# **UV-Protecting and Antibacterial Finishing of Cotton Knits**

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ABSTRACT: This article deals with enhancing the UVprotecting properties as well as the antibacterial activity of knitted cotton fabrics against two kinds of bacteria: grampositive bacteria (G +ve), i.e., Staphylococcus aureus (S. aureus), and gram-negative bacteria (G -ve), i.e., Escherichia coli (E. coli). Results showed that the extent of improvement in the UPF values are determined by: the fabric structure, i.e., Interlock > Pique > Parasol, pretreatment history, i.e., gray > scoured > bleached, type of softening agent, incorporation of the UV-absorber in the softening bath as well as sequence of addition, in addition to the nature of the deposited metal-oxide, i.e.,  $Cu > Zr > Zn \gg$ Al  $\approx$  none. On the other hand, the antibacterial activities of the treated substrates against G +ve and G -ve bacteria are outstandingly improved by using the proper: fabric structure, i.e., Parasol > Interlock > Pique, state of the

#### **INTRODUCTION**

Extensive efforts have been made to produce textile materials and clothing, based on natural fibres such as cotton, of high quality, high functional performance along with high value added taking in consideration technical, economical, and ecological aspects.<sup>1–3</sup> Demanding and sophisticated consumers as well as fashion designers are always looking for new finish effects, e.g., protective finishes, wellness finishes, self-cleaning finish, soft-hand finishes,....etc.<sup>1–9</sup>

UV-radiation is one of the major causes of degradation of textile materials because of photo oxidation. On the other hand, UVB-radiation, 280–315 nm, can penetrate into the top layer of the skin causing a range of effects from simple tanning to highly malignant skin cancers, if unprotected. Ultraviolet protection factor (UPF) is determined by the nature of the textile fibres, their chemical structure, fabric construction, presence of UV-absorbers, coloring, and/ or finishing agents. The use of UV-protecting fabrics, avoiding sunlight at its maximum as well as reducing the UV-radiation exposure can provide excellent protection against the harmful effects of sunlight.<sup>4,5</sup> untreated substrate, i.e., bleached > gray, finishing additives and regime, i.e., soft finishing (using polysiloxame softener—Adasil<sup>®</sup> SM) and UV-protecting (using UV-absorber, Tinofast<sup>®</sup> CEL) in one step > Tinofast<sup>®</sup> CEL-finish > Adasil<sup>®</sup> SM-finish > full-bleaching, as well as deposited metal oxide, i.e., Zn > Cu > Zr > Al > none. Combined soft-finishing and UV-cutting as well as *in* situ deposition of proper metal oxides, onto and/or within the knitted substrates, options exhibited both an excellent UV-protection and prominent antibacterial activities. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3589–3596, 2009

**Key words:** cotton knits; chemical modification; UVabsorber; metal oxides; softener; UV-protection; antibacterial

On the other hand, cellulose-based textiles are carriers of micro-organisms and more susceptible to microbial attack than man-made ones, as a direct consequence of their porous structure, hydrophilic nature along with their ability to retain water, oxygen, and nutrients, thereby leading to bacterial growth, body odor, and loss of their performance properties. Adversely affecting the vitality of microorganisms is generally referred to as antimicrobial. Antimicrobial functions can either inhibit the growth of micro-organisms without much destruction, i.e., biostats, or significant destruction of microbes, i.e., biocides. Antimicrobial chemicals can either work by controlled release mechanisms, or which remain fixed to textile substrates. Antimicrobial finishes add value to the textile products for both the producer as well as the human hygiene.<sup>1,2,6,7,10</sup>

The present study is concerned mainly with the enhancement of UV-protection and anti-microbial properties of knitted cotton fabrics to cope with the increasing needs for protection against solar UVradiation as well as micro-organisms.

#### **EXPERIMENTAL**

#### Materials

Mill-scoured and bleached knitted cotton fabrics (pique, 205 g/m<sup>2</sup>; interlock, 232 g/m<sup>2</sup>; and parasol,

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158 g/m<sup>2</sup>), used in underwear, T-shirts, and Poloshirts were taken for the study.

