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Plasma induced nano-finish for multifunctional properties on cotton fabric

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Atmospheric pressure dielectric barrier discharge plasma treatment for fabric surface activation to facilitate deposition of nano silicon oxide, and nano-titanium dioxide onto cotton fabric has been studied. It is aimed to study the possibility of engineering a multifunctional cotton fabric. The treated fabric is evaluated for ultraviolet protection factor (UPF), antimicrobial activity, and flame retardancy as a functional finish. Surface morphology (SEM), thermo-gravimetric analysis (TGA), and mechanical properties are also studied. Scanning electron microscopy shows deposition of nano particles onto the fabric. He-O_2 plasma pre-treatment improves the flame retardancy, UPF, antibacterial activity and thermal stability of the samples as compared to untreated samples. In order to improve the wash fastness of the finish, HMDSO plasma polymer is deposited on the surface of the finished fabric which acts as a barrier layer and imparts durable finish on cotton textiles.

Keywords: Antibacterial activity, Atmospheric pressure plasma, Cotton, Flame retardant, Plasma treatment, TiO_2/SiO_2 nano composite, UV protection

1 Introduction

Increasing concern over damage caused by exposure to microbes, chemicals, pesticides, UV light and pollutants in the last few years, has boosted the demand for protective garments. Clothing today is expected to be waterproof, flame resistant, self cleaning, insect repellent and antimicrobial to protect human beings from infection, UV light, chemical and biological agents[1].

Cellulose dominates the apparel industry with the king cotton taking the center stage. Cotton has some unique properties such as soft handle, breathable, strong, durable, and comfortable, making it ideal for apparel purpose. However, due to its glucose ring it is prone to microbial attack, and also catches flame easily. Therefore, multifunctional textiles could fulfill the requirement of ultraviolet protection, antimicrobial functionality and anti flammable textiles.

Plasma technologies can help in retaining inherent advantages of the substrates while enhancing material properties[2,3]. Plasma is partially ionised gas, which contains ions, electrons, and charged neutral particles. The active species produced in plasma carry high energy that causes etching or cleaning effect, which alters the characteristics of fibre surface. The treatment roughens the surface of the materials and is favourable to subsequent process to enhance the effectiveness[4-7]. Among various types of plasma treatments, atmospheric pressure plasma (APP) is widely used in the textile industry to modify the fabric surface in an environment friendly process that helps in reducing use of chemicals and energy[4,8,9]. On the other hand, plasma polymerization has shown tremendous potential for sustainable innovation and value creation in the area of textile processing operations including finishing[10]. The films produced by plasma polymerisation are usually insoluble, pinhole free, highly cross-linked and adhere well to substrates[11]. Therefore, attempt was made to deposit a barrier film of plasma polymer on the surface of finished fabric to improve the durability of finish.

In this study, the experimental data on plasma treatment for multifunctional finishing of cotton to impart UV protection, flame retardancy and antibacterial properties have been discussed. The changes in surface morphology and surface chemistry of the fabric samples due to plasma finishing are discussed in relation with their performance properties.

2 Materials and Methods

Commercially available RFD (ready for dyeing) 100% cotton fabric with warp and weft count 40Ne, GSM 132, EPI × PPI 144 × 72 and width 50cm was

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used for the experiments.TiO_2 and SiO_2 (15nm) nano particles were procured from Nanostructured and Amorphous Material (NonaAmor) Inc. Houston, USA. Hexamethyldisiloxane (HMDSO 99.5%, Sigma- Aldrich) was used as a monomer precursor for plasma polymerization. Helium + oxygen (99.9% purity) was used as plasma gases.

2.1 Plasma Treatment and Nano-particles Application

Atmospheric pressure plasma reactor Platex 600 (Grinp S.R.L., Torino, Italy) was used for the plasma treatment of cotton fabric. The detailed features of the plasma reactor are described elsewhere[12]. Fabric samples of about 50cm width were passed continuously between top and bottom electrodes, where dielectric barrier discharge (DBD) was generated from the mixture of He + O_2 gases. Plasma pre-activation of samples was carried out with 2500W power, 1min treatment time; helium and oxygen flow rate was kept at 5 and 0.5 litters/ min respectively. The plasma pre-activated samples were padded with finishing solution at 100% pick-up followed by drying and curing at 85°C for 5min and at 180°C for 2min respectively. Plasma polymer was deposited on the finished sample (Sample No. 3). Monomer flow rate 0.5 mL/min. power 3.5 kW, and polymer deposition time 1min, were maintained for polymer deposition.

