Proper Finishing Treatments for Sun-Protective Cotton-Containing Fabrics

N. A. Ibrahim,[1] R. Refai,[1] M. A. Youssef,[2] A. F. Ahmed[1]

[1]*Textile Research Division, National Research Centre, Dokki, Cairo, Egypt*
[2]*Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt*

Received 15 June 2004; accepted 19 November 2004
DOI 10.1002/app.21840
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To enhance both the performance and ultraviolet-protection properties of cotton-containing fabrics, attempts have been made to use poly(carboxylic acid)s as non-formaldehyde durable-press finishing agents alone or in combination with certain additives followed by posttreatment with metal salt solutions. Furthermore, simultaneous dyeing and resin finishing in the presence of triethanolamine hydrochloride (TEA · HCl) or citric acid (CA) as a reactive additive along with different anionic or cationic dyestuffs have been examined. The results reveal that the ester crosslinking of cotton-containing fabrics in the absence or presence of chitosan (5 g/L), β-cyclodextrin (20 g/L), or choline chloride (20 g/L) as an additive results in an improvement in the fabric resiliency as well as the ultraviolet-protection properties. The extent of the improvement is determined by the type of poly(carboxylic acid), type of additive, type of substrate (i.e., cotton or cotton/polyester blend), and pretreatment history (i.e., grey, bleached, or bleached and mercerized). The posttreatment of easy-care finished fabric samples with a copper acetate solution (5 g/L) results in a dramatic improvement in the ultraviolet-protection factor, especially with bleached cotton, grey cotton/polyester blend, and bleached cotton/polyester fabric samples, regardless of the additive. Simultaneous dyeing and resin finishing with Reactive Black 5 and Direct Violet 31, in the presence of TEA · HCL as a reactive additive, or with Basilene Red PB, in the presence of CA as a reactive additive, result in a sharp increase in both the depth of shade and the ultraviolet-protection values, regardless of the substrate. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1024–1032, 2005

Key words: additives; blends; crosslinking; UV-barrier

INTRODUCTION

Ultraviolet (UV) radiation falls into three categories: longer wavelength/low-energy-fraction UV-A ($\lambda = 320–400$ nm), shorter wavelength/high-energy-fraction UV-B ($\lambda = 280–320$ nm), and the highest energy fraction UV-C ($\lambda < 280$ nm).[1,2] Too much exposure to the shorter wavelength component of solar UV radiation, that is, UV-B, can result in the greatest skin damage.[3,4] Accordingly, the awareness of the need for protection against harmful UV radiation is rapidly increasing. The protective properties of clothing against UV radiation have been the subject of considerable research.[5–9] UV protection, to a greater or lesser extent, is determined by the fiber type and chemical composition, fabric construction, additives, textile processing aids, color, and fabric finish.[1–13]

This work focuses on enhancing UV-protection properties of cotton-containing fabrics via ester crosslinking as well as simultaneous dyeing and resin finishing.

Correspondence to: N. A. Ibrahim (nabibrahim@hotmail.com).

EXPERIMENTAL

Materials

The specifications of woven fabrics are given in Table I.

Citric acid (CA), 1,2,3,4-butanetetracarboxylic acid (BTCA), sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$), ammonium sulfate [$(NH_4)_2SO_4$], copper acetate [$Cu(CH_3COO)_2 \cdot 2H_2O$], and zinc acetate [$Zn(CH_3COO)_2$] were reagent-grade.

Choline chloride, β-cyclodextrin (Waker-Chemie GmbH, Germany), chitosan [β-(1,4)-2-amino-2-deoxy-D-glucopyranose with a degree of deacetylation of 82.9% and a molecular weight of 140,500 Da; Vanson, Inc., United States], poly(ethylene glycol) (PEG-600), and triethanolamine hydrochloride (TEA · HCl) were used as reactive additives.

Arkofix NG [dimethylol dihydroxyethylene urea (DMDHEU); Clariant], C.I. Reactive Red 63, Color Index (C.I.) Reactive Black 5, C.I. Direct Violet 31, C.I. Acid Red 1, and Basilene Red PB (Chemische Fabriken, Germany) were commercial-grade.

Methods

Ester crosslinking

The fabric samples were padded twice to a wet pickup of 70% with an aqueous formulation composed of a

TABLE I
Fabrics Specifications

No.	Substrate	Weight (g/m^2)	Weave	Threads/cm Ends	Threads/cm Picks	Thickness (mm)
I	Grey cotton	230	1/1 (plain)	114	54	0.47
II	Mill-scoured and bleached cotton	220	1/1 (plain)	114	54	0.38
III	Grey cotton/polyester blend (65/35)	120	1/1 (plain)	111	72	0.28
IV	Mill-scoured and bleached cotton/ polyester blend (65/35)	111	1/1 (plain)	120	70	0.23

poly(carboxylic acid) (PCA) as a crosslinker and sodium hypophosphite as a catalyst along with other additives. The padded fabric samples were mounted on pin frames, dried at 85°C for 3 min, and cured at 180°C for 90 s in a circulating air oven. The cured fabric samples were then washed at 50°C for 15 min to remove excess and unfixed reactants along with soluble byproducts and then finally dried at 85°C/5 min. Typical formulations used in the finishing treatments are given in the text.

