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April 1993

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Influence of Shade Depth on the Effectiveness of Selected Ultraviolet Absorbers in Reducing Fading*

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ABSTRACT: This study evaluates the ability of seven ultraviolet (UV) absorbers to reduce fading of nylon colored with nine synthetic acid dyes applied at 0.5% and 0.05% owf concentrations. By including two concentrations, we could evaluate the influence of depth of shade on the absorbers' effectiveness. Specimens were treated with UV absorbers using one of two application methods: an exhaust bath at 100°C or an immersion treatment at room temperature. After treatment, specimens were exposed to 160 AFUs of light in a xenon-arc Weather-Ometer, then evaluated instrumentally to determine the amount of color change. The UV absorbers examined here provided only very limited beneficial effects. Only two had no detrimental effects on all dye/shade combinations to which they were applied, and their beneficial effects were limited to four to seven of the eighteen dye/shade combinations evaluated. Based on this research, we cannot make general recommendations regarding UV absorber use because some of the acid-dyed nylon specimens treated with UV absorbers exhibited no improvement in lightfastness, while other treated specimens actually exhibited greater fading or color change than their respective untreated controls. Further testing is needed to determine the effects of specific absorbers on specific dyes not examined in this study, because the effectiveness of each absorber appears to be dye and shade specific.

Many factors influence the lightfastness of dyes, including the chemical state of the dye, the physical state of the dye within the fiber, the fiber substrate, environmental factors, the source and intensity of illumination, and the presence of UV absorbers and other additives in the dyebath. The chemical structure of the dye molecule can be represented in two parts: the nucleus characteristic of a particular dye class and the substituent groups present. In general, the nucleus determines the average lightfastness properties of a chemical class of dyes, but the substituent groups strongly influence lightfastness properties. For this reason, dyes with a wide range of lightfastness properties are present within a single chemical class [10]. The physical state of a dye within a fiber also affects its lightfastness. Darker shades or heavier dye concentrations are more lightfast than lighter shades or lighter concentrations, because larger dye aggregates form at heavier dye concentrations and these aggregates are less vulnerable to the action of light [12, 14]. The fiber substrate to which a dye is applied also influences its lightfastness. Some dyes are more lightfast on one fiber type than another [4, 12]. The environment surrounding the dyed fibers during light exposure can influence lightfastness. Relative humidity levels, temperature, atmospheric gases such as oxygen and sulphur dioxide, all influence the lightfastness of the dyed fiber [10, 12, 13,21,25].

The intensity and spectral constitution of the light to which a dye is exposed significantly influences the fading rate. Researchers Russell and Abney (cited in reference 12) determined as early as 1888 that the fading rate of a dye is inversely proportional to light intensity. In 1957 the Delaware Valley and New York Sections of AATCC [2] demonstrated that there is no level of light below which fading ceases to occur. Photodegradation of polymers and dyes occurs when the light energy absorbed by the molecule is greater than the bond energies of the molecule, resulting in broken bonds [16]. Radiation with wavelengths measuring up to 400 nm has sufficient energy to break covalent bonds as well as ionic and hydrogen bonds, which have less strength [23]. Since visible light encompasses wavelengths of the electromagnetic spectrum between 400 to 700 nm, photodegradation can be caused by visible as well as ultraviolet radiation [6], but ultraviolet radiation is the most destructive. McLaren [18] and Crews [7] found that lightfast synthetic dyes are faded

* Published in *Textile Research Journal* 63, no.4 (April 1993), pp. 231–238.
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primarily by ultraviolet radiation, whereas fugitive synthetic and natural dyes are susceptible to fading by both visible light and ultraviolet radiation.

UV absorbers inhibit photodegradation of polymeric materials in several ways. Some additives preferentially absorb most of the ultraviolet radiation reaching the substrate and convert it to harmless infrared radiation. Other additives function by interacting with the photoexcited molecule before any other reaction occurs. By quenching the excited states of molecules, the UV absorbers prevent or minimize polymer degradation and color loss [16].

Chemical compounds suitable for use as UV absorbers must be strong absorbers of ultraviolet radiation and stable to ultraviolet light [6]. An effective UV absorber should meet three criteria: it should absorb effectively throughout the near UV region of the electromagnetic spectrum (290–400 nm, but especially 350–400 nm), it must be UV-stable itself, and it must dissipate the absorbed energy in such a manner as to cause no degradation or color change in the medium it protects [11]. The most important chemical classes of UV absorbers are hydroxy-benzophenone derivatives, benzotriazoles, and phenyl esters. Minor chemical classes include cinnamic acid derivatives, s-triazines, and other compounds with nitrogen acceptors [16, 19].