Three commercial grad softeners namely Cellolube<sup>®</sup> THS (a nonionic softener based on fatty acid condensation product-Sybron/Tanatex), Cellolube<sup>®</sup> CRS (nonionic/ cationic softener based on fatty acid condensate/microemulsion of aminofunctional of polysiloxane, Sybron/Tanatex), and Adasil<sup>®</sup> SM (a nonionic modified polysiloxane, Cognos<sup>®</sup>-Japan) as well as Ciba<sup>®</sup> Tinofast<sup>®</sup> CEL (reactive UV-absorber based on an oxalanilide-Ciba) were used.

Other chemicals used: sodium hydroxide (NaOH), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 35%), zirconiumoxy chloride (ZrOCl<sub>2</sub> · 8H<sub>2</sub>O), zinc chloride (Zn Cl<sub>2</sub>), copper chloride (Cu Cl<sub>2</sub> · 2H<sub>2</sub>O), and aluminum chloride (AL Cl<sub>3</sub> · 6H<sub>2</sub>O) were of laboratory grade.

# Methods

#### Soft finish

Soft finish was performed by immersing the knitted fabrics samples into a 3% (owf) aqueous solution of the softening agent, using a sample dyeing machine, at: pH 5 (using acetic acid), LR 20/1 (w/v) at 50°C for 20 min, followed by air drying.

# Tinofast<sup>®</sup> CEL application

Application was carried out, using a sample dyeing machine, at: a LR 20/1 (w/v),  $50^{\circ}$ C for 20 min in the presence or absence of the UV-absorber 0–3% (owf) followed by washing and air drying.

# One step soft finishing/UV-Protecting

Simultaneous finishing of the knitted fabric samples were performed in aqueous media using a solution containing 1–3% (owf) Tinofast<sup>®</sup> CEL and 1% (owf) of the softening agent, maintaining of fabric-to-liquor ratio (LR) of 20/1 (w/v) for 30 min in a sample dyeing machine beakers at 50°C. The pH of the aqueous solutions was adjusted to 5 using acetic acid. Thereafter, the treated fabric samples were air dried.

#### In situ deposition of metal oxides

Metal oxides deposition was performed by padding the knitted fabric samples in aqueous solution of metal salts (50, 100, 150 mmol/L), to a wet pick up of 80% followed by padding twice in the oxidizing bath [4 g/L NaOH + 5 mL H<sub>2</sub>O<sub>2</sub> (35%)], and wet batching for 30 min at 25°C. Treated samples were then thoroughly washed with running water, rinsed with distilled water, and dried at 100°C for 3 min. Fabric evaluation

Drop absorbency time (AT): AT of the treated fabric samples was determined according to AATCC Test Method 79–1992.

The whiteness index (WI): WI was measured using a Datacolor Ultra scan PRO E 313, D65/10 made in USA.

Surface roughness (SR): SR was measured according to JIS 94 standard, using surface roughness measuring instrument, SE 1700α made in Japan.

Air permeability (AP): AP was measured according to ASTM D737, by Toyoseik<sup>®</sup> Tester, made in Japan.

Bursting strength (BS): BS was measured according to ASTM D3786-87 by the Mullen<sup>®</sup> Tester, made in USA.

The oily stain release rating (OSR): OSR was assessed according to AATCC Test Method 130–1974.

Fabric thickness (FT): FT was assessed according to ASTM D1777-96 using a dial thickness Gouge H (Teclcock<sup>®</sup>-Japan).

UV-protection factor (UPF): 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, and excellent protection if their UPF values range from 15 to 24, 25 to 39, and above 40, respectively. In no event was a fabric assigned a UPF rating greater than 50.<sup>5,11</sup>

The metal content of the treated fabric samples: The metal content expressed as mmol/100 gm fabric sample, was quantitatively determined by using flame atomic absorption spectrophotometer, GBC-Avanta Australia, as follow: 0.5 g from dried fabric samples was dissolved in 10 mL of 72% H<sub>2</sub>SO<sub>4</sub> at 3°C, followed by taking 0.5 mL of this solution and diluting up to 25 mL using buffer solution (0.06*M* Na<sub>2</sub>HPO<sub>4</sub> + 0.02*M* NaOH) before analysis.