Posttreatment with metal salts

Portions of the ester-crosslinked fabric samples were treated twice with an aqueous solution of a metal salt, that is, zinc acetate or copper acetate (5 g/L), along with a nonionic wetting agent (2 g/L) at 25°C to a wet pickup of 70%, dried at 85°C for 5 min, thoroughly washed to remove excess and unfixed metal salt, and finally dried and conditioned for evaluation.

Combined resin finishing and dyeing

The cellulose-containing fabric samples were padded twice through a solution containing Arkofix NG (50 g/L), $(NH_4)_2SO_4$ (5 g/L), PEG-600 (10 g/L), amine or CA (20 g/L), a nonionic wetting agent (2 g/L), and acetic acid (1 mL/L) to a wet pickup of 70%. After being dried at 100°C for 3 min, the fabric samples were thermofixed at 160°C for 3 min, washed thoroughly, soaped at 50°C for 15 min, rinsed, and finally dried.

Measurements

Standard methods were used to measure the conditioned dry wrinkle recovery angle [WRA; $(W + F)°$, where W = warp and F = weft; AATCC Test Method 66-1996], nitrogen content (Kjeldahl method),[14] carboxyl content (Cirino method),[15] and absorbency value (AATCC Test Method 39-1980).

The color strength, K/S, of the dyed/finished fabric samples was measured at the wavelength of maximum absorbance with an automatic filter spectrophotometer and calculated with the Kubelka–Munk equation:[16]

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

where K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance of the dyed/finished fabric samples at the wavelength of maximum absorption. The higher the K/S value was, the

TABLE II
Effect of the Type and Concentration of PCA on Some Performance and UV-Protection Properties of Finished Cotton Fabric Samples

PCA/SHP concentration (g/L)	—COOH content (mequiv/100 g of fabric sample) CA	—COOH content BTCA	WRA $(W + F)°$ CA	WRA BTCA	Absorbency (s) CA	Absorbency (s) BTCA	UPF rating CA	UPF rating BTCA
Blank	2.20	2.20	137	137	1	1	7	7
25/25	30.05	22.15	224	240	3	2	9	9
50/50	52.50	42.03	242	255	3	4	9	9
75/75	80.62	66	263	276	4	4	11	12

Mill-scoured and bleached cotton fabric samples were treated to a wet pickup of 70% with CA or BTCA, SHP, PEG-600 (10 g/L), and a nonionic wetting agent (2 g/L) and were then dried at 85°C for 3 min and cured at 180°C for 90 s; they were rinsed at 50°C for 15 min and dried at 85°C for 3 min. Protection levels: good (UPF = 15–24), very good (UPF = 29–39), and excellent (UPF > 40).

TABLE III
Effect of the Type and Concentration of PCA on Some Performance and UV-Protection Properties of Finished Cotton/Polyester (65/35) Blend Fabric Samples

PCA/SHP concentration (g/l)	—COOH content (mequiv/100 g of fabric sample)		WRA ($W + F$)°		Absorbency (s)		UPF rating		Protection level	
	CA	BTCA	CA	BTCA	CA	BTCA	CA	BTCA	CA	BTCA
Blank	2.80	2.20	175	175	1	1	14.0	14.0	—	—
25/25	20.25	15.02	240	270	2	2	17.8	17.0	Good	Good
50/50	38.59	30.40	265	280	3	3	18.5	18.0	Good	Good
75/75	62.69	52.61	278	289	4	5	19.0	18.6	Good	Good

Mill-scoured and bleached cotton/polyester fabric samples were treated to a wet pickup of 70% with CA or BTCA, SHP, PEG-600 (10 g/L), and a nononic wetting agent (2 g/l) and were then dried at 85°C for 3 min and cured at 180°C for 90 s. They were rinsed at 50°C for 15 min and dried at 85°C for 3 min. Protection levels: good (UPF = 15–24), very good (UPF = 25–39), and excellent (UPF > 40).

greater the dye receptivity was of the treated fabric samples.

Ultraviolet-protection factor (UPF) values were calculated according to the Australian/New Zealand standard (AS/NZS 4366-1996) with a UV-Shimadzu 3101 PC spectrophotometer. According to the Australian classification scheme, fabrics can be rated as providing good protection, very good protection, and excellent protection if their UPF values are 15–24, 25–39, and greater than 40, respectively.[2]

RESULTS AND DISCUSSION

With a view toward improving the UV-protective properties, meeting aesthetic requirements, and ensuring adequate wear comfort for the end use, attempts have been made to explore the effect of (1) ester crosslinking formulations followed by a posttreatment with a metal salt solution (5 g/L) and (2) simultaneous dyeing and resin finishing with different dyestuffs and additives on the extent of protection against solar UV radiation as well as the improvement in other performance properties of treated fabric samples. The obtained results, along with appropriate discussion, follow.