In the current experiment, three different samples were prepared, and effect of plasma pre-activation and plasma polymerization on the functional properties was studied. The details of the experiments are given in Table 1.

2.2 Characterization Techniques

Ultraviolet protection factor (UPF) values of untreated and treated cotton samples were measured as per AU/NZS 4399-1996 standard with Labsphere UV-2000F ultraviolet transmittance analyzer. The instrument operates by measuring the diffuse transmittance of a fabric sample as a function of wavelength in the ultraviolet spectrum. The UPF measurements were carried out in the weave length range of 280-400nm. Protection was evaluated by good, very good and excellent when the values of UPF was 15 - 24, 25 - 39 and >40 respectively.

Table 1—Samples processing details

Specifications	Sample 1	Sample 2	Sample 3
Plasma preactivation	-	Yes	Yes
Tio_2/ SiO_2	1%	1%	1%
BTCA/ SHP	8%	8%	8%
HMDSO polymerization	-	-	Yes

Flame retardant properties of treated samples were measured in terms of limiting oxygen index (LOI) as per the ASTM 2863-08 with oxygen index tester from Fire Testing Technology LID. 45° inclined flammability was studied as per IS 11871B-04 test method using Govmark instrument USA. The test method was slightly modified, as samples were not ignited in 1s. Therefore, the flame application time was increased to 3 s, and burn time was measured for each sample.

Thermo-gravimetric analysis (TGA) was carried out using TGA instrument (SDT Q 600, USA). The thermal degradation was studied up to 700°C under nitrogen atmosphere at a heating rate of 10 °C/min, loss in weights of the samples were recorded against temperature from 30°C to 700°C.The quantitative measurement of the antibacterial activity of the untreated and treated cotton sample was evaluated as per the AATCC 100-04.

The topographical modification on the cotton sample after plasma treatment and after nano finishing was investigated by scanning electron microscopy (SEM) on JEOL SEM model JSM 5400 (Tokyo, Japan). The crease recovery angle (CRA) was measured as per IS 4681 using Shirly crease recovery tester. Fabric tensile strength was measured as per test method ASTM D- 5035-08 by ravel trip method. Mean of five specimens was considered. In addition, durability to washing of treated samples was evaluated by subjecting the samples to the repeated number of washing cycles as per AATCC 61 (2A-06).

3 Results and Discussion

3.1 Ultra Violet Protection

Ultraviolet protection factor measures the effectiveness of textile fabrics in protecting the human skin from harmful ultraviolet radiations. It is expressed as the ratio of extent of time required for the skin to show redness (erythema) with and without protection, under continuous exposure to solar radiation. Effect of plasma preactivation and plasma polymerization on UV protection has been studied. Figure 1 shows the UPF of the samples treated and subjected to washing cycles up to 20 washes.

It can be seen from Fig. 1 that the control sample is not capable to protect from the UV radiations. However, initially all the samples treated with TiO_2/SiO_2 show the UPF value of 50+, which can be considered as excellent protection against the

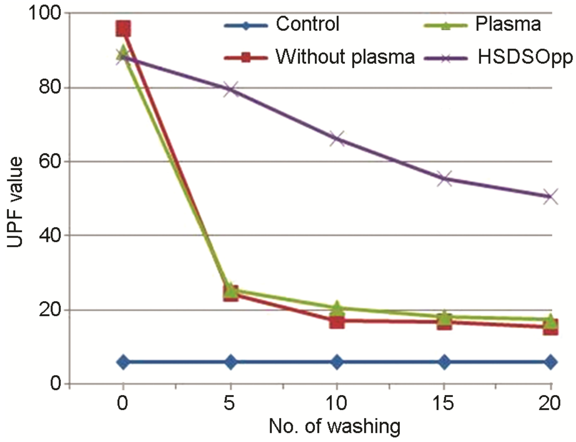

Fig. 1—Effect of washing on UPF of finished fabric

UV radiation. This increase in the UPF can be due to the natural attribute of TiO_2 for UV-absorption property, which can be explained by the solid band theory[13]. The samples were washed as per AATCC standard test method. The UPF of finished samples reduces significantly only after 5th wash and further reduces after every wash and finally shows only good protection after 20th wash (without plasma and with plasma treated samples). On the other hand, the sample treated with HMDSO plasma polymer (HMDSOpp) shows the excellent protection against UV radiations even after 20 washing cycles. This increase in durability may be attributed to deposition of plasma polymer which is insoluble in water[11]. Plasma polymer servers as a barrier to washing and hence the finish is not leached out.

