER APPLICATION RECIPE

Material amount	5 g
Bath ratio	1:50
UV absorbent (Rayocan C)	1, 2, 3 and 4
Na_2SO_4	70 g/L
Na_2CO_3	2 % + % Rayosan C
Rinsing after application	5 min at 30 ºC with 250 mL water

Percentage transmittance measurements of test samples: Percentage transmittance measurements of test samples were carried out with UV-visible spectrophotometer according to AS/NZS 4399:1996 standard. The transmittance

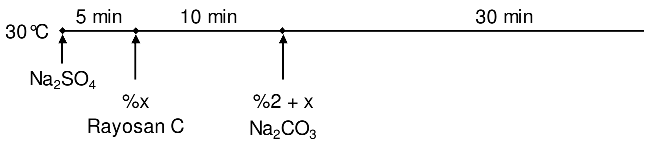

Fig. 1. UV absorber application process

measurements were performed in the range of 290-400 nm at 5 nm intervals and UPF (ultraviolet protection factor) values of each sample were calculated[19] using eqn. 1.

$$UPF = \frac{E_{eff}}{E} = \frac{\sum_{290}^{400} E_\lambda \cdot S_\lambda \cdot \Delta\lambda}{\sum_{290}^{400} E_\lambda \cdot S_\lambda \cdot T_\lambda \cdot \Delta\lambda} \quad (1)$$

E_λ = Relative eritemal spectral effects, S_λ = spectral radiation of the sun (W m^{-2} nm^{-1}), T_λ = spectral transmittance of the material, $\Delta\lambda$ = wavelength interval (nm), λ = wavelength (nm).

Eqns. 2 and 3 were used for the calculation of UVA and UVB transmittance average values[19].

$$UVA_{AV} = \frac{T_{315} + T_{320} + T_{325} + \ldots + T_{395} + T_{400}}{18} \quad (2)$$

$$UVB_{AV} = \frac{T_{290} + T_{295} + T_{300} + T_{305} + T_{310} + T_{315}}{6} \quad (3)$$

The classification system described in AS/NZS 4399:1996 standard for labeling of sun protected fabrics is shown in Table-4.

TABLE-4
CLASSIFICATION FOR LABELING OF SUN PROTECTED FABRICS[19]

UPF Range	UVR protection category	UVR trans. (%)	UPF (°)
15 – 24	Good protection	6.7 – 4.2	15, 20
25 – 39	Very good protection	4.1 – 2.6	25, 30, 35
> 40	Perfect protection	≤ 2.5	40, 45, 50, 50+

Colour measurements of test samples: The colour measurements of dyed samples were carried out with Datacolor Spectra Flash 600 plus reflectance spectrophotometer using the Datamaster program according to the CMC 2:1 CIELab and CIELch. The colour measurements were made using a D_{65} light source with 10° observer and the dyed samples without UV-absorbent were adopted as standard in the measurements. In order to identify the colours, three coordinates in the form of L*, a* and b* that can be calculated from tristimulus values are used (Fig. 2) and a* and b* axes that are perpendicular to each other and that are intersecting at the neutral point and the L* axis that is perpendicular to the plane formed by them are taken into consideration.

Different shades of the same colour are located on a line extending outward from the neutral point in the plane formed by a* and b* axes. Here, the rotation angle "h" indicating an increase from red to yellow is a measure of colour. For example, h = 0° corresponds to a red colour hue, h = 90° corresponds to a yellow colour hue and h = 270° corresponds to a blue colour

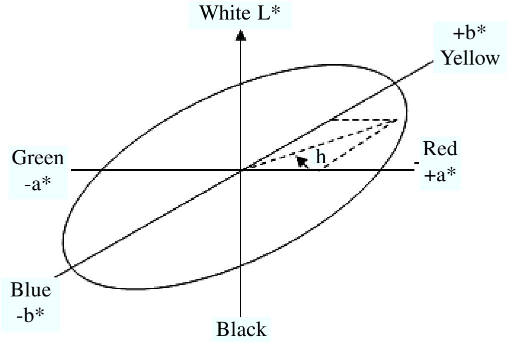

Fig. 2. Three-dimensional colour space

hue. A point distant from the neutral point implies "chroma (C*) and this is a measure of colour brightness at a certain L* value. The colour differences in CIELab units are calculated by using formula 4[20].