Some researchers found UV absorbers to be very effective in reducing dye fading, while others found them ineffective or detrimental. Maerov and Kobsa [15] observed improvements in lightfastness of basic dyes on polyester in the range of 200 to 300% when 2,2'-dihydroxy, 4,4'-dimethoxybenzophenone was applied in the dyebath. Coleman and Peacock [6] found 24 to 86% improvement in the lightfastness of disperse dyes on acetate and reduced strength losses on nylon when 2,2'-dihydroxy-4,4'-methoxybenzophenone was applied in an aqueous dyebath. Gantz and Sumner [11] contended that substituted benzophenone absorbers markedly improve the lightfastness of dyes faded by ultraviolet radiation. Reinert and Thommen [20] observed dramatic improvement in the lightfastness of pale shades of dyed nylon when an UV absorber was applied during dyeing with another lightfastness improver, but the effect was obvious on dark shades only after prolonged exposure. On the other hand, Cegarra and Ribe [5] found only slight, but not statistically significant, lightfastness improvements of acid-dyed wool treated with 2,4-dihydroxybenzophenone-2'-ammonium sulphonate applied in a dyebath.

Crews and Reagan [9] found modest reduction of fading of some natural dyes on wool, but observed increased fading of others when treated with selected alkyl-hydroxybenzophenone absorbers by an immersion procedure. Giles and McKay [13] and Maerov and Kobsa [15] also found little reduction of fading of direct dyes on cotton and observed increased fading on modified polyester dyed with methylene blue as a result of application of substantive UV absorbers (fluorescent photostabilizers). Woepfel [27] found no significant reduction in color change of acid-dyed nylon when three hydroxybenzophenone absorbers were applied by immersion treatment. Lappin [16] noted that many compounds absorb radiation in the desired region, but do not provide protection when applied to fibers. Furthermore, some compounds and some dyes sensitize the fibers to ultraviolet radiation, increasing the amount of fading and degradation [11, 16]. Gantz and Sumner [11] note that the problem is complex, and years of testing under practical conditions may be required to prove the merits of a stabilizer system.

Because UV absorber type, application method, dye class, shade depth, and length of exposure varied in the published studies, generalizations regarding the beneficial effects of UV absorbers on consumer textiles are limited, and the reasons for the contradictory reports about the effectiveness of UV absorbers in reducing fading remain unclear. However, J. Lee Rush [22], senior scientist at Allied Fibers in dye applications and dyeing technology, suggested that differences in depth of shade are likely one reason for the contradictory reports. Others suggested that application methods might contribute to the differing findings on UV absorber effectiveness.

In this study, we have tried to identify some of the possible causes for these conflicting reports on UV absorbers, and to demonstrate whether or not they provide sufficient benefits to warrant their use in finishes for consumer textiles such as carpeting. Specifically, we have examined the influence of shade depth and application method on the effectiveness of UV absorbers in reducing fading of red, yellow, and blue acid dyes applied to nylon. Because pastel shades usually fade more rapidly, we have hypothesized that the beneficial effects of the UV absorbers might be more clearly demonstrated on lighter shades. Furthermore, because a more intimate dispersion of the UV absorber within the fiber should, theoretically, better reduce fading, we hypothesized that UV absorbers exhaust-applied to nylon in the dyebath would prove more ef-

fective than UV absorbers applied by immersion procedures at room temperature.

Materials and Methods

The fabric we selected for this study was 100% nylon 6 Superba Twistset tubular filling knit (444 g/m²) constructed of a two-ply Anso IV bulked continuous, filament carpet yarn (Allied Fibers Corp., Petersburg, VA) and treated with a fluorochemical finish. The filament fibers did not contain the delusterant titanium dioxide (TiO₂). This fabric represents the fiber content and yarn type used in most U.S. carpeting, but in a form that facilitates laboratory testing.

The nine dyes included in this study are listed in Table I; they are representative of acid-leveling dyes widely used by U.S. mills for dyeing nylon carpeting. All dyes with known Colour Index (CI) lightfastness ratings included in the study had AATCC lightfastness ratings less than L6 on pale shades [24]. We selected dyes with lightfastness ratings below L6 so that the specimens would show visually appreciable color change during the exposure period of 160 AATCC fading units (AFUs). The fabrics were dyed at concentrations of 0.5% and 0.05% based on the weight of fabric (owf) for all dyes.

The fabric was cut into specimens, which were randomly assigned to replications, dyes, and treatments. Specimens were scoured in an 0.5% AATCC detergent solution to remove impurities from manufacturing and immediately dyed according to the manufacturer's recommendations.

Table I. Levelling acid dyes.

