Investigation of Wash Durability of Silica Nanoparticle Coated 100% Cotton Reactive Dyed Fabric Treated by Sol-Gel Technique

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ABSTRACT

In this research a hydrophobic surface of 100% cotton woven fabric was developed by sol-gel technique.

Fabric samples were dyed with Drimarene Reactive Red 5B and Drimarene Reactive Blue BR dyes (0.5% and 3% o.w.f) and then treated with a combination of silica nanoparticles, silane hydrophobes (alkyltrialkoxysilanes), and silane cross-linkers i.e, tetraethoxysilane (TEOS) and teramethoxysilane (TMOS) by dip-dry-cure process.

After coating, wash durability of dyed samples was investigated for water repellency and water uptake according to AATCC standards. The effect of coating on dyeing behavior was assessed by measuring the $(K/S)_{\lambda max}$ value, while change in color (ΔE) and fastness properties of coated fabric also investigated.

It has been observed that durable hydrophobicity achieved on cotton reactive dyed fabric through non-fluorine sol-gel route with silica nanoparticles with better fastness properties with little effect on shade.

INTRODUCTION

Hydrophobic textiles such as rainwear, upholstery, sportswear, and interior fabrics are need of today's world [1-3]. Different finishing agents may be used to attain desired hydrophobic properties, such as fluoro chemicals, silicones, PVA (polyvinylalchohol) and waxes are used to make the cotton fabric hydrophobic, except fluoro base chemicals other treatments are non-durable; whereas fluoro base chemicals are expensive and environmentally hazardous [2, 4]. Because during curing process due to the emission of non-volatile fluorinated compounds it can yield the risk for health and skin [4]. It was reported that perfluoroalkylsilane contains linear chains with CF_2-CH_2 bonds which tend to develop an undesirable and dangerous hydrogen fluoride (HF) gas on heating [5].

Treatment with nano-particles was not only maintained the existing properties of textile material but also imparted other textile properties such as repellency, soil release and UV-resistance [6]. When silica nanoparticles were applied on dyed cellulosic substrate by sol-gel cross linking process, it forms thin smooth film on fabric surface with high degree of homogeneity but it can alter color of dyed substrate [7]. Furthermore, durability towards repellency of textile coated material was improved using silica nanopaticles and silane additives and in early days sol-gel coatings were applied to change the nature of desized, scoured and bleached cotton fabric from hydrophilic to hydrophobic [3]. However, due to the increased demand of colored hydrophobic textiles; it is preferred to dye the cotton textiles prior to finishing with sol-gel coating. Water repellency of sol-gel coated textiles was assessed by measuring contact angle but the durability of coating was not assessed because when water was sprayed on fabric with pressure, have no effect on coating, hence this method of assessing the durability is not suitable for some end uses such as fabric for umbrella [8].

Much work has been carried out to make the cellulosic fabrics hydrophobic using chemical treatments. These chemical treatments were carried out on bleached fabric in most cases. While the effect of hydrophobic treatment with tetraethoxysilane (TEOS) and teramethoxysilane (TMOS) cross linkers on dyed fabric has not been studied to its scope. Therefore, in this research hydrophobe with cross-linkers (TMOS and TEOS) silica nano-particle sols were applied on 100% cotton reactive dyed (0.5%

and 3% o.w.f) fabric samples. The durability of these coating before and after wash, color strength, color difference values and fastness properties were also investigated.

EXPERIMENTAL

Materials

100% bleached cotton plain woven fabric of 139 g m^{-2} was kindly supplied by M/S Popular Textile Mills Pvt: Ltd Karachi, Pakistan. Drimarene Reactive Red-5B and Drimarene Reactive Blue-BR was supplied by Clariant, Pakistan.

Cross-linkers, Tetraethoxysilane (TEOS) and Tetramethoxysilane (TMOS) and hydrophobe, n-octyltriethoxysilane were supplied by M/S Hangzhuo Feidian Chemical Co. Ltd Shanghai China. Silica nanoparticals (Aerosil® 200) was supplied by M/S Jawa Pharmaceutical Industry Pvt: Ltd Lahore, Pakistan. Other chemicals solvent, