## **Multifunctional Anionic Cotton Dyeings**

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**ABSTRACT:** Anionic cotton dyeings with anti-ultraviolet and antibacterial functions were prepared by the posttreatment of direct and reactive cotton dyeings with a zirconium oxychloride salt solution. The extent of improvement in the functional properties was governed by the structure and pretreatment history of the knitted cotton fabric, the kind and concentration of the anionic dye, and the dyeing regime. The chelation and fixation of the positively charged zirconium ions onto and/or within the dyed substrate resulted in an enhancement in the ultraviolet absorption capacity of the treated substrate and interaction with the thiol groups of the cellular protein; this imparted antibacterial activity against Gram-positive and Gram-negative bacteria without adverse effects on the hue of the obtained dyeings. Both the anti-ultraviolet and bacterial functions of the post-treated dyeings survived through 15 washing cycles. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 3249–3255, 2010

Key words: dyes/pigments; fibers; modification

#### INTRODUCTION

Production of cotton-containing textiles generally includes the following stages: yarn formation, fabric formation (i.e., woven, nonwoven, or knitted), wet processing (i.e., pretreatment, coloration, and/or finishing), and textile fabrication.<sup>1</sup> Pretreatment is mainly concerned with the removal of noncellulosic and added impurities to get high and uniform water absorption and the oxidation of colored impurities to attain a sufficiently high and uniform degree of whiteness and to prepare the cotton substrate for subsequent dyeing and/or finishing.<sup>2</sup> The dyeing of pretreated substrates with direct, reactive, vat, or sulfur dyestuffs is carried out to add color to textiles and to increase their added values.<sup>3</sup> On the other hand, new quality requirements and a growing awareness of health and hygiene have increased the demands for novel finishes, such as protective finishes, wellness finishes, medical finishes, and biofinishes, which take into consideration both the economical and ecological aspects.<sup>4</sup>

Cotton fabrics used in summertime apparel often provide poor protection against harmful ultraviolet (UV) radiation, especially UVB radiation (280–315 nm), and are also an excellent environment for microorganism growth. Many attempts have been made to enhance the UV protection and the antibacterial properties of cotton textiles.<sup>5–15</sup>

In this research, an attempt was made to enhance both the UV protection and antibacterial properties of cotton knits dyed with direct and reactive dyes via post-treatment with zirconium oxychloride salt. The relationship of the fabric structure, pretreatment history, type and concentration of the dye, and postdeposition of zirconium ions onto and/or within the dyed substrates to the UV protection factor (UPF) along with the antibacterial activity against Grampositive bacteria, that is, *Staphylococcus aureus*, and Gram-negative bacteria, that is, *Escherichia coli*, was investigated.

#### **EXPERIMENTAL**

## Materials

The specifications of the mill-scoured and halfbleached knitted cotton fabrics are shown in Table I. Details of the commercial anionic dyes used in this study are given in Table II.

Gisapal ECO 160 (a multifunctional detergent and nonionic wetting agent based on fatty alcohol ethoxylate; Rotta), Cibanpon R [a postclearing agent based on a sodium salt of modified poly(acrylic acid), anionic; Ciba, Egypt], and Alvirol AGK (a sequestering agent based on polyacrylates and carboxylic acid derivates, Texticolor, Switzerland) were commercial grade.

The other chemicals used [zirconium oxychloride (ZrOCl<sub>2</sub>·8H<sub>2</sub>O), sodium hydroxide (NaOH),

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Substrate	Pretreatment	Count (Ne)	Weight (g/m²)	Thickness (mm)	Absorbency time (s)	Whiteness index	Bursting strength (kg/cm <sup>2</sup> )	UPF
Pique	Scouring	30/1	198.2	0.700	3	25.7	7.08	11.5
-	Half-bleaching		204.4	0.721	<1	54.3	5.70	9.0
Interlock	Scouring	30/1	228.3	0.826	5	20.3	7.88	32.2
	Half-bleaching		231.3	0.833	<1	50.2	6.08	21.0
Parasol	Scouring	30/1	152.9	0.697	2	32.8	6.45	7.0
	Half-bleaching		157.7	0.700	<1	58.1	5.95	6.0

TABLE I Characteristics of the Substrates Used

disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>), acetic acid, and sodium chloride] were laboratory grade.