CI acid dye	Chemical class	Trade name	Manufacturer
Red 337	monoazo	Supernylite red GN	Crompton & Knowles
Red 57	monoazo	Erio Rubine 3 GP	Ciba-Geigy
Red 266	azo	Nylanthrene red B-2BSA	Crompton & Knowles
Red 361	monoazo	Tectilon red 2B-KWL	Ciba-Geigy
Blue 25	anthraquinone	Telon blue ANL	Mobay Chemical
Blue 40	anthraquinone	Telon blue 2GL 200	Mobay Chemical
Blue 277	anthraquinone	Tectilon blue 4R	Ciba-Geigy
Yellow 49	azo	Telon yellow FGL 200	Mobay Chemical
Yellow 219	disazo	Tectilon yellow 4R 250	Ciba-Geigy

Shade Depth and Ultraviolet Absorbers

The ultraviolet absorbers we used in this study are listed in Table II. We selected them on the basis of their commercial availability, commercial use, and reported effectiveness. One absorber, Cibafast W, reportedly is widely used by carpet manufacturers to reduce fading [22], but we did not locate any published reports about its effectiveness. We added absorber UA7, Uvinul M-40, to the study to replicate previous work, but we did not apply it to dye CI acid red 266 or blue 277 due to limited quantities available in our lab. The water-soluble UV absorbers were applied to 26 x 10.5 cm knitted tubes at 1% owf during an exhaust dyeing process to simulate industry application procedures. Technical literature for water-soluble UV absorbers suggested that 1–3% owf of the UV absorbers be used. Reinert and Thommen [20] stated that 0.5–1% owf of UV absorbers applied during dyeing is enough for most nylon and nylon 66 applications.

Table II. Ultraviolet absorbers used in experiment.

Code and application method*	Trade name	Chemical formula	Manufacturer
UA1 E	Uvinul DS-49	Disodium 2,2'-dihydroxy-4,4'-dimethoxy-5,5'-disulfobenzophenone	BASF Wyandotte
UA2 E	Uvinul MS-40	2-hydroxy-4-methoxybenzophenone-5-sulfonic acid	BASF Wyandotte
UA3 E	Tinuvin P Paste	2(2'-hydroxy-5-methylphenyl)benzotriazole	Ciba-Geigy
UA4 E	Cibafast VI	proprietary	Ciba-Geigy
UA5 I	Cyasorb UV531	2-hydroxy-4-n-octoxybenzophenone	American Cyanamid
UA6 I	Givisorb UVI	N-(p-ethoxycarbonylphenyl)-N'-methyl-N'-phenylfonnamidine	Givaudan
UA7 I	Uvinul M-40	2-hydroxy-4-methoxybenzophenone	BASF

* E = applied in an exhaust dye bath

I = applied by immersion in UV absorber/TCE solution.

The water-insoluble UV absorbers were dissolved in tetrachloroethylene (TCE) and then applied to fabric specimens by an immersion treatment at room temperature, duplicating an application method described in some published reports [3, 8, 9, 27]. Each 6.5 x 18 cm specimen was gently agitated in 50 ml of a 2% UV absorber/TCE solution (2g UV absorber in 98 ml TCE) for 60 seconds on each side. Specimens were allowed to air dry at room temperature for 24 hours on suspended nylon netting. A 2% UV absorber/TCE solution was used for the immersion treatments to duplicate previous research [8, 9, 27]. We expected an add-on of 3% ± 1% based on previous work [9].

Following UV absorber application, we made spectrophotometric analyses of one replication of each dye at the 0.05% owf concentration for each absorber treatment, the TCE control, and the untreated control using a Varian DMS 200 UV-visible spectrophotometer with a diffuse reflectance accessory. Analysis was performed from 200 to 500 nm with readings taken every five nm. These analyses confirmed the presence of UV absorbers on all of the dyed fabrics.

The specimens were mounted in exposure masks and exposed to light for 160 AFUs, according to AATCC test method 16-E, colorfastness to light: water-cooled xenon-arc lamp, continuous light in an Atlas (Chicago, IL) 6500 watt xenon arc Weather-Ometer [1]. Borosilicate inner filters and soda lime outer filter glasses surrounded the lamp to simulate daylight through window glass. L-7 blue wool standards were used to control the length of exposure.