3.2 Flame Retardancy

Cotton is a combustible textile that ignites and burns easily when subjected to external sources of ignition, while flame retardant systems are intended to delay or stop the combustion process. Flame retardant systems act either physically or chemically and can interfere with various processes involved in combustion[14]. Phosphorus-based flame retardant agents can be used as additives and are known to be active in the condensed and/or vapour phase[15]. In the present study, flame retardancy of treated fabric is evaluated by limiting oxygen index (LOI) and 45° inclined flammability measurements (Fig. 2 and Table 2).

Figure 2 shows the LOI values of different finished samples before and after 20 washes. The LOI values of samples treated with TiO_2/SiO_2 nano composite increase significantly. Moreover, a noticeable difference is observed in the LOI values of without plasma treated and with plasma treated samples. For

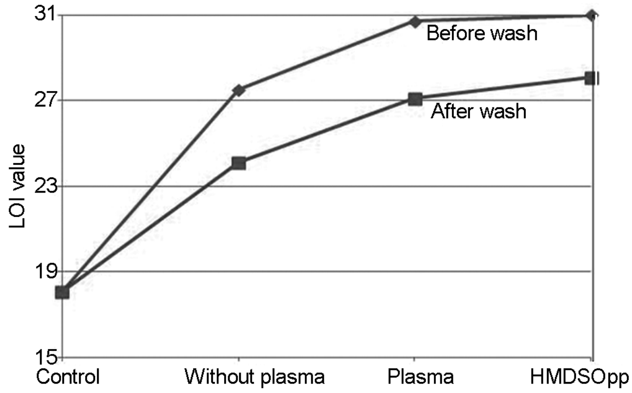

Fig. 2—Effect of washing on LOI values of the finished samples

Table 2—LOI and 45° flammability of finished samples

Sample	LOI	Flame application time , s	Burning time , s	Pass/fail
Control Cotton	18.1	2	3.5	Fail
Without plasma	27.5	3	24.2	Pass
Plasma	30.7	3	27.3	Pass
HMDSOpp	31	3	28.2	Pass

example, the control cotton shows the LOI value of 18.1 which is increased to 27.5 and further increased to 30.7 after plasma treatment. This may be attributed to the formation of reactive species on the surface of plasma treated samples or surface cleaning/etching effect of plasma treatment, which makes fibres more accessible for the diffusion of chemicals inside the fibres. Moreover, with use of HMDSOpp treatment the LOI value slightly improves.

Lam *et al*[15]. in their studies on the effect of plasma treatment and TiO_2 on the flame retardancy of cotton fabric report that the flame-retardancy improves by plasma pre-treatment and by the addition of metal oxide as a co-catalyst. They have also reported that both plasma pre-treatment and metal oxide co-catalyst added in the flame-retardant finishing improve the crosslinking process between FR and cotton fabric, minimizing the formation of free formaldehyde.

The ease of ignition and the relative ability to sustain combustion measure the flammability characteristics of a material. 45° flammability test was carried out according to the IS 11871B standard. Table 2 shows the correlation between 45° flammability and LOI.

As can be seen from Table 2 that the time required to burn specific length of fabric is drastically improved, and plasma treatment further improves the effectiveness of the finish. As the LOI values increase the burning time is also increased. Therefore, it may be inferred that LOI values and time required to burn specified length of the fabric are directly proportional. This increase in the LOI can be attributed to the presence of phosphorous and silicon compounds on the treated samples which act as a thermal barrier.