Ester crosslinking

Type and concentration of PCA

Tables II and III show the effects of the type and concentration of PCA on some performance and UV-protection properties of the treated cotton and cotton/polyester (65/35) fabric samples. Increasing the PCA concentration in the finishing bath results in the following:

1. There is a significant increase in the carboxyl content along with a noticeable improvement in the fabric resiliency.
2. The extent of the increase in the carboxyl content is determined by the type of PCA, that is, CA > BTCA, as well as the kind of finished substrate, that is, cotton > cotton/polyester (65/35) blend.
3. The improvement in WRA is governed by both the type of crosslinker, that is, BTCA > CA, and the nature of the substrate, that is, cotton/polyester blend > cotton.
4. Ester crosslinking has practically a marginal effect on the extent of wettability.
5. Increasing the crosslinker concentration from 0 to 75 g/L has a slight effect on the UPF values and the protection level, regardless of the crosslinker and substrate.

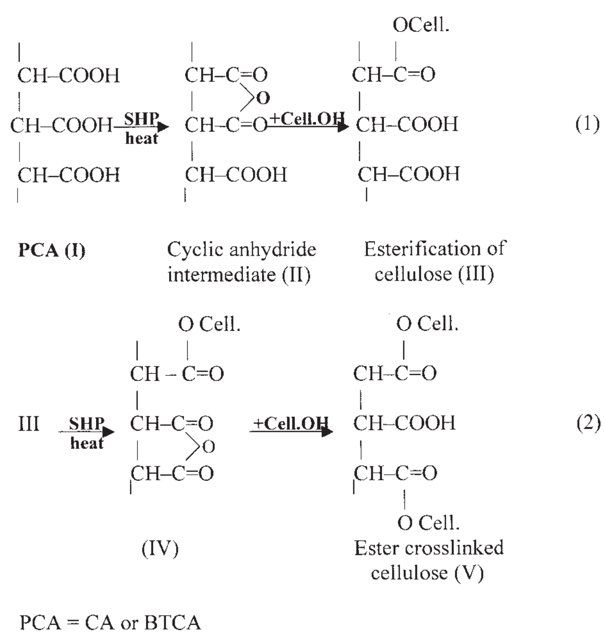

Figure 1 Ester crosslinking of the cellulose structure.

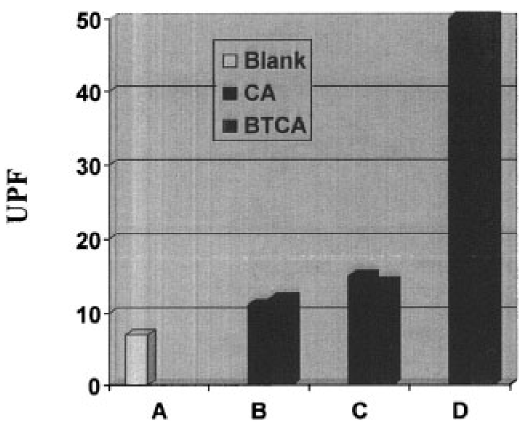

Figure 2 UPF rating of bleached cotton fabric samples: (A) untreated fabric, (B) ester-crosslinked fabric, (C) ester-crosslinked fabric posttreated with zinc acetate (5 g/L), and (D) ester-crosslinked fabric posttreated with copper acetate (5 g/L). The finishing included PCA/SHP (75/75 g/L each), PEG-600 (10 g/L), a nonionic wetting agent (2 g/L), 70% wet pickup, drying at 85°C for 3 min, and curing at 180°C for 90 s. The posttreatment included a metal salt (5 g/L), 70% wet pickup, drying at 85°C for 5 min, and thorough washing and drying.

6. The presence of a polyester component in the cotton/polyester blend has a positive impact on WRA and UPF-rating values.

The enhancement of both the carboxyl content and the fabric resiliency with increasing PCA/sodium hypophosphite monohydrate (SHP) concentration is a direct result of enhancing the extent of crosslinking of the cellulose structure and creating free —COOH groups on the finish fabric matrix, as shown in Figure 1.[17]

The degree of ester crosslinking of the cellulose structure is determined by the type of PCA, that is, the molecular weight, chemical structure, number of carboxylic groups, and reactivity.[17–22]

Type of metal salt

As for the variation in the UPF rating of the finished fabric samples as a function of the treatment sequence as well as the type of salt in the posttreatment bath, Figures 2 and 3 show the following:

1. The UPF rating of untreated fabric samples is governed by the nature of the substrate, that is, cotton/polyester blend > cotton, and this can be attributed to the better UV absorption capacity of the polyester component.[1]
2. Ester crosslinking of the substrates results in a marginal improvement in the UPF-rating values as a direct result of fabric modification along with minimization of the holes in the fabric structure.
3. The posttreatment of ester-crosslinked fabric samples has a positive impact on the UV protection, and its extent follows a descending order, copper acetate ≫ zinc acetate > none, regardless of the substrate.
4. Posttreatment with copper acetate is accompanied by a sharp increase in the sun-protection property of the finished fabric samples, and this improvement is generally higher in the cotton fabric than that in the blended fabric. This can be discussed in terms of a higher extent of crosslinking as well as the fixation and binding of copper onto the finish/cotton fabric matrix due to salt and/or complex formation with its free carboxyl groups [eq. (3)].[23,24]
5. The highest UPF rating obtained by posttreatment with copper acetate reflects its positive impact as an effective UV-radiation absorber.[25]
6. A posttreatment with metal salts has practically no effect on the performance properties of the precrosslinked fabric samples.