Fabric specimens were evaluated after 160 AFUs of exposure to xenon light with a Hunter Labscan II spectrophotometer according to AATCC test method 153-1985, color measurement of textiles: instrumental [1]. Measurements were taken from the top, middle, and bottom in both the course and wale directions of each specimen on both the exposed and unexposed areas. Total color difference was calculated using the CIELAB system 10 degree observer data and illuminant D65 with a 2.54 cm viewing aperture. Total color difference was calculated using the color measurement committee (CMC) formula shown in Equation 1 [17]:

$$\Delta E_{CMC}(l : c) = [(\Delta L^*/lS_L)^2 + (\Delta C^*/cS_C)^2 + (\Delta H^*/S_H)^2]^{1/2} \quad (1)$$

We chose the CMC color difference formula rather than the CIELAB formula because recent studies have shown that the CMC formula gives better correlation with visual judgments than the CIELAB formula [17]. We corroborated this by computing all total color difference values in both CMC units and CIELAB units, followed by a statistical analysis of the results. We observed that there were many more statistically significant color differences based on CIELAB ΔE s. However, many of the statistically significant color differences based on CIELAB data were not visually perceptible, whereas the statistically significant differences based on CMC data were, with a few exceptions. Consequently, we statistically analyzed and reported only the ΔE CMC values in this paper.

The research design for this study was a completely randomized factorial design to test the effects of dye, shade, and UV absorber on color change. Since it is well known that different dyes fade at different rates, and since the dyes in this study have different lightfastness ratings, the researchers knew the dye effects would be a significant variable. Therefore, we tested factorial designs within each dye rather than among all dyes.

Results and Discussion

COLOR DIFFERENCES IN ACID DYED NYLON

We made a general linear model (GLM) factorial analyses within each dye to test the effects of shade, treatment, and shade by treatment interaction. The effect of shade, treatment, and the interaction between shade and treatment were all significant at $\alpha = 0.001$ for all dyes. Post-hoc analyses using Tukey's HSD were done within each dye and shade level; treatment was the only variable tested in the model for each analysis. Tukey's groupings are shown in Table III. The reported means are the average of six color difference readings on each of three replicate specimens.

We made the following observations regarding the effect of shade on the untreated controls. At the 0.05% owf shade depth, CI acid blue 277 ($\Delta E_{CMC} = 5.0$) exhibited the most color change while CI acid yellow 219 ($\Delta E_{CMC} = 1.2$) exhibited the least. Darker shades associated with heavier dye concentrations are known to be more lightfast than lighter

shades or lighter dye concentrations [12, 14]. As expected, within each dye the medium shades (0.5% owf) exhibited less color change (lower M CMC values) than the light shades (0.05% owf). It was evident that the dyes in this study faded at different rates, as expected, and that the effect of shade was also significant. Therefore, we made factorial analyses within each dye/shade level as planned. The mean color difference values (ΔE CMC) for each dye/shade combination plus the results of the statistical analysis are shown in Table III.

Results showed that some UV absorber treatments significantly reduced color change, while other treatments significantly increased fading or color change. Only nylon specimens treated with absorbers UA5 and UA7, both benzophenones, exhibited no detrimental effects. Absorbers UA5 and UA7 significantly decreased color change or had no significant effects on all dye/shade combinations. All other UV absorbers were detrimental (increased fading or color change) to at least two dye/shade combinations. Three absorbers (UA3, UA4, and UA6) significantly decreased color changes on some dyes, while significantly increasing color change on others. Treatment UA6 (phenylformamidine) significantly increased color changes on 11 out of 18 dye/shade combinations to which it was applied. The instances where UA3 (benzotriazole) and UA4 (chemical class unknown – proprietary) significantly increased color change were applications to medium shade depths (0.5% owf). Treatments UA1 (benzophenone) and UA2 (benzophenone) exhibited no beneficial protective effects. They significantly increased color change or had no significant effects on color change in all dye/shade combinations to which they were applied.

Shade Depth and Ultraviolet Absorbers

TABLE III. Tukey's grouping for mean color difference values for acid dyed nylon fabrics treated with seven UV absorber treatments plus TCE and untreated controls after 160 AFU's of xenon light exposure.^a

Treatment	Mean ΔE	CMC Group	Treatment	Mean ΔE	CMC Group
CI acid red 337/0.5% owf			CI acid red 337/0.05% owf		
UA4	3.3	A	UA6	6.2	A
UA3	3.0	A B	UA2	3.0	B
UA2	2.9	A B	UA3	2.8	B
UAI	2.6	B C	UAI	2.8	B C
CTRL	2.3	C D	CTRL	2.7	B C
UA7	2.2	C D	UA4	2.6	B C
UA6	2.2	C D	TCE	2.5	B C
TCE	2.0	D	UA5	2.0	C
UA5	1.9	D	UA7	1.0	D
CI acid red 361/0.5% owf			CI acid red 361/0.05% owf		
UA4	4.1	A	UA6	8.1	A
UA6	3.1	A B	CTRL	3.8	B
UA2	2.7	A B	UA3	3.4	B
UAI	2.7	A B	UA1	3.3	B
CTRL	2.6	A B	UA2	3.2	B
UA3	2.6	B	UA7	3.1	B
TCE	2.0	B C	UA4	3.1	B
UA5	1.7	B C	TCE	3.0	B
UA7	1.0	C	UA5	2.4	B
CI acid blue 25/0.5% owf			CI acid blue 25/0.05% owf		
UA6	4.6	A	UA6	11.0	A
UA2	3.8	A B	CTRL	4.9	B
UA1	3.8	A B	UA2	4.7	B
CTRL	3.6	B	TCE	4.6	B
TCE	3.3	B	UAI	4.1	B C
UA5	3.0	B	UA7	3.9	B C
UA3	3.0	B	UA3	3.1	C
TC7	2.1	C	UA5	2.7	C
UA4	1.4	C	UA4	1.2	D

^a Means with same letter are not significantly different at alpha = 0.01

Table III. cont.