## Methods

#### Dyeing

The knitted fabric samples were dyed with the aforementioned dyestuffs according to the recommended amounts of alkali and salt and dyeings and postwashing conditions given by the dye suppliers by the exhaustion technique in Launder-Ometer (Atlas, Germany) at a material-to-liquor ratio of 1/10 w/v.

## Post-treatment with zirconium oxychloride

The predyed fabrics samples were treated in a Launder-Ometer dye pot with an aqueous solution of the zirconium salt (50 mmol/L) in the presence of a nonionic wetting agent (2 g/L) at 25°C for 20 min with constant stirring; the material-to-liquor ratio was kept at 1/20 w/v, and the fabric was subsequently washed three times with deionized water to remove the excess and unfixed metal salt and finally dried and conditioned for evaluation.

#### Fabric evaluation

The fabric thickness was assessed according to ASTM D 1777-96 with a Dial Thichness Gauge, supplied by TeClock, Japan. The drop absorbency time of the treated fabric samples was determined accord-

ing to AATCC test method 79-1992. The whiteness index of scoured and half-bleached substrates were evaluated with an UltraScan PRO (HunterLab, USA) E 313, D65/10-USA. The bursting strength was measured according to ASTM D 3786-87 by a Mullen tester (Standex Company, USA).

UPF values were assessed according to the Australian/New Zealand standard AS/NZS 4399-1996. According to the Australian classification scheme, fabrics can be rated as providing good, very good, or excellent protection if their UPF values range from 15 to 24, 25 to 39, or above 40, respectively. In no event can a fabric be assigned a UPF rating greater than 50.<sup>5,16</sup>

The color strength [K/S (where K is the light absorption coefficient and S is the scattering coefficient)] of the obtained dyeings were obtained from the reflectance (R) values at the wavelength of maximum absorption with the Kubelka Munk equation:<sup>17</sup>

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

*R* was determined with a Color-Eye 3100 spectrophotometer (SDL Inter, England).

Fastness properties to washing and the crocking of dyed fabric samples were evaluated according to AATCC test methods 61-1972 and 8-1972, respectively.

The metal content (mmol/100 g of fabric sample) of the dyed samples post-treated with the zirconium salt was quantitatively determined with a Flame

TABLE II Anionic Dyestuffs

	j		
Dyestuff	Class	Color index	Supplier
Procion Crimson H-Exl	Reactive	Reactive Red 231	Dystar
Procion Yellow H-Exl	Reactive	Reactive Yellow 138	Dystar
Cibacron Red FN-R	Reactive	Reactive Red 238	Ciba
Cibacron Blue FN-R	Reactive	Reactive Blue 235	Ciba
Remazol Red RR	Reactive	Not available	Dystar
Remazol Blue RR	Reactive	Not available	Dystar
Solophenyl Turquoise BRLE	Direct	Direct Blue 189	Ciba
Solophenyl Bordeaux Red 3BLE	Direct	Direct Red 83	Ciba
Solophenyl Yellow AGL	Direct	Direct Yellow169	Ciba