$$2 \sim\!\sim COOH + Cu^{2+} \rightleftharpoons (\sim\!\sim COO)_2 Cu + 2H^{+} \quad (3)$$

Ester-crosslinked cellulose — Crosslinked-cellulose structure containing copper

Effect of the preparation history

The effects of the preparation history and the type of substrate on some performance and UV-protection properties of finished fabric samples are given in Table IV. For a given set of finishing conditions, the data indicate the following:

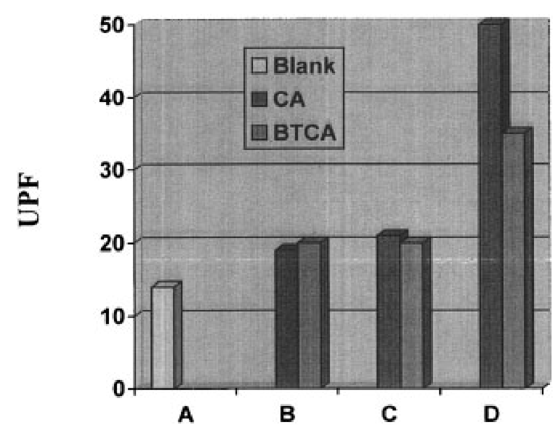

Figure 3 UPF rating of bleached cotton/polyester (65/35) blend fabric samples: (A) untreated fabric, (B) ester-crosslinked fabric, (C) ester-crosslinked fabric posttreated with zinc acetate (5 g/L), and (D) ester-crosslinked fabric posttreated with copper acetate (5 g/L). The finishing included PCA/SHP (75/75 g/L each), PEG-600 (10 g/L), a nonionic wetting agent (2 g/L), 70% wet pickup, drying at 85°C for 3 min, and curing at 180°C for 90 s. The posttreatment included a metal salt (5 g/L), 70% wet pickup, drying at 85°C for 5 min, and thorough washing and drying.

TABLE IV
Effect of Pretreatment Steps and Type of Substrate on Some Performance and UV-Protection Properties of Finished Fabric Samples

Pretreatment	Substrate	Finish	—COOH content (mequiv/100 g of fabric)	WRA $(W + F)°$	Wetting (s)	UPF rating	Protection level
Grey	Cotton	−ve	2.30	153	16	37.7	Very good
		+ve	60.52	271	5	48.0	Excellent
	C/PET	−ve	2.00	190	10	21.7	Good
	65/35	+ve	55.81	277	5	25.5	Good
	C/PET	−ve	1.50	196	8	13.3	—
	50/50	+ve	57.31	280	6	21.4	Good
Scoured and bleached	Cotton	−ve	2.20	137	1	7.0	—
		+ve	80.62	263	4	11.0	—
	C/PET	−ve	2.80	175	1	14.0	—
	65/35	+ve	62.69	278	4	19.0	Good
	C/PET	−ve	1.51	183	3	12.0	—
	50/50	+ve	60.2	265	3	18.0	Good
Scoured, bleached, and mercerized	Cotton	−ve	2.10	115	2	5.6	—
		+ve	60.12	250	2	10.4	—
	C/PET	−ve	1.80	179	3	5.9	—
	65/35	+ve	59.01	287	3	8.4	—
	C/PET	−ve	2.01	197	2	8.5	—
	50/50	+ve	60.10	263	2	12.0	—

CA/SHP = 75/75 g/L; PEG-600 = 10 g/L); nonionic wetting agent = 2 g/L. Samples were dried at 85°C for 3 min, cured at 180°C for 90 s, rinsed at 50°C for 15 min, and dried at 85°C for 3min. −ve = without finish; +ve = with finish. Protection levels: good (UPF = 15–24), very good (UPF = 25–39), and excellent (UPF > 40).

1. Ester crosslinking of the substrates brings about a remarkable increase in the carboxyl content as well as fabric resiliency; this is a direct result of increasing the extent of crosslinking along with building free carboxyl groups onto the finish/fabric matrix, regardless of the substrate and the pretreatment step.
2. Ester crosslinking of grey fabrics is accompanied by an improvement in fabric wettability along with an increase in the UPF rating.
3. The extent of the improvement in the UPF rating is determined by the pretreatment step (grey cotton ≫ scoured and bleached cotton ≥ scoured, bleached, and mercerized cotton) in the absence or presence of the crosslinking agent, reflecting the positive role of the noncellulosic impurities acting as UV-radiation absorbers and thereby upgrading the UV-protection property of grey fabrics, especially cotton fabric.[1,4]
4. Bleaching cotton-containing fabrics has a negative impact on their UV-protection property because of the high permeability of bleached substrates to solar UV rays.[1]
5. The pretreatment of cotton fabric samples results in a sharp improvement in their wettability along with a decrease in their resiliency as a result of the removal of the hydrophobic natural impurities, that is, waxes, fats, and oils, which act as lubricating and softening agents, thereby minimizing the fabric resiliency.[26]
6. The extent of variation in the performance and UV-protection properties of the finished fabrics under investigation is determined by the nature of the substrate, that is, the chemical composition, fabric components, yarn count and structure, weave construction, thickness, and cover factor.[13]