Antibacterial activity: Antibacterial activity against Gram-positive bacteria (*S. aureus*) and Gram-negative bacteria (*E. coli*) was tested quantitatively by AATCC Test Method 100–1999.

The durability: The durability to wash was determined according to AATCC method 124.

The obtained results of the aforementioned analysis and test methods are the average of triplicate tests.

# **RESULTS AND DISCUSSION**

Since the main task of the present work is to searching for the proper treatment formulations and conditions for upgrading and enhancing the UVprotective and antibacterial functional properties of bleached knitted cotton fabrics for producing textile articles with higher protection capacity, a wide range of factors have been examined. Results obtained along with their appropriate discussion follow.

Knitted fabric	Count Ne	Thickness (mm)	Weight (g/m <sup>2</sup> )	AT (s)	AP $[cm^3/(cm^2 s)]$	BS (kg/cm <sup>2</sup> )	UPF rating
Pique							
Ġray	30/1	0.663	187.7	>120	218	7.68	12.8
Scour	30/1	0.700	198.2	3	107.72	7.08	9.2
Full bleach	30/1	0.710	205	<1	55.25	6.48	6.00
Interlock							
Gray	30/1	0.755	192.6	>120	137.7	8.48	44.4
Scour	30/1	0.826	228.3	5	82.94	7.88	32.2
Full bleach	30/1	0.838	232.4	<1	45.18	6.98	12.0
Parasol							
Gray	30/1	0.502	125.9	>120	238.5	7.20	7.8
Scour	30/1	0.697	152.9	2	119.6	6.45	7.0
Full bleach	30/1	0.703	158.3	<1	66.3	5.83	4.0

TABLE I Effect of Fabric Parameters on Some Physico-Mechanical and UV-Protective Properties

AT, absorbency time; AP, air permeability; BS, bursting strength; UPF, ultraviolet protection factor

# **UV-Protection**

#### Fabric parameters

The physico-mechanical and UV-protective properties, UPF, of the used knitted substrates are listed in Table I. It is clear that: (i) the thickness, weight, bursting strength as well as the UPF values are determined by the natural of the knitted substrate and follow the decreasing order: Interlock > Pique > Parasol, (ii) contrarily, the air permeability values follow the increasing order: Parasol > Pique > Interlock, (iii) pretreatment, i.e., scouring and bleaching, of the gray substrates results in an increase in their thickness and weight, a sharp decrease in wetting time as well as in air permeability along with a gradual decrease in bursting strength and UPF values, regardless of the used substrate, (iv) the enhancement in fabric thickness and weight is determined by the extent of shrinkage and the subsequent change in fabric density and thickness during the scouring and full bleaching steps, (v) the remarkable improvement in fabric hydrophilicity along with a decrease in UPF values can be discussed in terms of better removability of noncellulosic and hydrophobic impurities along with other natural coloring matters, which act as UVabsorbers during scouring and bleaching, (vi) the decrease in bursting strength reflects the chemical damage of the pretreated substrates along with removal of their natural adhesives, and (vii) the outstanding UV-protective properties of interlock class, especially the gray one, reflects its higher ability to absorb and/or reflect UV-radiation thereby offering better protection capacity.<sup>4,5,12,13</sup>

# Softener type

Physico-mechanical and UV-protective properties of treated and untreated substrates as a function of softener type are shown in Table II. For a given set of softening conditions, it is clear that: (i) incorporation of the softening agent in the finishing bath has practically no or slight negative effects on fabric wettability or a slight positive effect on UPF rating, along with an improvement in softness and a reduction in OSR values, regardless of the used substrate and the type of softener, (ii) the decrease or the increase in the aforementioned properties indicates possible thin film formation, of the added softener, onto and/or within the substrate, (iii) the extent of variation in this properties is governed by the fabric nature,<sup>4,14</sup> e.g., construction, thickness, porosity, surface area, and geometry, hydrophilicity,...etc., as well as the type of softening agent, e.g., chemical composition, location, and extent of distribution, functionality, and mode of interaction (physically and/or chemically), hydrophilic/hydrophobic nature of the formed film, ability to pick-up and retain the oily stain, extent of modification, and lubrication of the fabric structure,....etc.<sup>12,15,16</sup>