Treatment	Mean ΔE	CMC Group
CI acid blue 40/0.5% owf		
UA6	2.8	A
UA2	2.1	B
UA7	2.1	B C
UAI	1.7	B C D
TCE	1.6	C D
CTRL	1.6	C D
UA5	1.6	D
UA4	1.6	D
UA3	1.4	D

Treatment	Mean ΔE	CMC Group
CI acid blue 40/0.05% owf		
UA6	8.8	A
UA7	4.3	B
CTRL	3.6	B C
UA2	3.6	B C
TCE	3.5	B C
UAI	2.7	C
UA5	2.3	C
UA3	2.2	C D
UA4	.8	D

CI acid yellow 49/0.5% owf

UA2	5.5	A
UA3	5.2	A
UAI	4.7	A
UA6	3.7	B
UA4	3.3	B
CTRL	3.3	B
UA5	3.2	B
TCE	3.1	B
UA7	.6	C

CI acid yellow 49/0.05% owf

UA2	6.8	A
UAI	5.5	B
UA3	5.3	B C
CTRL	4.7	B C D
UA4	4.7	B C D
TCE	4.5	C D
UA5	4.2	D E
UA6	3.6	E F
UA7	2.8	F

CI acid blue 277/0.5% owf

UA6	4.0	A
UA2	3.9	A
UAI	3.5	A B
CTRL	3.5	A B
TCE	3.2	B
UA5	3.1	B
UA3	2.5	C
UA4	1.4	D

CI acid blue 277/0.05% owf

UA6	8.6	A
UA2	5.2	B
CTRL	5.0	B
TCE	4.8	B
UAI	3.9	B C
UA3	2.5	C D
UA5	2.3	C D
UA4	1.5	D

Table III. cont.

Treatment	Mean ΔE	CMC Group
CI acid red 57/0.5% owf		
UA4	4.6	A
UA6	3.2	B
UA3	3.2	B
UA2	3.1	B
UAI	2.9	B C
CTRL	2.1	C D
UA5	1.6	DE
TCE	1.6	DE
UA7	1.0	E

Treatment	Mean ΔE	CMC Group
CI acid red 57/0.05% owf		
UA6	8.4	A
UA2	4.1	B
CTRL	3.8	B C
UA4	3.6	B C D
UAI	3.4	B C D
UA 7	3.3	B C D
TCE	3.3	B C D
UA3	3.0	C D
UA5	2.5	D

CI acid red 266/0.5% owf

IUA3	2.5	A
UA2	2.3	A B
UAI	2.2	A B C
UA6	2.1	A B C
CTRL	2.0	B C
TCE	1.8	C D
UA5	1.7	C D
UA4	1.4	D

CI acid red 266/0.05% owf

UA6	7.8	A
CTRL	3.1	B
UA2	3.1	B
UAI	2.7	B C
UA3	2.6	B C
TCE	2.6	B C
UA5	2.3	C
UA4	1.5	D

CI acid yellow 219/0.5% owf

UA6	1.8	A
UA7	1.3	A B
UA4	1.1	A B
UA3	1.0	A B
TCE	.8	B
UA2	.7	B
CTRL	.7	B
UAI	.6	B
UA5	.5	B

CI acid yellow 219/0.05% owf

UA2	1.8	A
UA3	1.5	A B
UAI	1.4	A B C
UA6	1.3	B C
CTRL	1.2	B C
TCE	1.1	B C D
UA4	1.1	B C D
UA5	.9	C D
UA7	.8	D

^a Means with same letter are not significantly different at alpha = 0.01^a Means with same letter are not significantly different at alpha = 0.01

Based on these results, we could not identify a chemical class of UV absorber that consistently reduced fading or at least had no effect. The most effective UV absorber, UA7, was a benzophenone, but some of the least effective absorbers, UA1 and UA2, were also benzophenones. The least effective absorber was a phenylformamidine (UA6), which was associated with more yellowing and increased fading than any other UV absorber. Consequently, based on this research, we recommend that UA6 not be used on nylon colored with red and blue acid dyes. Since we examined only one phenylformamidine absorber in this study, however, we could not conclude that phenylformamidine absorbers as a chemical class are always detrimental. This merits further investigation.