As for the variation in the UPF rating of the obtained products as a function of the pretreatment and the finishing sequence, Figures 4 and 5 show the following:

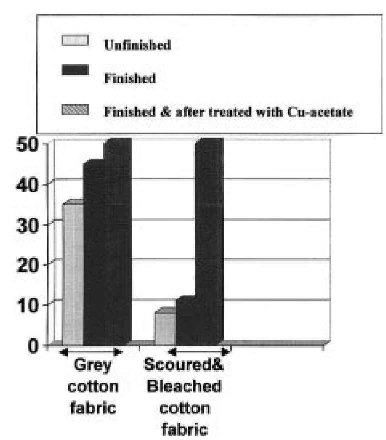

Figure 4 Effect of the preparation history and finishing sequence on the UPF rating of finished fabric samples. The finishing included CA/SHP (75/75 g/L each), PEG-600 (10 g/L), a nonionic wetting agent (2 g/L), 70% wet pickup, drying at 85°C for 3 min, and curing at 180°C for 90 s. The posttreatment included copper acetate (5 g/L), 70% wet pickup, drying at 85°C/3 min, and thorough washing and drying.

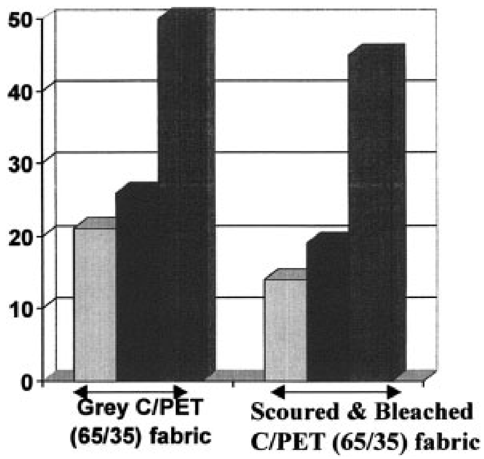

Figure 5 Effect of the preparation history and finishing sequence on the UPF rating of finished C/PET (65/35) fabric samples. The finishing included CA/SHP (75/75 g/L each), PEG-600 (10 g/L), a nonionic wetting agent (2 g/L), 70% wet pickup, drying at 85°C for 3 min, and curing at 180°C for 90 s. The posttreatment included copper acetate (5 g/L), 70% wet pickup, drying at 85°C/3 min, and thorough washing and drying.

1. The UPF rating is governed by the finishing sequence, finishing followed by posttreatment > finishing > without finishing, regardless of the substrate.
2. Posttreatment with a copper acetate solution has a positive impact on enhancing the extent of the UV-protection property of the treated substrates, and this indicates that copper acts as an UV absorber and makes the posttreated fabric samples less permeable to solar UV rays.
3. The extent of the improvement is determined by the preparation history of the used substrate and follows a descending order, grey > scoured and bleached substrate, with a fixed finishing treatment as well as no copper acetate posttreatment.
4. When copper acetate is used after the treatment, the preparation history of the substrate has practically no effect.

Additives

As for the variation in the performance and UV-protection properties of the obtained products as a function of the additive type, with and without posttreatment with copper acetate, the data in Table V demonstrate the following:

1. Ester crosslinking of the substrates improves the resiliency, wettability, and UV-protection property of these substrates, regardless of the substrate.
2. The incorporation of any of the additives into the ester crosslinking formulations results in a decrease in WRA, a marginal increase in the wetting time, and an improvement in the UPF rating, and the extent of the variation in the aforementioned properties is determined by the nature of the additive, that is, the chemical composition, molecular weight, reactivity, and functionality, the mode of interaction, the fixation onto the finish/fabric matrix, and the extent of the modification of the fabric structure along with its ability to absorb the UV rays or increase the cover factor, thereby minimizing or preventing the permeability of UV rays.
3. Posttreatment of the scoured and bleached cotton, grey cotton/polyester (65/35) blend, and scoured and bleached cotton/polyester (65/35) blend fabric samples with copper acetate solutions (5 g/L) is accompanied by a remarkable improvement in the UPF-rating values, regardless of the additive.
4. The extent of the improvement in the UPF rating is governed by the ability of the prefinished

TABLE V
Effect of the Incorporation of Certain Additives in the Finishing Formulation on Some Performance and UV-Protection Properties of Fabric Samples

	Cotton fabric						Cotton/polyester (65/35) blend fabric					
	Grey			Scoured and bleached			Grey			Scoured and bleached		
Additive	WRA $(W + F)^\circ$	Absorbency (s)	UPF	WRA $(W + F)^\circ$	Absorbency (s)	UPF	WRA $(W + F)^\circ$	Absorbency (s)	UPF	WRA $(W + F)^\circ$	Absorbency (s)	UPF
Untreated	153	16	37.7	137	1	7.0	190	10	21.7	175	1	14
None	271	5	48	263	4	11 (50^+)	277	5	25.5 (50^+)	278	4	19 (48)
Chitosan (5 g/L)	210	8	50^+	226	6	12.3 (50^+)	245	6	30.6 45	236	4	22.5 (34.3)
β-cyclodextrin (20 g/L)	220	7	50^+	240	3	12.4 (50^+)	242	5	32.4 (50^+)	250	3	24 (36)
Choline chloride (20 g/L)	210	6	50^+	240	6	11.5 (50^+)	235	4	26.6 (50^+)	245	3	20 (33.4)