# One bath two-stage: UV-Protecting followed by soft finishing

To evaluate the potential effectiveness of incorporating Ciba Tinofast<sup>®</sup> CEL, as a UV-absorber, in softening formulation, an approach was carried out to show the ability to run single bath two-stage; i.e., UV-Protecting followed by subsequent addition of the nominated softener to the same bath (Fig. 1).

For a given finishing sequence, data in Table III show that: (i) treatment with Tinofast<sup>®</sup> CEL alone has practically no or slight negative or positive effects on the evaluated properties along with an outstanding improvement in UV-protecting properties, expressed as UPF rating, regardless of the used substrate, i.e., treated substrate (very good, excellent)  $\gg$  control  $\approx$  untreated (not good), (ii) the extent of improvement is determined by the nature of the substrate as discussed before, and can be ranked as follow: Interlock [UPF (151.17-grade excellent)] > pique [UPF (41.8-grade (very good)]  $\geq$ 

8.6

9.8

11.5

12.0

13.6

15.017.5

19.6

4.0

5.0

6.5

8.0

9.9

Piqu

Interlock full-bleach

Parasol full-bleach

Effect of Softe	ner Type on Some Phy	sico-Mechanica		ective Properties	of Treated Su	bstrates
Fabric	Softener type	AT (s)	WI	SR (µm)	OSR	UPF rating
ue full-beach	Untreated Control	<1	64.41 64.04	23.49 21.88	4–5 4–5	6.0 7 1

62.72

63.86

63.19

72.75

71.10

69.94

71.00

70.82

60.36

60.00

58.25

59.85

59.62

18.82

21.00

19.36

18.09

17.22

14.43

16.90

13.39

22.21

18.22

15.90

17.55

16.04

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1

1

TABLE II

Softening Bath: Softener (3% owf) pH (5); LR (1/20 w/v); at 50°C for 20 min.

Softeners: Cellolube® THS (nonionic), Cellolube® CRS (nonionic/cationic), Adasil® SM (nonionic).

Untreated, full bleached fabric; Control, treated in absence of softener.

CRS

THS

SM

CRS

THS

SM

CRS

THS

SM

Untreated

Untreated

Control

Control

AT, absorbency time; WI, whiteness index; SR, surface roughness; OSR, oily stain release.

parasol [UPF (35.6-grade very good)],<sup>5,11,12</sup> (iii) the remarkable change in UPF rating as well as in protection category can be discussed in terms of higher extent of UV-absorption and cutting effect of the used UV-absorber, (iv) incorporation of the softening agent in the UV-absorber bath, one bath-two stages, brings about no or slight changes in AT, WI, and OSR values along with an improvement in SR values, regardless of the used softening agents, (v) subsequent addition of the used softeners to the Tinofast<sup>®</sup> CEL bath results in no changes in UV-protecting category, as in case of Pique (41.8-31.9, very good) as well as in case of Interlock substrate (151.7– 128.5, i.e., > 50: excellent), or a decrease in extent of protection as in case of parasol substrate (35.6–25.2, very good to good), depending on the nature of the used softener, i.e., its chemical structure, compatibility with the used UV-absorber, extent of location, distribution, and interaction, as well as its negative or positive impact on the location and function of the UV- absorber.