			lne	Piq			lock	Inter			asol	Para	
	Shade	ured	Scou		Ha blea	ured	Scot	alf- ched		ured	Scot		Ha blead
Reactive dye	(% owf)	K/S	UPF	UPF K/S		K/S	UPF	PF K/S UPF K/S UPF		UPF	K/S	UPF	
Procion	0.5	4.45	36.8	4.15	28.7	3.8	$50^{+}$	3.58	$50^{+}$	4.62	30.1	4.30	20.4
Crimson H-Ex	1.0	9.02	$50^{+}$	8.25	50	8.78	$50^{+}$	7.16	$50^{+}$	9.36	50	8.99	45
	3.0	18.62	$50^{+}$	18.24	$50^{+}$	17.95	$50^{+}$	17.48	$50^{+}$	18.99	$50^{+}$	18.63	$50^{+}$
Procion	0.5	3.93	50	3.65	42.6	3.69	$50^{+}$	3.36	$50^{+}$	4.16	$50^{+}$	3.73	39.2
Yellow H-Exl	1.0	6.00	$50^{+}$	5.80	$50^{+}$	5.78	$50^{+}$	5.52	$50^{+}$	6.73	$50^{+}$	5.99	50
	3.0	15.84	$50^{+}$	15.39	$50^{+}$	14.99	$50^{+}$	14.68	$50^{+}$	16.35	$50^{+}$	15.73	$50^{+}$
Cibacron	0.5	3.41	44.5	3.15	$50^{+}$	3.14	$50^{+}$	3.00	$50^{+}$	3.69	37.5	3.40	50
Red FN-R	1.0	7.12	$50^{+}$	6.21	$50^{+}$	6.80	$50^{+}$	5.86	$50^{+}$	7.40	49.2	6.63	$50^{+}$
	3.0	16.61	$50^{+}$	16.10	$50^{+}$	15.19	$50^{+}$	14.64	$50^{+}$	16.88	$50^{+}$	16.25	$50^{+}$
Cibacron	0.5	5.76	43.9	5.50	32.9	5.02	$50^{+}$	4.70	$50^{+}$	6.02	33.5	5.66	26.5
Yellow FN-R	1.0	10.15	$50^{+}$	9.80	42.6	9.46	$50^{+}$	9.16	$50^{+}$	10.40	48.8	10.00	40.6
	3.0	19.09	$50^{+}$	18.26	$50^{+}$	18.09	$50^{+}$	17.39	$50^{+}$	19.42	$50^{+}$	18.80	$50^{+}$
Remazol	0.5	3.44	36.9	3.12	28.2	3.10	$50^{+}$	2.65	$50^{+}$	3.75	26.3	3.30	20.0
Red RR	1.0	6.85	50	6.15	46.0	6.08	$50^{+}$	5.39	$50^{+}$	7.12	46.8	6.48	40.2
	3.0	16.80	$50^{+}$	15.98	$50^{+}$	14.54	$50^{+}$	13.80	$50^{+}$	17.17	$50^{+}$	16.24	$50^{+}$
Remazol	0.5	1.97	34.0	1.60	25.2	1.60	$50^{+}$	1.42	$50^{+}$	2.29	22.3	1.80	15.0
Blue RR	1.0	3.80	44.3	3.50	37.0	3.50	$50^{+}$	3.29	$50^{+}$	3.96	38.8	3.57	32.3
	3.0	9.66	$50^{+}$	9.31	$50^{+}$	9.30	$50^{+}$	9.00	$50^{+}$	9.86	$50^{+}$	9.61	$50^{+}$
None	0		11.5	_	9.0		32.2		21.0		7.0		6.0

 TABLE III

 Effects of the Substrate Type and the Nature and Concentration of the Reactive Dyes on the K/S and UPF Values

Atomic Absorption Spectrophotometer (GBC-Avanta Australia) as follows: 0.5 g of dried fabric samples was dissolved in 10 mL of 72%  $H_2SO_4$  at 3°C; then, 0.5 mL of this solution was taken and diluted up to 25 mL with a buffer solution (0.06M Na<sub>2</sub>HPO<sub>4</sub> and 0.02M NaOH) before analysis.

The reduction of the bacterial count (RBC) of the dyed and dyed/post-treated fabric samples against Gram-positive bacteria (*S. aureus*) and Gram-negative bacteria (*E. coli*) was determined quantitatively with the AATCC test method 100-1999.

Durability to washing was evaluated according to AATCC method 124.