Finishing: CA/SHP = 75/75 g/L; PEG-600 = 10 g/L; nonionic wetting agent = 2 g/L; wet pickup = 70%. Samples were dried at 85°C for 3 min, cured at 180°C/90 s, and then rinsed and dried. Posttreatment: Copper-acetate = 5 g/L; nonionic wetting agent = 2 g/L; wet pickup = 70%. Samples were dried at 85°C for 3 min and were then rinsed and dried. Values in parentheses indicate UPF ratings of posttreated finished fabric samples with copper acetate for solution (5 g/L).

TABLE VI
Effect of Reactive Dyeing/Resin Finishing on Some Performance and UV-Protection Properties of Treated Fabric Samples

Dye (g/L)	Substrate	N (%)	WRA ($W + F$)°	K/S	Absorbency (s)	UPF Rating	Protection level
0	Cotton	0.346	230	—	2	13.5	—
	Blend	0.320	250	—	2	20.6	Good
10	Cotton	0.363	239	1.16	2	38.9	Very good
	Blend	0.335	262	0.70	2	28.5	Good
20	Cotton	0.385	250	1.75	2	46.5	Excellent
	Blend	0.356	273	1.08	3	36.7	Very good

Finishing formulation: Arkofix NG = 50 g/L; $(NH_4)_2SO_4$ = 5 g/L; PEG-600 = 10 g/L; TEA · HCl = 20 g/L; nonionic wetting agent = 2 g/L; Reactive Red 63 = 0–20 g/L; wet pickup = 70%. Samples were dried at 85°C for 3 min and cured at 160°C for 3 min, followed by washing and drying. Cotton = scoured and bleached cotton fabric; blend = scoured and bleached C/PET (65/35) blend fabric.

fabric samples to pick up and fix the Cu^{2+} cations onto the finish/fabric matrix.

Simultaneous dyeing and resin finishing

Trials have been made to enhance the UV-protection properties of cotton-containing fabrics via the incorporation of certain anionic and cationic dyestuffs into the resin finishing formulations. As far as changes in some performance and UV-protection properties are concerned, upon the inclusion of certain reactive dyes, namely, C.I. Reactive Red 63 and C.I. Reactive Black 5, in the finishing formulations, the results in Tables VI and VII demonstrate the following:

1. Increasing the dye concentration up to 20 g/L slightly improves the nitrogen content and the fabric resiliency, and there is a remarkable improvement in both the K/S and UPF-rating values without an adverse effect on the fabric wettability, regardless of the substrate.
2. The extent of variation in the aforementioned properties is determined by the type of substrate, that is, the cellulose content, extent of crosslinking, and fixation of triethanolamine in the finish/fabric matrix, along with its ability to pick up and fix the reactive dye onto the cellulose structure, regardless of the reactive dye.[27]
3. The enhancement of the UV-protection property is governed by the nature of the reactive dye, that is, the chemical structure, molecular geometry, transmission/absorption characteristics, steric effect, location and aggregation, and uniformity across the fiber/fabric,[1,2,13] and follows a descending order, C.I. Reactive Black 5 > C.I. Reactive Red 63, regardless of the dye concentration.
4. The incorporation of C.I. Reactive Black 5 up to 10 g/L results in a dramatic improvement in the UPF rating [from 13.5 to 50^+ for treated cotton fabric samples and from 20.6 to 50^+ for treated cotton/polyester (65/35) blend fabric samples].

The data in Table VIII show the effect of the Direct Violet 31 concentration on some performance and UV-protection properties of cotton and cotton/polyester (65/35) blend fabric samples. It is clear, within the range examined, that

1. Increasing the direct dye concentration in the finishing formulations improves both the nitro-

TABLE VII
Effect of Reactive Dyeing/Resin Finishing on Some Performance Properties of Treated Fabric Samples

Dye (g/L)	Substrate	N (%)	WRA ($W + F$)°	K/S	Absorbency (s)	UPF rating	Protection level
0	Cotton	0.346	230	—	2	13.5	—
	Blend	0.320	250	—	2	20.6	Good
10	Cotton	0.372	241	2.41	3	50^+	Excellent
	Blend	0.341	260	1.80	4	50^+	Excellent
20	Cotton	0.390	255	3.82	3	50^+	Excellent
	Blend	0.364	272	2.52	4	50^+	Excellent

Finishing formulation: Arkofix NG = 50 g/L; $(NH_4)_2SO_4$ = 5 g/L; PEG-600 = 10 g/L; TEA · HCl = 20 g/L; nonionic wetting agent = 2 g/L; Reactive Black-5 = 0–20 g/L; wet pickup = 70%. Samples were dried at 85°C for 3 for min and cured at 160°C for 3 min, followed by washing and drying. Cotton = scoured and bleached cotton fabric; blend = scoured and bleached C/PET (65/35) blend fabric.