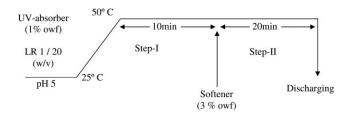
#### Combined soft finishing and UV-protecting

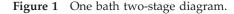
The impact of combined soft finishing and UV-protecting in one step on the UPF rating as well as the degree of protection against UV- $\beta$  is shown in Table IV. The obtained results brings into focus the following points: (i) the higher the UV-absorber dose, the more enhanced would be the extent and degree of protection, regardless of the history of the used substrates, and (ii) the extent of improvement is governed by the type of substrate, i.e., Interlock > Pique > Parasol, as well as the pretreatment step as mentioned before.

On the basis of the Tables III and IV, UPF values as well as degree of protection especially for full bleached substrates and keeping the UV-absorber dose fixed at 1% (owf), it is possible to state that the sequence of addition of the softening agent to the UV-absorber bath has practically no significant effect except in case of using the parasol substrate the UPF rating follows the descending order one step-two stages (UPF 30.3, very good ) > simultaneous process (UPF 18.9, good).

# Effect of in situ deposition of metal oxides

To evaluate the potential effectiveness of *in* situ deposition of certain metal oxides onto and/or within the treated substrate, as a new option for enhancing the UPF values of cotton knits, five metal oxides were screened for their ability to upgrade the inherent UV-protection against the harmful UV-radiation. The treatment regime comprises the following steps: salt treatment followed by alkali treatment (to form metal hydroxide)/H<sub>2</sub>O<sub>2</sub>—oxidation to form the metal oxide within and/or onto the fabric structure. Results of Table V indicate that: (i) increasing the salt concentration in the padding bath results in a





Fabric	Treatment bath	AT (s)	WI	SR (µm)	O SR	UPF rating
Pique full-beach	Untreated	<1	64.41	23.49	4–5	6.0
1	Control	<1	64.04	21.88	4–5	7.1
	Tinofast <sup>®</sup> CEL	<1	63.74	21.43	4	41.8
	Tinofast <sup>®</sup> CEL $^{a}(\rightarrow)$ CRS	3	62.23	18.56	3–4	31.9
	Tinofast <sup>®</sup> CEL <sup>a</sup> ( $\rightarrow$ ) THS	<1	63.63	20.90	4	39.2
	Tinofast <sup>®</sup> CEL $^{a}(\rightarrow)$ SM	<1	62.99	19.19	4	36.3
Interlock full-bleach	Untreated	<1	72.75	18.09	4–5	12.0
	Control	<1	71.10	17.22	4–5	13.6
	Tinofast <sup>®</sup> CEL	<1	71.00	17.66	4	131.7
	Tinofast <sup>®</sup> CEL <sup>a</sup> ( $\rightarrow$ )CRS	3	69.74	14.24	3–4	100.8
	Tinofast <sup>®</sup> CEL $^{a}(\rightarrow)$ THS	<1	70.82	17.02	4	115.5
	Tinofast <sup>®</sup> CEL <sup>a</sup> ( $\rightarrow$ ) SM	<1	70.69	13.25	4	105.70
Parasol full-bleach	Untreated	<1	60.36	22.21	4–5	4.04
	Control	<1	60.00	18.22	4–5	5.0
	Tinofast <sup>®</sup> CEL	<1	59.89	18.00	4	35.6
	Tinofast <sup>®</sup> CEL $^{a}(\rightarrow)$ CRS	2	58.01	16.00	3–4	25.2
	Tinofast <sup>®</sup> CEL <sup>a</sup> ( $\rightarrow$ ) THS	<1	59.70	17.41	4	30.3
	$Tinofast^{\circledast} CEL \ ^{a}(\to) \ SM$	<1	59.51	16.13	4	29.6

TABLE III Effect of Finishing Sequence, One Bath-two Steps, on Some Physico-Mechanical and UV-Protective Properties of Bleached Substrates

For explanation of abbreviation, see footnote to Table II.