3.3 Thermo-gravimetric Analysis

TGA of the untreated cotton fabric and treated sample with plasma- SiO_2 were studied. The peak temperature, corresponding loss in weight, and the residue of untreated and treated samples are given in Table 3. These values indicate that the thermal stability of the treated fabric increases due to the increase in residue accompanied by a significant decrease in the corresponding weight loss. The plasma-SiO_2 treatment causes a significant change in thermal behaviour of cotton fabric. This change can be attributed to silicon dioxide as it significantly changes the thermal stability of cotton[16-19]. Silica acts as a physical barrier (thermal insulator), being able to protect cotton from heat and oxygen transfer and favouring the formation of a carbonaceous residue[20]. The increase in thermal stability of treated sample is also reflected by the enhanced flame retardancy of cotton fabric as shown by the results of LOI and 45° flammability.

3.4 Surface Morphology

The extent of deposition on the surface of finished cotton samples is studied by using SEM. Figure 3 shows typical SEM micrographs of samples treated with TiO_2/ SiO_2. Figure 3A shows that the micrograph of untreated cotton fibres is without any sign of deposition. SEM images of all finished cotton samples exhibit the deposition of nano material on the fibre surface. Furthermore, the fibrillar structure of the cotton is fully covered due to the deposition of the nano material and crosslinking agent on the surface. In addition, the samples treated with plasma show the higher deposition than that of the without plasma treatment. Moreover, the samples treated with HMDSOpp show the smooth coating on the surface. The deposition as seen in the SEM micrographs is responsible for conferring UV protective and flame retardant characteristics to the cotton sample.

Table 3—TGA data of finished samples

Sample	Peak temperature, °C	Weight loss % (at 700°C)	Residue, % (at 700°C)
Control cotton	368	93.45	6.55
Without plasma	337	73	27
Plasma	335	69.5	30.5
HMDSOpp	336.2	68.28	31.72

3.5 Antibacterial Properties

The quantitative AATCC Test Method 100 has been used to assess the antibacterial properties of the fabric against Gram-positive *staphylococcus aureus* and Gram-negative *klebsiella pneumonia* (Table 4). The results indicate that the treated sample with plasma and nano TiO_2/SiO_2 have an excellent antibacterial activity against both Gram-positive and Gram-negative bacteria. This improvement can be attributed to plasma treatment as it cleans the surface and causes the penetration of the chemicals inside the material[21]. HMDSOpp treated samples show the good durability to washing, and more than 80% bacterial reduction for both the bacteria after 20 washes.

3.6 Crease Recovery Angle

In this study, BTCA has been used as a binder or crosslinker which is well known for its reactivity with cotton. It binds the free hydroxyl groups of cotton to impart the crease recover[22,23]. It is observed that after plasma pre-activation, CRA increases and further treatment with HMDSOpp decreases the CRA slightly (Fig. 4), this may be due to the softening of the samples after HMDSO treatment. Moreover, it can be seen from figure that without plasma treated samples show 20% reduction in CRA after 20 washes. The reduction in CRA decrease after HMDSO

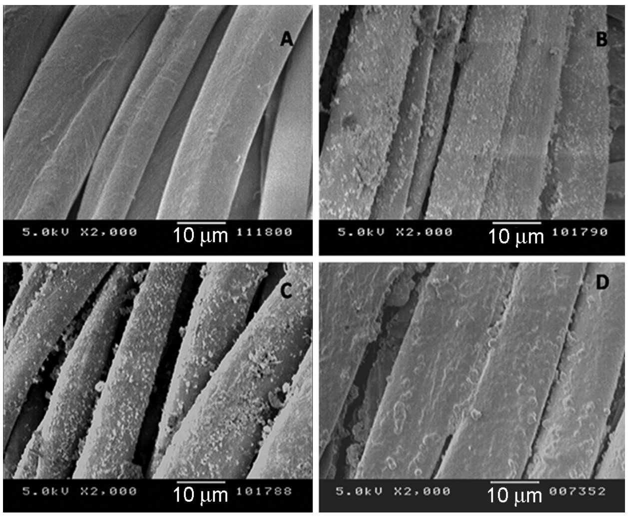

Fig. 3—SEM images of (A) control cotton, (B) TiO_2/SiO_2 without plasma, (C) TiO_2/SiO_2 with plasma, and (D) TiO_2/SiO_2 with plasma and polymer deposition

Table 4—Antibacterial activity of the different finished samples before and after 20 washes

Sample	% Reduction			
	Before wash		After 20 washes	
	S. aureus	*K. pneumonia*	*S. aureus*	*K. pneumoniae*
Control cotton	No reduction	No reduction	No reduction	No reduction
Without plasma	85.45	86.55	No reduction	No reduction
Plasma	99.95	99.96	88.62	78.61
HMDSOpp	99.59	99.41	99.04	83.02