TABLE VIII
Effect of Direct Dyeing/Resin Finishing on Some Performance and UV-Protection Properties of Treated Fabric Samples

Dye (g/L)	Substrate	N (%)	WRA (*W* + *F*)°	*K/S*	Absorbency (s)	UPF rating	Protection level
0	Cotton	0.346	230	—	2	13.5	—
	Blend	0.320	250	—	2	20.6	Good
10	Cotton	0.365	240	2.35	3	50^+	Excellent
	Blend	0.330	260	1.40	3	38.6	Very good
20	Cotton	0.385	255	3.39	3	50^+	Excellent
	Blend	0.361	272	1.92	3	45.5	Excellent

Finishing formulation: Arkofix NG = 50 g/L; $(NH_4)_2SO_4$ = 5 g/L; PEG-600 = 10 g/L; TEA · HCl = 20 g/L; nonionic wetting agent = 2 g/L; Direct Violet 31 = 0–20 g/L; wet pickup = 70%. Samples were dried at 85°C for 3 min and cured at 160°C for 3 min, followed by washing and drying. Cotton = scoured and bleached cotton fabric; blend = scoured and bleached C/PET (65/35) blend fabric.

gen content and the fabric resiliency, WRA, along with a noticeable increase in the depth of the obtained dyeings, with the wetting time remaining practically unchanged.

2. This improvement in the aforementioned properties may be attributed to the dye fixation onto the grafted cationic sites along with the dye retention within the cellulose structure, which minimizes its basicity, increases its acidity, and enhances its extent of crosslinking, via the polyfunctional crosslinking agent, during the curing step.[28]
3. The higher the dye concentration is, the greater the UPF rating is, regardless of the substrate, which can be discussed in terms of lower transmission of UV rays within the darker fabric.[3,29]
4. The extent of dye fixation onto the cotton structure is higher than that on the cotton/polyester blend, and this leads to greater dye absorption, even at a 10 g/L dye concentration, and less ray transmission, that is, excellent UV protection.

As for the change in the percentage of N, WRA, *K/S*, absorbency, and UPF rating as a function of the acid dye (Acid Red 1) concentration, Table IX shows that increasing the acid dye concentration up to 20 g/L enhances the percentage of N and WRA and results in a considerable improvement in both the *K/S* and UPF rating without adversely affecting the wettability of the obtained products. The higher the extent is of dye fixation onto the amine-containing crosslinked cellulose, the greater the shade depth and the UPF rating are.

Current data also show that both C.I. Reactive Black 5 (Table VII) and C.I. Direct Violet 31 (Table VIII) are effective additives in combination with other finishing bath ingredients for simultaneous dyeing and resin finishing of cotton-containing fabrics to produce easy-care finished dyeings with greater UV protection in comparison with the other used anionic dyes, even at a 10 g/L dye concentration. This reflects their unique UV-radiation absorbing properties.

Table X also shows that increasing the Basilene Red PB basic dye concentration from 0 to 10 g/L in the finishing formulation brings about an increase in the percentage of N, a slight decrease in WRA, and a sharp increase in *K/S* without affecting the absorbency values of the treated fabric samples. On the other hand, the addition of the basic dye up to 10 g/L results in a dramatic improvement in UPF-rating val-

TABLE IX
Effect of Acid Dyeing/Resin Finishing on Some Performance Properties of Treated Fabric Samples

Dye (g/L)	Substrate	N (%)	WRA (*W* + *F*)°	*K/S*	Absorbency (s)	UPF rating	Protection level
0	Cotton	0.346	230	—	2	13.5	—
	Blend	0.320	250	—	2	20.6	Good
10	Cotton	0.362	238	1.95	2	33.6	Very good
	Blend	0.341	264	1.32	2	27.2	Good
20	Cotton	0.380	250	2.70	3	40.9	Excellent
	Blend	0.359	276	1.79	3	32.0	Very good

Finishing formulation: Arkofix NG = 50 g/L; $(NH_4)_2SO_4$ = 5 g/L; PEG-600 = 10 g/L; TEA · HCl = 20 g/L; nonionic wetting agent = 2 g/L; Acid Red 1 = 0–20 g/L; wet pickup = 70%. Samples were dried at 85°C for 3 min and cured at 160°C for 3 min, followed by washing and drying. Cotton = scoured and bleached cotton fabric; blend = scoured and bleached C/PET (65/35) blend fabric.