#### **RESULTS AND DISCUSSION**

With a view toward conferring particular functions, such as anti-ultraviolet and antibacterial abilities on cotton knits dyed with anionic dyes, that is, reactive and direct dyes, to cope with the urgent needs of customers for effective protection and cutting-edge cotton clothing widely useable for various inner and outer garments, an attempt was made to examine the effect of the post-treatment of anionic cotton dyeings with zirconium oxychloride salt solution on the enhancement of their anti-ultraviolet and antibacterial properties without adverse effects on their dyeing properties. The results obtained along with their appropriate discussion follow.

# Effect of the type of substrate and dye nature and concentration

As far as the changes in the K/S and UPF values of the dyed substrates as a function of the type of substrate, chemical pretreatment (i.e., scouring or scouring/half-bleaching), nature of the dyestuff (i.e., reactive or direct), and depth of shade (0–3% owf), Tables III and IV reveal the following:

- 1. The UPF value of the undyed pretreated substrates followed a decreasing order, Interlock > Pique  $\approx$  Parasola, regardless of the pretreatment step. This reflected the differences among the used substrates in fabric structure and construction, weight, thickness, porosity, and ability to block the UV transmission and/or to absorb the harmful UV radiation.<sup>18</sup>
- 2. The scoured fabric samples showed a darker depth of shade along with better UPF values, which may have been due to the presence of natural coloring matters, which acted as UV absorbers.<sup>6,18</sup>
- 3. Increasing the dye concentration (from 0 to 3% owf) resulted in a remarkable improvement in the *K*/*S* values of the obtained dyeing as a direct consequence of the greater availability and accessibility of dye molecules in the vicinity of the cellulose active sites, —OH group; this enhanced the extent of dye fixation, regardless of the used dyestuff and the substrate.

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	Par	asol			Inter	rlock							
	alf- ched Scoured		ured		alf- ched	Scoured		Half- bleached		Scoured		Shade	
UPF	K/S	UPF	K/S UPF K/S		UPF K/S		UPF	UPF K/S		K/S	(% owf)	Direct dye	
50	5.00	50	5.50	$50^{+}$	4.45	$50^{+}$	5.05	$50^{+}$	4.62	$50^{+}$	5.27	0.5	Solophenyl
$50^{+}$	8.06	$50^{+}$	8.43	$50^{+}$	7.08	$50^{+}$	7.40	$50^{+}$	7.50	$50^{+}$	8.09	1.0	Boraleaux
$50^{+}$	17.23	$50^{+}$	17.70	$50^{+}$	15.96	$50^{+}$	16.13	$50^{+}$	16.85	$50^{+}$	17.35	3.0	Red 3BLE
30	7.37	40	7.80	$50^{+}$	6.59	$50^{+}$	7.09	38	7.04	48	7.54	0.5	Solophenyl
50	10.86	$50^{+}$	11.48	$50^{+}$	9.73	$50^{+}$	10.23	$50^{+}$	10.38	$50^{+}$	11.04	1.0	Yellow AGL
$50^{+}$	19.45	$50^{+}$	19.94	$50^{+}$	16.36	$50^{+}$	16.74	$50^{+}$	18.24	$50^{+}$	18.69	3.0	
0.6		7.0		21.0		32.2		9.0		11.5		0.0	None

 TABLE IV

 Effect of the Substrate Type and the Nature and Concentration of the Direct Dyes on the K/S and UPF Values

- 4. The extent of dye fixation, expressed as *K/S* values, was determined by the nature of the used dye, that is, the molecular size, chemical structure, functionality, substantivity/exhaustion/fixation profile, mode of interaction (via covalent and/or physical bonds), stability to hydrohysis,<sup>19,20</sup> and type of substrate (i.e., Parasol > Pique > Interlock); this reflected the differences among this substrates in the extent of penetration and diffusion of the dye molecules within their structures and the availability and accessibility of their hydroxyl groups.
- 5. Dyeing of the aforementioned substrates with the nominated reactive (Table III) and direct (Table IV) dyes brought about dramatic improvements in the UPF values of the obtained dyeings, regardless of the used dye; this reflected the greater ability of the dyed substrates to absorb harmful UV radiation, which thereby led to substantial improvements in their UV protection properties.<sup>18</sup>
- 6. The degree of UV protection was governed by the kind of dye, nature of substrate, and pre-treatment regime, especially at lower depths of shade (0.5–1% owf).