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (4)$$

L*a*b* cartesian coordinates can be converted into L*C*h* cylindrical coordinates with the help of formula 5 and 6.

$$C^* = [(a^*)^2 + (b^*)^2]^{1/2} \quad (5)$$

$$h = \arctan \frac{b^*}{a^*} \quad (6)$$

The positive L^*_{sample} - $L^*_{standard}$ value indicates that the samples were lighter than standard and the negative L^*_{sample} - $L^*_{standard}$ value indicates that the samples were darker than standard.

In C^*_{sample} - $C^*_{standard}$ value, the positive ΔC^* value indicates that the samples had higher chroma (saturation) and the negative ΔC^* value indicates that the samples had lower chroma.

Fastness tests: The washing and perspiration fastnesses of test samples were tested according to ISO standards and they were evaluated with the help of gray-scale[21,22].

RESULTS AND DISCUSSION

The amount of UV radiation passing through the dyed samples is less than bleached samples, because the dyestuffs itself has protection affects against UV radiation depending on their own colours and dyestuffs concentrations[23] (Fig. 3). UV absorbers converts the induced-state molecules back to their basic forms by capturing them through the effects of polymer degradation blocking by absorbing UV rays, converting UV-energy into heat form and energy transfer and thus they prevent bond fragmentation. In the study, UV-absorbent materials have reduced the amount of radiation passing through the material depending on the increased concentrations of substances in the conventional and ultrasonic methods (Fig. 3).

In the ultrasonic probe and ultrasonic bath methods, in which ultrasonic energy was utilized, a very good degree of protection in material was ensured while the amount of UV absorbent was decreased as 1, 2 and 3 % (Fig. 3). This is because in the direction that possibly the amount of UV-absorbent materials defunded from the surfaces of fibers into fibers may be increased with the effect of ultrasonic cavitation[24]. Some fall occurred in the degree of protection against UV radiation with only 4 % UV-absorbent concentration and some of the