TABLE X
Effect of Basic Dyeing/Resin Finishing on Some Performance Properties of Treated Fabric Samples

Dye (g/L)	Substrate	N (%)	WRA $(W + F)°$	K/S	Absorbency (s)	UPF rating	Protection level
0	Cotton	0.368	235	—	1	11.0	—
	Blend	0.330	248	—	2	14.3	—
10	Cotton	0.380	226	7.82	2	50^+	Excellent
	Blend	0.346	240	4.05	2	50^+	Excellent
20	Cotton	0.395	220	8.40	2	50^+	Excellent
	Blend	0.359	230	4.96	3	50^+	Excellent

Finishing formulation: Arkofix NG = 50 g/L; $(NH_4)_2SO_4$ = 5 g/L; CA = 20 g/L; nonionic wetting agent = 2 g/L; Basilene® Red PB = 0–20 g/L. Samples were dried at 85°C for 3 min and cured at 160°C for 3 min, followed by washing and drying. Cotton = scoured and bleached cotton fabric; blend = scoured and bleached C/PET (65/35) blend fabric.

ues, from less than 15 to 50^+ (excellent UV protection), regardless of the substrate; this reflects the outstanding ability of the dye to absorb and hinder the transmission UV radiation. A further increase in the dye concentration has a positive impact on the shade depth of the obtained products along with a negligible effect on the other performance properties.

Table X shows that the sharp increase in the K/S and UPF-rating values is a direct result of fixation of the basic dye onto the carboxyl-containing crosslinked cellulose structure.[30]

CONCLUSIONS

Grey cotton fabric (100%) provides greater UV protection than the other fabrics, regardless of the finishing formulations. A posttreatment of ester-crosslinked fabric samples with a copper acetate solution (5 g/L) results in a remarkable improvement in the UV-protection values of grey cotton/polyester blend and bleached cotton and cotton/polyester blend fabric samples without adversely affecting other performance properties. Simultaneous reactive dyeing (with Reactive Black 5), direct dyeing (with Direct Violet 31), or basic dyeing (with Basilene Red PB) and resin finishing with DMDHEU as a reactant resin, in the presence TEA · HCl or CA, respectively, produces dyed easy-care finished cotton-containing fabrics with outstanding UV-protection properties.

References

1. Ghosh, S. B.; Bajaj, P.; Kothari, V. K. Indian J Fibre Text Res 2003, 28, 431.
2. Srinivasan, M.; Gatewood, B. M. Text Chem Color Am Dyestuff Rep 2000, 32(4), 36.
3. Reinert, G.; Fuso, F.; Hilfiker, R.; Schmidt, E. Text Chem Color 1997, 29(12), 36.
4. Rupp, J.; Böhringer, A.; Yonenaga, A.; Hilden, J. Int Text Bull 2001, 6, 8.
5. Sharma, D. K.; Singh, M. Colourage Annu 2001, 48, 69.
6. Hilfiker, R.; Kaufmann, W.; Reinert, G.; Schmidt, E. Text Res J 1996, 66, 61.
7. Pailthorpe, M. Text Horizons 1996, 16(5), 11.
8. Reinert, G.; Schimdt, E.; Hilfiker, R. Melliand Textilber 1994, 75(7), 607/E-151.
9. Bohringer, B.; Schindling, G.; Shon, U.; Hanke, D.; Hoffmann, K.; Alfmeir, P.; Koltz, M. L. Melliand Int 1997, 3, 165.
10. Bayer, A. G.; Cox-Crews, P. Proc Int Conf Exhib 1997, 175.
11. Eckhardt, C.; Rohwer, H. Text Chem Color Am Dyestuff Rep 2000, 32(4), 21.
12. Algaba, I.; Riva, A. Color Technol 2002, 118, 52.
13. Gies, P. H.; Roy, C. R.; Toomey, S.; McLennan, A. Mutat Res 1998, 422, 15.
14. Vogel, A. I. Elementary Practical Inorganic Chemistry, 2nd ed.; Longman: London, 1975; Part 3, p 652.
15. Cirino, O. V.; Rowland, S. P. Text Res J 1976, 46, 272.
16. Kubelka, P.; Munk, F. Z Tech Phys 1931, 12, 593.
17. Ibrahim, N. A.; Abo-Shosha, M. H.; Elnagdy, E. I.; Gaffar, M. A. J Appl Polym Sci 2002, 84, 2243.
18. Xu, W. I.; Cui, W.; Li, W.; Guo, W. Color Technol 2001, 117, 352.
19. Welch, G. M.; Peters, J. G. Text Chem Color 1997, 29, 22.
20. Xu, W. I.; Li, Y. Text Res J 2000, 70, 588.
21. Xu, W. I.; Li, Y. Text Res J 2000, 70, 957.
22. Andrews, B. A. K. Text Chem Color 1990, 22, 63.
23. Rowland, S. P.; Cirino, V. O. Am Dyestuff Rep 1977, 65(7), 46.
24. Gaffar, M. A. Ph.D. Thesis, Cairo University, 2000.
25. Reinert, G.; Thommen, F. Text Chem Color 1991, 23(1), 31.
26. Prabaharan, M.; Rao, J. V. Indian J Fibre Text Res 2003, 28, 437.
27. Blanchard, E. J.; Grawes, E. E.; Reinhardt, R. M. Colourage Manual 1999, 46, 55.
28. Ibrahim, N. A.; El-Zairy, M. R.; Allam, E.; Hassan, T. M. Colourage 1996, 43(4), 21.
29. Perenich, T. A. Colourage Annu 1998, 45, 71.
30. Ibrahim, N. A.; El-Zairy, M. R.; Allam, E.; Hassan, T. M. Colourage 1996, 43(5), 23.