<sup>a</sup> ( $\rightarrow$ ): Followed by softening (Fig. 1).

significant increase in the metal content, after the oxidation alkaline step, along with a slight decrease, as in case of Zr, Al, and Zn salts, or a noticeable reduction, as in case of Cu-salt, in the WI value of the treated substrate, (ii) the higher UPF values as well as the better sun-protection category are attributed to the presence of higher metal content compared with the untreated substrate, (iii) the extent of improvement in the UV-protecting properties is determined by the type of metal oxide and follows the descending order: Cu > Zr > Zn >> Al  $\approx$ None, and (iv) the variation in the UV-screening power of treated fabric samples in presence of the aforementioned metal oxides, reflects the differences among them in: molecular weight, content, particle size, surface area, location and extent of distribution, blocking property, and absorbing capacity.<sup>16,17</sup>

### Antibacterial activity

In this part, the effectiveness of peroxide bleaching, soft, and/or UV-protection finish as well as *in* situ deposition of certain metal oxides on the antibacterial properties of knitted substrates were evaluated.

# Finishing regime

Antibacterial activity, expressed as percent reduction in bacterial count (% RBC), towards *S. aureus* (G +ve) and *E. coli* (G –ve) of treated samples along with their UV-screening capacity, expressed as UPF rating and UV-protection grade, are shown in Table VI. The data so obtained signify that: (i) full bleaching of the pique substrate results in a remarkable reduction in both the G +ve and G –ve count

 TABLE IV

 Effect of Variation of the UV-Absorber Dose in the Softening Bath on UPF Rating and UV-Protection Category

		UPF								
Tinofast®		Pique			Interlock			Parasol		
CEL (% owf)	Scoured	Half- bleach	Full- bleach	Scoured	Half- bleach	Full- bleach	Scoured	Half- bleach	Full- bleach	
0 1 2	24.2 (G) 42.6 (Excell) 67.9 (Excell)	( )	9.8 (L) 30.2 (V.G) 45.1 (Excell)	76.4 (Excell) 181.9 (Excell) 220.8 (Excell)	110.0 (Excell)	95.5 (Excell)	· · · ·	· · ·	8.0 (L) 18.9 (G) 30.0 (V.G)	

Finishing bath [Cellolube<sup>®</sup> THS (3% owf), Tinofast<sup>®</sup> CEL (0–2% owf); pH 5; LR 1/20 (w/v); at 50°C for 20 min. Values in brackets represent the UV-protection category, i.e., L (little protection, <15); G (good, 15–24); V. G (very good, 25–39); and Excell (excellent >40).

Metal-salt	Metal conc (mmol/L)	Metal content (mmol/100 g sample)	WI	UPF rating	UV-protect. category
None	_	_	64.41	6.0	L
Zr-oxy chloride	50	4.7	64.20	30.2	V.G
,	100	11.0	63.66	37.0	V.G
	150	14.4	63.32	40.2	Exc
Al-chloride	50	3.6	64.01	10.2	L
	100	8.2	63.02	12.3	L
	150	11.6	62.53	15.8	G
Cu(II)-chloride	50	3.5	58.71	34.5	V.G
	100	6.8	57.30	40.8	Exc
	150	10.5	55.55	50.3	Exc
Zn-chloride	50	2.8	64.05	20.3	G
	100	5.0	63.30	26.7	V.G
	150	8.0	63.00	30.2	V.G

 TABLE V

 Effect of In Situ Deposition of Metal Oxides on UPF Rating and UV-Protection Category of Full Bleached Pique Substrate

L, little-protection; G, good-protection; V.G, very good-protection; Exc, excellent-protection.

compared with the gray one (from zero up to 80 and 70.5%, respectively), reflecting the disinfection effect of the remnant  $H_2O_2$  in the bleached substrate and its harmful effect to the cells of living micro-organisms through attacking the cell membrane followed by affecting the enzymes of the micro-organisms,<sup>10,18</sup> (ii) fabric structure have practically a positive effect on the reduction in bacterial count of the bleached substrates and follows the descending orders: Parasol > Interlock > Pique, regardless of the used bacteria (G +ve or G -ve), (iii) soft finishing of the bleached substrates with the modified polysilioxane softener brings about a significant reduction in both the G +ve and G -ve bacterial count, reflecting the ability of the used softener to modify the fabric surface via film formation or coating to be more hydrophobic thereby making the softened substrates unsusceptible to bacterial growth along with the possibility of disrupting the cell membrane through physical and ionic phenomena during the direct contact of bacteria with the functional groups of the softener film,<sup>18,19</sup> (iv) post-treatment of the bleached cotton knitted substrates with Tinofast® CEL is accompanied by a significant decrease in both the antibacterial activity as well as the UV-protecting properties, regardless of the used substrate, most probably because of the chemical composition of the Tinofast<sup>®</sup> CEL, which is a bireactive oxalic acid dianilide derivative,<sup>20</sup> and its functionality as a UVabsorber and as a bactericide agent, and the extent of protection against the G +ve and G -ve bacteria, as well as against the harmful UV-radiation is