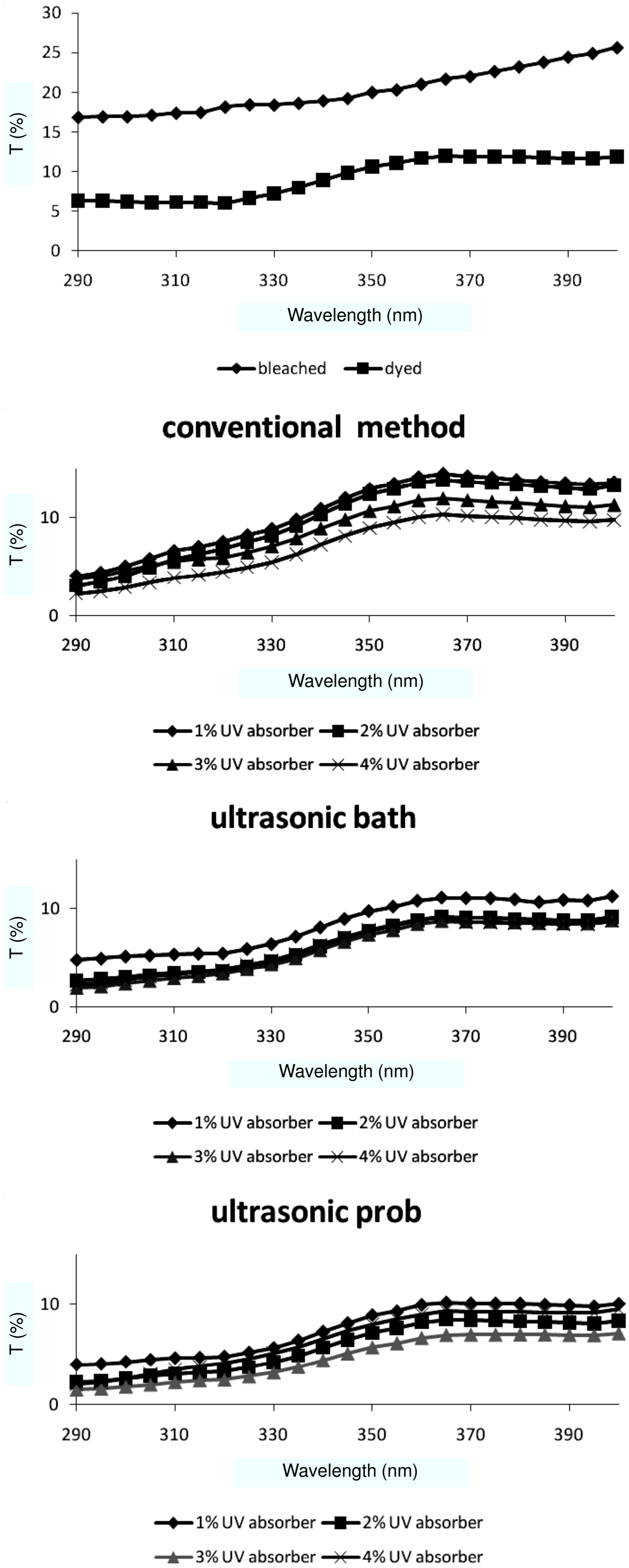

Fig. 3. Transmittance curves of samples

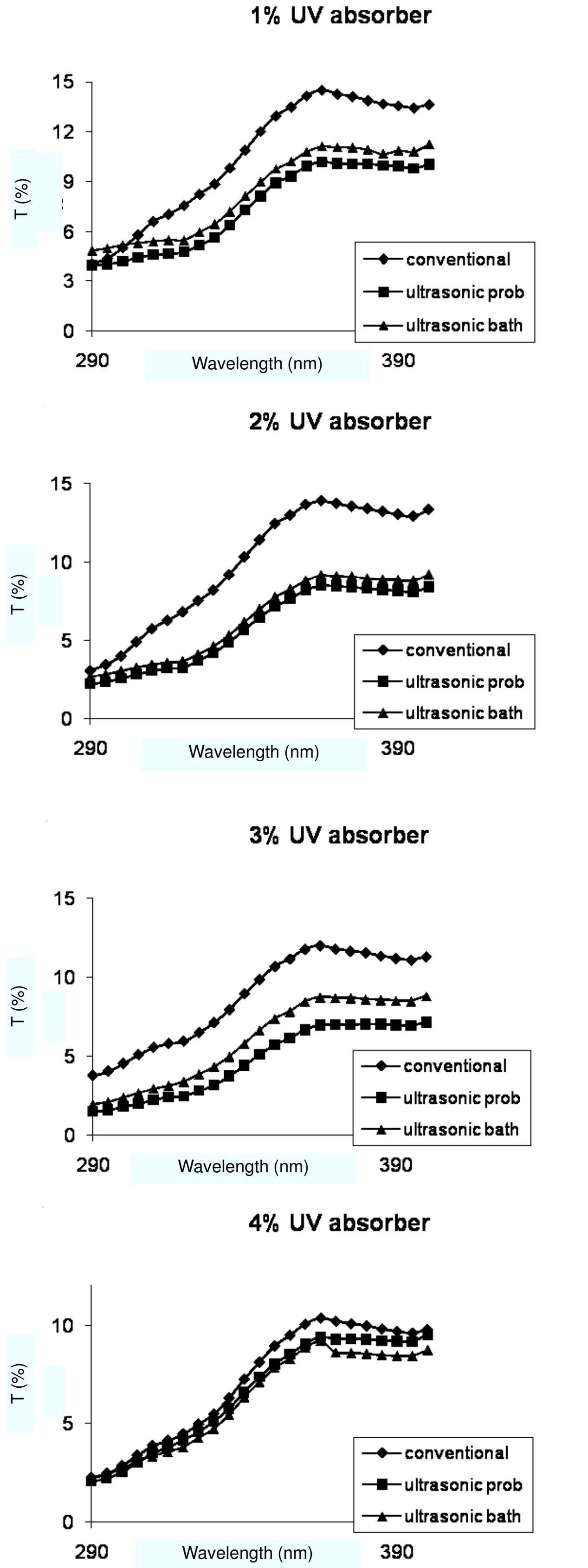

Fig. 4. Transmittance curves of samples

material was still determined to exhibit good protection. When the ultrasonic methods compared, the highest UPF value (3 % UV absorber) was obtained from the ultrasonic probe method (Fig. 4). It is believed that the sonication directly provided by the ultrasonic probe might have increased this effect in protecting against UV radiation.

The best result for the transmittance of UVB radiation is known to be much more harmful than UVA was obtained from the 3 % UV absorbent concentration in the ultrasonic probe method (UVB_{AV} % = 1.91 %). For the same UV-absorbent concentration, the ultrasonic probe method was less than the conventional method and the ultrasonic bath method for UVB transmittance at the rates of 150 and 31.4 %, respectively and thus it provided a very good protection against UVB (Table-5).