## Post-treatment with zirconium oxychloride

With regard to the changes in the K/S and UPF values as a function of post-treatment with the zirconium oxychloride salt solution (50 mmol/L), Table V shows the following:

- 1. The K/S and UPF values and the zirconium content of the dyed/post-treated fabric samples were higher than those of the untreated sample.
- 2. The extent of variation was governed by the fabric structure and its ability to pick up and interact with the dye in addition to the extent of take-up and absorption of the zirconium ions by the used reactive and direct dyes in the knitted substrate.
- 3. The enhancement in both the K/S and UPF values by post-treatment with the zirconium oxychloride salt solution was a result of the formation of a complex salt between the dye functional and solubilizing groups and zirconium ions,<sup>21</sup> along with the ability of the cellulose structure itself to take up and retain these ions, and the positive roles of the formed metal chelates in darkening the shade without

TABLE V

Effect of the Post-Treatment with the Zirconium Salt on the K/S and UPF Values of the Half-Beached Substrate

		Cibacr	on Blue	FNR (1%owf)			Solophenyl Turquoise RBLE (1%owf)									
	Dye	ed		Post-tro with zirco	Dye	ed		Post-treated with zirconium salt								
Half- bleached substrate	Zirconium content (mmol/100 g		Zirconium content (mmol/100 g of sample) K/S UPF			Zirconium content (mmol/100 g of sample)	K/S	UPF	Zirconium content (mmol/100 g of sample) K/S UP.							
Pique Interlock Parasail	0.0 0.0 0.0	6.95 6.70 7.19	$48 \\ 50^+ \\ 40$	4.60 4.45 4.75	7.28 6.95 7.50	$50^+ \\ 50^+ \\ 50^+ \\ 50^+$	0.0 0.0 0.0	3.58 3.30 3.86	$42 \\ 50^+ \\ 35$	3.60 3.42 3.72	3.77 3.48 4.09	$50^+ \\ 50^+ \\ 50^+ \\ 50^+$				

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			Fast	ness I	Proper	rties o	f the	Untr	eate	d and	Treat	ed Co	tton I	Dyei	ngs					
	Cibacron Blue FNR (1%owf)							Solophenyl Turquoise RBLE (1%owf)												
	Dyed				Post-treated			Dyed					Post-treated							
Half-bleached		W	/F	R	F		I	VF		RF		W	/F		RF		V	VF	R	F
substrate	K/S	St	Alt	D	W	K/S	St	Alt	D	W	K/S	St	Alt	D	W	K/S	St	Alt	D	W
Pique Interlock Parasail	6.95 6.70 7.19	5 4–5 5	5 4–5 5	4–5 4–5 5	4 4 4–5	7.28 6.95 7.50	5 5 5	5 5 5	5 5 5	4–5 4–5 5	3.58 3.30 3.86	3–4 3–4 3–4	3–4 3–4 3–4	$\begin{array}{c} 4\\ 4\\ 4\end{array}$	3–4 3–4 3–4	3.77 3.48 4.09	$\begin{array}{c} 4\\ 4\\ 4\end{array}$	4 4 4	4–5 4–5 4–5	$\begin{array}{c} 4\\ 4\\ 4\end{array}$

TABLE VI astness Properties of the Untreated and Treated Cotton Dyeings

Alt = alteration; D = dry; RF = rubbing fastness; St = staining on cotton; W = wet; WF = wasting fastness.

adversely affecting the hue and in upgrading the UV protection class by acting as UV absorbers.<sup>6,8,18</sup>

4. The kinds of dyes, that is, their chemical structures, their mode of interaction, and extent of fixation, and the number and presence of groups, such as  $-SO_3H$  and -OH, in the appropriate orientation and in a favorable position, governed both the extent of fixation and the ability to form a stable chelates with the zirconium metal ions and certainly affected the aforementioned dyeing and protection properties.