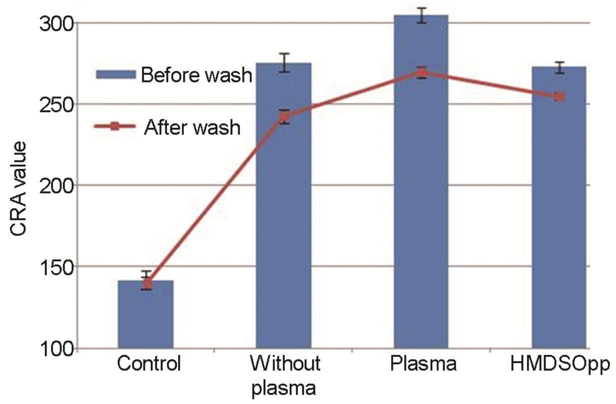

Fig. 4—Crease recovery angle of control and finished samples

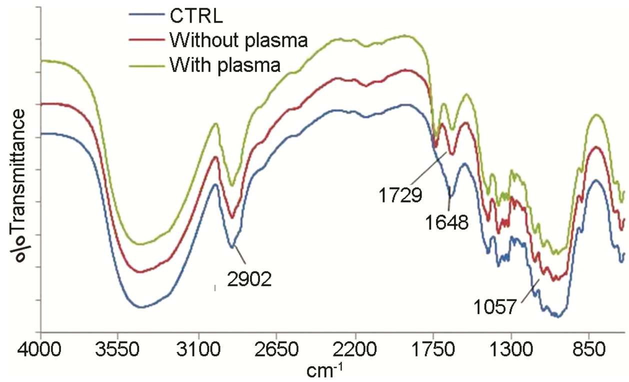

Fig. 5—FTIR spectra of BTCA treated samples, control cotton, without plasma and plasma

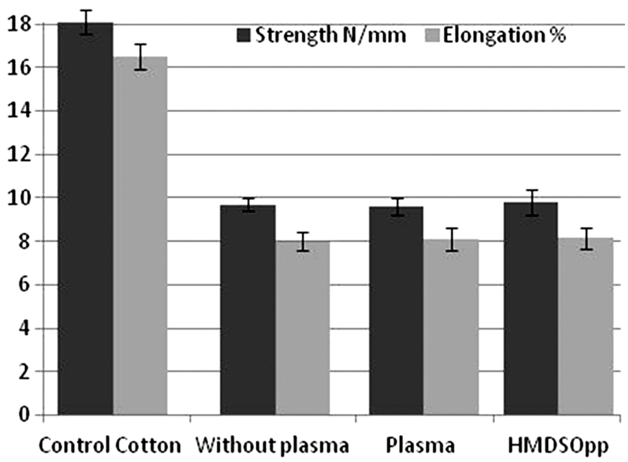

Fig. 6—Tensile strength and elongation of finished samples

treatment to 4%. These results can correlate well with the results of UPF, LOI and antibacterial properties. It can be inferred that with the use of HMDSO plasma treatment, the durability of the treatment is improved. This can be ascribed to the hydrophobic nature of the HMDSO polymer which restricts the leaching of finish during washing.

3.7 Surface Chemical Changes

The FTIR spectra of cotton fabric (Fig. 5) show strong absorption near 3433 cm^{-1}, attributed to O-H stretching vibration.

The peak at 2902 cm^{-1} is due to the presence of C-H carbon hydrogen bond of cellulose. The peak located at 1648 cm^{-1} is attributed to O-H bending of adsorbed water molecules. The peaks at 1432 cm^{-1} and 1372 cm^{-1} can be attributed to CH_2 scissoring and hydroxyl group bending. The spectra of treated samples shows the distinct peak at 1729 cm^{-1} which can be ascribed to C=O stretching vibration of the ester carboxyl band due to crosslinking of cotton with polycarboxylic acid (BTCA) [24]. The occurrence of the peak at 1729 cm^{-1} is prominent especially in the case of plasma treated sample. This infers that the higher cross linking of the BTCA occurs due to the plasma pre-activation of cotton sample.