Furthermore, UV absorbance did not appear to be a reliable predictor of UV absorber effectiveness. Spectrophotometric analyses done on one specimen for each dye at the 0.05% shade depth confirmed the presence of UV absorbers on all specimens. Treatments UA5 and UA6 had poorer levels of UV absorbance than other UV absorbers in the study. As might be predicted, based on levels of absorbance, UA6 was one of the least effective absorbers, but surprisingly, UA5 was one of the more effective absorbers. The reason for this unexpected result is unclear.

As postulated, UV absorber treatments significantly reduced color changes on more dyes at the 0.05% owf concentration than at the 0.5% owf concentrations. Recently published research [20] has shown that UV absorbers are more effective on pale shades than on deeper shades. Our work further supports the published findings [20] and unpublished industry observations [22].

To further examine the effects of the UV absorbers on the acid-dyed nylon, we made visual evaluations of all treated specimens identified as being significantly different from their respective controls following light exposure. Most of the specimens with color difference measurements that were significantly different than their respective controls exhibited visually perceptible differences, as would be desired. Out of 122 dye/shade/UA treatment combinations evaluated, our results showed that only 46 dye/shade/UA treatment combinations were significantly different from their untreated controls after 160 AFUs of light exposure. The limited effectiveness of UV absorbers is illustrated by the fact that only about one third of the treated specimens were significantly influenced by the treatment. Furthermore, visual examination of these 46 dye/shade/treatment combinations showed that only 22 of the treatment

combinations exhibited decreased color change, while 19 exhibited increased color change. The 46 dye/shade/treatment combinations with color difference values significantly different from their respective untreated controls are given in Table IV with observations based on visual evaluations. All but two of these statistically significant color differences were visually appreciable, which shows how well the color differences calculated by the CMC formula correspond with visual perception. Treatment UA3 reduced color changes on some of the light shades, but promoted uneven fading of three of the medium shades. These shades (0.5% owf) had an unlevel, spotty, fading appearance, as though UV absorber UA3 had not evenly penetrated the fibers. This spotting or uneven fading supports the suggestion given by Woepfel [27] that unevenly applied UV absorbers could result in uneven color change. The absorber solution before exhaust application was a milky color when mixed with water. The solution remaining after exhaust application of this treatment was very slightly cloudy, suggesting that some of the absorber may not have exhausted into the fibers. All other exhaust treatments, whether originally a clear or light yellow solution (UA2) before exhaust application, resulted in completely clear post-exhaust solutions.

Table IV. Visual observations about the 55 UV absorber treatments with significantly different color difference values than their respective untreated controls.

Treatment	CI acid dye/ concentration	Observations ^a
UA1	yellow 49/.5	increased
UA2	red 337/.5	increased
	red 57/.05	increased
	blue 40/.5	increased, darkened
	yellow 49/.5	increased
	yellow 49/.05	increased
	yellow 219/.05	increased
UA3	red 337/.5	uneven fading
	red 57/.5	increased
	red 266/.5	uneven fading
	blue 25/.05	decreased, slightly yellowed
	blue 277/.5	increased, darkened
	blue 277/.05	decreased, slightly yellowed

Table IV. (cont.)

Treatment	CI acid dye/ concentration	Observations ^a
UA4	yellow 49/.5	uneven fading
	red 337/.5	increased
	red 57/.5	increased
	red 266/.5	decreased
	red 266/.05	decreased
	blue 25/.5	decreased
	blue 25/.05	decreased
	blue 40/.05	decreased
	blue 277/.5	decreased
	blue 277/.05	decreased
UA5	red 57/.05	decreased, slightly yellowed
	red 266/.05	decreased, slightly yellowed
	blue 25/.05	decreased, slightly yellowed
	blue 277/.05	decreased, slightly yellowed
UA6	red 337/.05	much increased, very yellowed
	red 57/.5	increased, slightly yellowed
	red 57/.05	much increased, very yellowed
	red 266/.05	much increased, very yellowed
	red 361/.05	much increased, very yellowed
	blue 25/.5	increased, slightly yellowed
	blue 25/.05	much increased, very yellowed
	blue 40/.5	increased, yellowed
	blue 40/.05	increased, yellowed
	blue 277/.05	increased, yellowed
UA7	yellow 49/.05	decreased
	yellow 219/.5	no difference
	red 337/.05	decreased
	red 57/.5	decreased, slightly yellowed, darkened
	red 361/.5	decreased, slightly darkened
	blue 25/.5	decreased, darkened
	yellow 49/.5	decreased, color changed differently
yellow 49/.05	decreased	
	yellow 219/.05	no difference

^a No difference = not a visually perceptible difference from the control. Increased = increased fading or color changes compared to control. Decreased = decreased fading or color change compared to control.