#### **Fastness properties**

Table VI shows the variation in the washing and rubbing fastness properties of the obtained dyeings

subjected to post-treatment with the zirconium oxychloride salt solution. The following is clear:

- 1. The K/S values and the evaluated fastness properties were governed by the nature of the used dye, that is, Reactive > Direct; the dyeing regime, that is, Post-treated > Untreated; and the fabric structure, that is, Parsol > Pique > Interlock.
- 2. Post-treatment with the zirconium oxychloride salt solution resulted in an improvement in the fastness properties, especially for fabrics dyed with the direct dye.
- 3. The enhancement in the fastness properties was a direct consequence of the improvement of the extent of dye fixation<sup>20</sup> and entrapment.
- 4. The slightly lower ratings of the wet rubbing fastness properties of the obtained dyeings, untreated or post-treated with zirconium

	Half-bleached			Gram-pe (S. aut		Gram-negative (E. coli		
Dye (1% owf)	substrate	Post-treatment	K/S	Count/mL	RBC (%)	Count/mL	RBC (%)	
Cibacron Blue FN-R	Pique	Without (dyed only)	6.95	$11 \times 10^{6}$	93.5	$15 \times 10^{6}$	90.0	
		With	7.28	$15 \times 10^{6}$	96.6	$12 \times 10^{6}$	92.9	
	Interlock	Without (dyed only)	6.70	$2 \times 10^7$	86.6	$25 \times 10^6$	83.3	
		With	6.95	$15 \times 10^{6}$	90.0	$2 \times 10^7$	88.2	
	Parasol	Without (dyed only)	7.19	$8 \times 10^{6}$	95.2	$11 \times 10^{6}$	93.5	
		With	7.50	$5 \times 10^5$	99.6	$8 \times 10^{6}$	95.2	
Solophenyl Turquoise RBLE	Pique	Without (dyed only)	3.58	$25 \times 10^6$	83.3	$3 \times 10^7$	82.3	
*		With	3.77	$9 \times 10^{6}$	94.0	$14 \times 10^{6}$	91.7	
	Interlock	Without (dyed only)	3.30	$3 \times 10^7$	80.0	$35 \times 10^6$	79.4	
		With	3.48	$15 \times 10^{6}$	90.0	$2 \times 10^7$	86.6	
	Parasol	Without (dyed only)	3.86	$2 \times 10^7$	88.2	$25 \times 10^6$	85.2	
		With	4.09	$4 \times 10^{6}$	97.3	$8 \times 10^{6}$	95.2	

 TABLE VII

 Antibacterial Properties of the Dyed and Dyed/Treated Fabric Samples

The post-treatment was performed with the zirconium salt (50 mmol/L).

TABLE VIII
Effects of the Washing Cycles on the Zirconium Contents and K/S, UPF, and RBC Values of the Obtained Dyeings

		Cibacror	n Blue FN	R (1% ov	vf)	So	ise			
		Dyec	Post-treated			ved	Post-t	reated		
		Washing o	cycles	Washing cycles		Washing cycles		Washing cycles		
Property	1	15	1	15	1	15	1	15		
Zirconium content (mmol/100 g K/S UPF	7.19 40	4.86 30	$4.75 \\ 7.50 \\ 50^+$	$3.30 \\ 5.25 \\ 50^+$	3.86 35	2.02 22	3.72 4.09 50 <sup>+</sup>	1.85 2.64 42	—	
Antibacterial Gram negative [RBC (%)]	[RBC (%)] 87.6	95.2 92.2	90.5 91.8	99.6 85.2	95.5 81.3	88.2 93.3	84.5 90.1	97.3	92.0	

The substrate was half-bleached parasol.

oxychloride salt, relative to the dry fastness properties rating may have been related to the partial removal of the unfixed/loose dye molecules by wetting.