TABLE VI Effect of Finishing Regime on both the Antibacterial Activity and UV-Protection of Treated Substrates

	Type of	G +Ve S. aureus		G –Ve E. coli		UPF	UV-protection
Treatment bath	substrate	Count/mL	RBC (%)	Count/mL	RBC (%)	rating	category
Gray	Pique	$15 \times 10^7$	0.0	$17 \times 10^7$	0.0	12.8	L
Full-bleached (control)	Pique	$3 \times 10^7$	80.0	$5 \times 10^7$	70.5	6.0	L
	Interlock	$25 \times 10^6$	83.0	$45 \times 10^{6}$	73.5	12.0	L
	Parasol	$3 \times 10^7$	84.0	$4 \times 10^7$	76.4	4.0	L
Adasil <sup>®</sup> SM (3% owf)	Pique	$14 \times 10^{6}$	90.6	$25 \times 10^6$	85.2	11.5	L
	Interlock	$15 \times 10^{6}$	91.0	$27 \times 10^{6}$	84.0	19.6	G
	Parasol	$11 \times 10^{6}$	92.6	$2 \times 10^7$	88.2	9.9	L
Tinofast <sup>®</sup> CEL (1% owf)	Pique	$1 \times 10^7$	92.5	$2 \times 10^7$	88.2	41.8	Exc
	Interlock	$8 \times 10^{6}$	94.6	$17 \times 10^{6}$	90.0	131.7	Exc
	Parasol	$6 \times 10^{6}$	96.0	$15 \times 10^{6}$	91.0	35.6	V. G
$Tinofast^{(\!R\!)} CEL + Adasil^{(\!R\!)} SM^a$	Pique	$7 \times 10^{6}$	92.8	$17 \times 10^{6}$	90.0	33.4	V. G
	Interlock	$1 \times 10^7$	95.0	$14 \times 10^{6}$	91.7	117.8	Exc
	Parasol	$6 \times 10^{6}$	96.2	$13 \times 10^{6}$	92.3	30.3	V. G

Finishing bath: Adasil<sup>®</sup> SM (3% owf), Tinofast<sup>®</sup> CEL (1% owf), pH (5), LR (1/20 w/v), at 50°C for 30 min. RBC (%), reduction in bacterial count percent; UPF, UV-protecting factor. <sup>a</sup> Combined soft finishing and UV-protecting in one step.

	Content of metals	G +Ve S. aut	reus	G –Ve E. coli		
Metal oxide	(mmol/100 g sample)	Count/mL	RBC (%)	Count/mL	RBC (%)	
None	0.0	$3 \times 10^7$	80.0	$5 \times 10^7$	70.5	
Zr-oxide	4.7 (4.2)	$8  imes 10^{6} \ (15  imes 10^{6}$ )	94.6 (91.0)	$15  imes 10^{6} \ (2  imes 10^{7} \ )$	91.0 (88.2)	
AL-oxide	3.6	$3 \times 10^7$	81.0	$4 \times 10^{7}$	76.4	
Cu-oxide	3.5 (3.0)	$25 \times 10^5 (8 \times 10^6)$	98.3 (94.6)	$7 \times 10^{6} (15 \times 10^{6})$	95.8 (91.0)	
Zn-oxide	2.8 (2.1)	$15 \times 10^5 (6 \times 10^6)$	99.0 (96.0)	$5 \times 10^6 (1 \times 10^7)$	97.0 (93.3)	