3.8 Tensile Properties

Results of the tensile strength and elongation study of the untreated cotton fabric and treated samples are shown in Fig. 6. Significant strength loss is noticed due to functional finishing of the cotton samples; this loss may be due to crosslinking of cotton with BTCA.

Crosslinking between cellulose molecules causes stiffening of the cellulosic macromolecular network and fibre embrittlement, thus reducing the mechanical strength of the treated cotton[25]. There is no change observed in the tensile properties of the plasma treated and without plasma treated samples, as plasma only modifies the surface and does not change the bulk properties of the material.

4 Conclusion

It has been observed that nano TiO_2/SiO_2 application imparts excellent UV protection, flame retardancy and antibacterial properties to cotton fabric. When compared between two treatments viz. with and without plasma, plasma treatment has better results compared to without plasma application. TiO_2 act as photocatylist to improve UV protection. TiO_2/SiO_2 acts as a physical barrier (thermal insulator), with SHP as an active in the condensed and/or vapour phase to improve the flame retardancy. Furthermore, it could be asserted that TiO_2/SiO_2 and BTCA show the best wrinkle recovery outcome since carboxylic acids would make crosslinking cellulose. Finally, it could be inferred that with the use of HMDSO plasma polymerization the durability of the finish improves. Plasma technology requires less chemicals, thus reduces the environmental pollution and cost effective solution for conventional finishing techniques.

References

1 Onar N, Aksit A C, Sen Y & Mutlu M, *Fibres Polym*, 12(4) (2011) 461.

2 Radetic M, Ilic V, Vodnik V, Dimitrijevic S, Jovancic P, aponjic Z S & Nedeljkovic J M, *Polym Advance Technol,* 19 (2008*)* 1816.

3 Lam Y L, Kan C W & Yuen C W M, *J Appl Polym Sci,* 124 (2012*)* 3341.

4 Hwang Y J & McCord G M, *Text Res J,* 75 (2005) 771.

5 Wang C X, Liu Y, Xu H L, Ren Y & Qiu Y P, *Appl Surf Sci* 254(8) (2008*)* 2499.

6 Kaplan S, *Surf Coat Technol,* 186 (2004) 214.

7 Rajpreet K V & Gita N R, *Text Res J.* 74(12) (2004*)* 1073.

8 Bourbigot S & Duquesne S, *J Material Chem,* 17 (2007*)* 2283.

9 Wang C X & Qiu Y P, *Surf Coat Technol,* 201 (2007*)* 6273.

10 Kale K H & Palaskar S, *Text Res J,* 81(6) (2011) 608.

11 Kale K H & Palaskar S S, *J Text Inst,* 103(10) (2012) 1088.

12 Palaskar S, Kale K H, Nadiger G S & Desai A N, *J Appl Polym Sci* 122(2) *(*2011) 1092.

13 Yang H, Zhu S & Pan N, *J Appl Polym Sci,* 92 (2004) 3201.

14 Laoutid F, Bonnaud L, Alexandre M, Lopez-Cuesta J M & Dubois Ph, *Material Sci Eng. R: Reports.* 63(3) (2009) 100.

15 Lam Y L, Kan C W & Yuen C W, *Bioreso uses,* 6(2) (2011) 1454.

16 Alongi J, Ciobanu M & Malucelli G, *Cellulose,* 18 (*2011)* 1335.

17 Alongi J, Ciobanu M & Malucelli G, *Cellulose* 18 (2011) 167.

18 Alongi J, Ciobanu M & Malucelli G, *Carbohyd Polym,* 85 (2011) 599.

19 Alongi J, Ciobanu M, Carosio F, Tata J & Malucelli G, *J Appl Polym Sci,* 19(4) (2011*)* 1961.

20 Alongi J, Ciobanu M & Malucelli G, *Carbohydrate Polym,* 87 (2012) 2093.

21 Kan CW & Yuen C W M, *Res J Text Appl Polym Sci,*. 10(1) (2006) 49.

22 Welch C M & Peters J G, *Text Chem Color.* 25(10) (1993) 25.

23 Yang Y & Li S, *Text Chem Color,* 26(5) (1994) 25.

24 Montazer M. Alimohammadi F & Shamei A & Rahimi M K, *Collul Surf B: Bio Interf,* 89 (2012) 196.

25 Yang C Q, Wei W & Lickfield G C, *Text Res J,* 70(2) (2000) 143.