Three UV absorbers (UA4, PA5, and UA7) reduced color change in more dye/shade combinations than the other absorbers, perceptibly reducing color change on four to seven dye/shade combinations. However, only absorbers UA5 and UA7 had no adverse effects; absorber UA4 increased fading on two dye/shade combinations. In general, the protective effects of the UV absorbers were most evident on the light shades, but absorber UA7 reduced color change on more medium shades than lighter shades (four medium versus two light shades).

The most obvious effects of any treatment were those of UA6, which unfortunately significantly increased color change on more than half (11 out of 18) of the dye/shade combinations evaluated. All but one of the statistically significant effects of increased color change attributed to UA6 were visually perceptible. UA6 frequently increased color changes through increased yellowness. Blue dyed fabrics, especially the lighter shades, were yellowed to a green color, and the reds, especially the lighter shades, yellowed to an orange color. The apparent effectiveness of UA6 on the CI acid yellow 49/.05% owf may have resulted from the specimens yellowing at nearly the same rate as the dyes faded.

Based on this research, we cannot make generalizations about the effectiveness of UV absorbers, nor can we recommend any of the absorbers we examined for use on all acid-dyed nylon. This is because acid-dyed nylon specimens treated with some of the UV absorbers exhibited no reduction in fading, while other treated specimens exhibited increased fading or color change rather than reduced fading. Only two UV absorbers (VA5 and VA7) had no detrimental effects on all of the dye/shade combinations to which they were applied, and their beneficial effects were limited to 4 to 7 of the 18 dye shade/combinations evaluated. Consequently, our research shows that, at best, the UV absorbers provide only modest benefits.

Although industrial technical representatives suggested quite logically that an exhaust application of UV absorbers would result in a more intimate dispersion of the UV absorber within the fiber substrate, thereby increasing the effectiveness of the UV absorber, this was not borne out by our results. For example, two of the least effective absorbers (UA1 and UA2) were exhaust-applied to the nylon, while the most effective absorbers UA5 and UA7 were applied by immersion treatments at room temperature. This should not be interpreted to mean that UV absorbers

applied by immersion treatments perform more effectively, because absorber UA4 was applied by an exhaust procedure and it was one of the more effective UV absorbers. Rather, the application method does not appear to be a useful predictor of UV absorber effectiveness based on this research. It also suggests that the reason for the very limited protective effects of UV absorbers described by several researchers [8, 9, 27] in earlier work should not be attributed to the application method (an immersion treatment) of the UV absorbers. In fact, it appears likely that UV absorbers have limited effectiveness when applied to some dye/fiber combinations, regardless of application method.

Conclusions

The UV absorbers we examined provided only very limited beneficial effects. UA4 and UA7 were the most effective. We could not recommend UA6 for any of the red or blue acid dyes evaluated. In general, UV absorbers were more effective at reducing color change on lighter shades than on darker shades. Application method (exhaust versus immersion treatment) did not appear to be a useful factor in predicting absorber effectiveness.

Further testing is needed to determine the effects of specific absorbers on specific dyes not examined in this study, because the effectiveness of each absorber appears to be dye and shade specific. This research further highlights the complexity of interactions in UV absorber/dye/fiber systems and provides additional insights into reasons for the contradictory reports about UV absorber effectiveness in published reports. Our findings serve to illustrate that the relationship between the chemical type and absorption properties of a UV absorber and its effectiveness on a variety of fiber types and dye classes remains tentative. The complex relationship that exists between those factors is further complicated by other factors such as shade depth, application method, and length of exposure. None of the factors alone is a sufficient explanation for the behavior of UV absorbers. Much work remains to elucidate the relationship between UV absorber effectiveness and dye/fiber substrates. Our work confirms once again that empirical testing remains necessary for predicting the effectiveness of UV absorbers in end-use applications.

ACKNOWLEDGMENTS

This research was made possible by research funds from the University of Nebraska-Lincoln, Nebraska Agricultural Research Division, and all AA TCC / HE Student Research Award. We appreciate contributions of fabric, dye and ultraviolet absorbers from the following companies: Allied Fibers Corporation, BASF Corporation, Ciba-Geigy Corporation, American Cyanamid Company, Crompton & Knowles Corporation, Givaudan Corporation, and Mobay Corporation. This report has been published as Journal Series Number 9925, Agricultural Research Division, University of Nebraska.