TABLE-5
UVA AND UVB PERMEATION VALUES OF SAMPLES %

		UVA_{AV} (%)	UVB_{AV} (%)
Bleached fabric		21.08	17.13
Dyed fabric without UV absorbent		10.05	6.23
UV absorbent			
Conventional method	1 %	12.01	5.49
	2 %	11.44	4.57
	3 %	9.87	4.79
	4 %	8.27	3.17
Ultrasonic Prob	1 %	8.36	4.32
	2 %	6.72	2.71
	3 %	5.48	1.91
	4 %	7.62	2.86
Ultrasonic Bath	1 %	9.23	5.20
	2 %	7.30	3.14
	3 %	6.93	2.50
	4 %	7.19	2.90

When the colour differences between the colours obtained after the applications of UV-absorbent substance with conventional and ultrasonic methods and the colours of samples without UV-absorbent application were examined, very low colour change was observed with the ultrasonic method. When UV absorbent applied with conventional methods, the colour of samples became considerably lighter and its hue changed and the colour became dull. In the ultrasonic methods, the colour saturation was increased, while the hue did not change significantly. So, the application of UV-absorbent with the ultrasonic method has appeared not lead to changes in colour, even it caused increase in brightness of the colours. There is no remarkable difference between the applications of ultrasonic probe and ultrasonic bath and similar positive results were obtained with both methods (Table-6).

In the applications of UV-absorbent, it was determined that the ultrasonic energy did not have a negative impact in washing and perspiration fastness values (Table-7).

TABLE-6
ΔE*, ΔL*, ΔC* AND ΔH* VALUES

Std: Dyed fabric		ΔE	ΔL*	ΔC*	ΔH*
	UV absorbent				
Conventional method	1 %	1.19	2.46	-0.23	0.62
	2 %	1.25	2.79	-0.04	0.47
	3 %	1.18	2.69	-0.05	0.36
	4 %	1.34	3.04	-0.21	0.43
Ultrasonic Prob	1 %	0.37	-0.54	0.36	0.18
	2 %	0.34	-0.27	0.50	-0.02
	3 %	0.56	-0.73	0.72	-0.02
	4 %	0.13	0.02	0.20	-0.01
Ultrasonic Bath	1 %	0.44	0.70	0.43	0.17
	2 %	0.56	0.02	0.70	0.34
	3 %	0.55	-0.97	0.52	0.17
	4 %	0.31	0.59	0.29	0.04

CMC 2:1.

TABLE-7

UV absorbent		Washing		Perspiration: Acid media		Perspiration: Alkaline media	
		l*	rd*	l	rd	l	rd
Conventional method	1 %	5	5	5	5	5	5
	2 %	5	5	5	5	5	5
	3 %	5	5	5	5	5	5
	4 %	5	5	5	5	5	5
Ultrasonic Prob	1 %	5	5	5	5	5	5
	2 %	5	5	5	5	5	5
	3 %	5	5	5	5	5	5
	4 %	5	5	5	5	5	5
Ultrasonic Bath	1 %	5	5	5	5	5	5
	2 %	5	5	5	5	5	5
	3 %	5	5	5	5	5	5
	4 %	5	5	5	5	5	5

*l: staining: rd: colour change.

Conclusion

Today, while so many conservations are taking place on damages of UV rays on human health rather than its benefits and thus those discussions are creating a conscious market for products to protect against the skin cancer, the UV protective products of textile materials providing a second skin over the skin are being developed every day. In this sense, as the UV absorbents have functions of reducing or eliminating negative effects of UV, the UV absorbent applications are using conventional methods. It was determined that while the highest UV-absorbent substance use (4 %) just reached the "good protection" value in the conventional method, even 2 % of the UV absorbent concentration was good enough for obtaining the "good protection" value in the ultrasonic bath and probe methods, that even ultraviolet protection force values was higher than the ones in ultrasonic bath method due to direct sonication effect in the ultrasonic probe method, that the UV absorbent application with the ultrasonic method did not cause colour change and even it caused increase in the colour brightness and that it did not affect the washing and perspiration fastness values. It is believed that the utilization of ultrasonic energy is an alternative method in terms of both the environment and the economy as better protection is ensured with less material.

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