 TABLE VII

 The Impact of In Situ Deposition of Metal Oxides on the Antibacterial Properties of Full Bleached-Pique Substrate

Values in brackets represent durability to wash after 10 laundering cycles.

determined by the type of substrate and follow the descending orders: Parasol > Interlock > Pique, regardless of the bacteria type, and Interlock > Pique > Parasol, respectively, (v) the aforementioned treatments were found to be more effective against G +ve bacteria, e.g., *S. aureus*, than for G –ve bacteria, e.g., *E. coli*, reflecting the differences between the two types in: the cell wall structure as well as amenability to oxidation, destruction, disruption, and/or poisoning,<sup>19,21</sup> and (vi) the improvement in both the antibacterial properties as well as in UV-properties as a function of the finishing regime can be ranked descendingly as follows:

Combined finish  $\geq$  Tinofast<sup>®</sup> CEL-finish > Adasil<sup>®</sup> SM-finish > None (full bleached), regardless of the used type of a bacteria, and Tinofast<sup>®</sup> CEL-finish  $\geq$  combined finish  $\gg$  Adasil<sup>®</sup> SM-finish  $\approx$  None, respectively.

#### Antibacterial activities of deposited metal oxides

For a given treatment conditions, the data in Table VII signify that: (i) post-treatment of the full bleached substrate with the nominated metal salts solutions followed by alkaline-H<sub>2</sub>O<sub>2</sub> treatment results in *in* situ deposition of the corresponding metal oxides, which in turn have a positive impact on enhancing the antibacterial activity for the full bleached substrate, (ii) the extent of improvement in the % RBC of both the G +ve and the G -ve bacteria is determined by the type of deposited metal oxide and follows the descending order: Zn-oxide > Cu-oxide > Zr-oxide > Al-oxide > None, i.e., the higher the % RBC values, the higher the antibacterial activity of the treated fabric samples, (iii) the outstanding effect of the deposited heavy metal oxides, i.e., Zn, Cu, and Zr, reflecting their ability to react with cellular proteins thereby inactivating and killing them more effectively than Al-oxide,<sup>22</sup> (iv) the synergistic effect of: the combination of heavy metals with the protein-thiol group, the interaction of metal oxide with the moisture retained by the cellulose to generate  $H_2O_2$ , which is harmful to the cells of living micro-organisms, in addition to the ability of heavy

metals to absorb UV-light and its contribution to enhance the antibacterial activity,<sup>23,24</sup> reflects the high potentially and usefulness of them as antibacterial/UV-protecting agents, and (v) the durability of deposited metal oxides to severe washing (10 laundering cycles) most probably because of their fixation onto and/or within the cellulose structure through hydrogen bonding.<sup>23</sup>

#### CONCLUSIONS

The fabric structure of cotton knits has a positive impact on UV-protection and the extent of protection follows the decreasing order Interlock > Pique > Parasol, as well as preparation history, i.e., gray > scored > bleached.

Soft finishing of the used substrates has practically no significant improvement effect on UPF values.

Incorporation of the Tinofast<sup>®</sup> CEL in the softening bath significantly improves the UPF values and protection grades.

Furthermore, institue deposition of metal oxides, especially heavy metals, in and/or onto the bleached substrates results in a remarkable improvement in both the UPF values and UV-protection grade.

The extent of improvement in the so-mentioned properties is determined by the type of oxides, i.e.,  $Cu > Zr > Zn \gg Al \approx None$ .

Remarkable antibacterial activities of the treated substrates could be obtained by: full bleaching followed by combined soft-finishing and UV-protecting finish in one-step or deposition of heavy metal oxides onto and/or within the bleached substrates, and the extent of improvement can be ranked as follow: Zn > Cu > Zr > None.

Finally, both one-bath/one-step finishing process and in-stiue deposition of heavy metal oxides are very effective options in providing UV-protection as well as antibacterial activities to cotton knits.

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