Literature Cited

1. AATCC Technical Manual, Research Triangle Park, NC, 1989.
2. AATCC Delaware Valley and New York Sections, A Study of the Variables Encountered in Natural Light Fading, *Am. Dyest. Rep.* 46, 861–883 (1957).
3. Asche, K., and Crews, P. C., An Evaluation of Antioxidants for the Conservation of Museum Textiles, *Clothing Textiles Res.* 1. 6 (3), 10–16 (1988).
4. Burgess, S., The Fastness to Light of Dyed Textiles, *J. Soc. Dyers Colour.* 65, 732–739 (1949).
5. Cegarra, J., and Ribe, J., Use of 2,4-dihydroxybenzophenone-2'-Ammonium Sulphonate to Prevent the Yellowing of Wool by Ultraviolet Radiation, *J. Soc. Dyers Colour.* 88, 293–296 (1972).
6. Coleman, R. A., and Peacock, W. L. J., Ultraviolet Absorbers, *Textile Res. I.* 27, 784–791 (1958).
7. Crews, P. C., A Comparison of Clear Versus Yellow ultraviolet Filters in Reducing Fading of Selected Dyes, *Stud. Conserv.* 33, 87–93 (1988).
8. Crews, P. C., and Clark, D. C., Evaluating UV Absorbers and Antioxidants for Topical Treatment of Upholstery Fabrics, *Textile Res. I.* 60, 172–179 (1989).
9. Crews, P. C., and Reagan, B. M., Evaluating UV Absorbers for Museum Textiles, *Textile Chem. Color.* 19 (11), 21–26 (1987).

10. Egerton, G. S., and Morgan, A. G., The Photochemistry of Dyes, Part II Some Aspects of the Fading Process, *J. Soc. Dyers Colour.* 86 (6), 242–249 (1970).
11. Gantz, G. M., and Sumner, W. G., Stable Ultraviolet Light Absorbers, *Textile Res. J.* 27, 244–251 (1957).
12. Giles, C. H., The Fading of Colouring Matters, *J. Appl. Chem.* 15, 541–550 (1965).
13. Giles, C. H., and McKay, R. B., The Lightfastness of Dyes: A Review, *Textile Res. J.* 33, 528–577 (1963).
14. Giles, C. H., Baxter, G., Black, W. A., Macauley, N., and Rahman, S. M. K., Lightfastness and Surface Activity of Dyes: The Effect of Alkylation and Sulfonation, *Textile Res. J.* 30, 934–943 (1960).
15. Maerov, S. B., and Kobsa, H., Lightfastness Studies of Basic Dyes on Acid-Modified “Dacron” Polyester Fiber, *Textile Res. J.* 31, 697–703 (1961).
16. Lappin, G. R., Ultraviolet Radiation Absorbers, in “*Encyclopedia of Polymer Science and Technology*,” vol. 14, N. M. Bikales, G. O. Schetty, J. Perlman, M. Bickford, and J. M. Ricciardi, Eds., Interscience Publishers, NY, 1971, pp. 125–148.
17. McDonald, R., Acceptability and Perceptibility Decisions Using the CMC Color Difference Formula, *Textile Chem. Color.* 20 (6), 31–37 (1988).
18. McLaren, K., The Spectral Regions of Daylight Which Cause Fading, *J. Soc. Dyers Colour.* 72, 86–99 (1956).
19. Ran by, B., and Rabek, J. F., “*Photodegradation, Photo oxidation, and Photostabilization of Polymers*,” John Wiley and Sons, NY; 1975.
20. Reinert, G., and Thommen, F., Lightfastness Improvers and Photostabilization of Textiles, *Textile Chem. Color.* 23 (1), 31–37 (1991).
21. Rush, J. L., and Hinton, E. H., Jr., How Dye bath Auxiliaries Can Affect the Lightfastness of Nylon, *Textile Chem. Color.* 11 (2), 26–30 (1979).
22. Rush, J. L., Personal communication, October 4, 1989.

23. Simpson, W. S., and Page, C. T., Inhibition of Light Tendering of Wool, in “*Proc. 6th Quinquennial International Wool Textile Research Conference, Pretoria*,” 1980, pp. 183–193.
24. Soc. Dyers Colour., *Colour Index*, 8 vols., The Society of Dyers and Colourists, London, 1971.
25. Van Beek, H. C. A., and Heertjes, P. M., Fading of Light of Organic Dyes on Textiles and Other Materials, *Stud. Conserv.* 11 (3), 123–131 (1966).
26. Woeppel, L. T., Evaluating the Potential Synergism of Selected Antioxidants and Ultraviolet Absorber Combinations Applied to Textiles, Masters thesis, University of Nebraska, 1988.
27. Woeppel, L. T., Evaluating UV Stabilizers for the Conservation of Museum Textiles, *Textile Chem. Color.* 22 (6), 31–37 (1990).

Manuscript received April 21, 1992; accepted September 14, 1992.