## Antibacterial activity

Table VII shows the antibacterial activity (RBC %) of both the dyed and dyed/post-treated fabric samples. For a given set of dyeing and post-treatment conditions, the following was clear:

- 1. The *K*/*S* of the treated fabric samples was governed by the nature of the dye, the dyeing regime, and the kind of anionic dye.
- 2. Post-treatment with the zirconium salt brought about a noticeable improvement in the antibacterial properties, regardless of the substrate and dyestuff used.
- 3. The extent of improvement in the antibacterial activity was determined by the chemical structure of the dye; the extent of dyeing, expressed as the K/S value; and the capacity/ability of the dyed substrate to take up, absorb, chelate, retain, and bind the zirconium ions onto and/ or within the structure.
- 4. The higher the K/S value was, the higher the extent of dye fixation was. That is, there were more reactive groups, such as sulfonate and hydroxyl; this, thereby bridged the positively charged zirconium ions to the cellulosic fiber.
- 5. The improvement in RBC % of the dyed fabric samples by post-treatment with the zirconium salt was a direct consequence of the combination of the zirconium metal ions with the cellular protein-thiol groups; this, thereby, inactivated and killed them.<sup>11</sup>
- 6. The antibacterial activity against Gram-positive bacteria was better than that against Gram-negative bacteria, regardless of the substrate used,

dyestuff, or dyeing regime, which reflected the lower sensitivity of the Gram-negative bacteria to biocides because of their outer membrane.<sup>22</sup>

7. The biological activity and the ability of the anionic dyes to attack microorganisms could not be ruled out,<sup>11,22</sup> that is, without posttreatment.

## Washing durability

For a given set of dyeing, postmordanting, and washing conditions, the data in Table VIII signify the following:

- Increasing the number of washing cycles up to 15 resulted in a decrease in the evaluated properties, and the extent of the decrease was determined by the nature of the anionic dye used, that is, Direct dyeings > Reactive dyeings, and the dyeing regime, that is, Dyeing without subsequent salt treatment > Dyeing followed by zirconium salt after treatment.
- 2. Fifteen repeated laundering cycles of the dyed/ post-treated fabric samples had no significant effect on either the anti-UV radiation. expressed as UPF values, or the antibacterial activity against the Gram-positive and Gramnegative bacteria under investigation, expressed as RBC%. This reflected the positive role of the chelated zirconium metal ions in enhancing the durability of the obtained dyeings to washing and in maintaining their protection properties against harmful UV radiation and microorganisms at high levels.
- 3. The decrease in the zirconium content, which, in turn, resulted in a slight decrease in both the UV protection and the antibacterial activity, was a direct consequence of the partial disruption of the ionic bridges between the dye anionic groups and the positively charged

zirconium ions, so it could dissociate during laundering, which thus minimized the extent of UV absorption and impeded the antibacterial durability.

#### CONCLUSIONS

A new approach was carried out to functionalize anionic cotton dyeings, through the use of reactive groups of direct and reactive dyes, such as sulfonate dyes, hydroxyl dyes that served as auxochromes as linkers for fixing and attaching the positively charged zirconium ions to the cellulosic fibers.

Post-treatment of the obtained anionic dyeings with the zirconium oxychloride salt solution resulted in

- There was a remarkable improvement in both the UV protecting properties and the antibacterial activity against Gram-negative and Grampositive bacteria without adverse effects on the visual color of the obtained direct and anionic dyeings.
- The fastness properties of the obtained dyeings, especially the direct dyeings, were enhanced.
- The enhancement and upgrading of the imparted properties were governed by the fabric structure, pretreatment steps, and nature of the dye functionality, its mode of interaction, and subsequent degree of fixation.
- Post-treatment with zirconium ions was an easy, very effective, and promising method for conferring anti-UV and anti-microorganism properties with laundering durability.

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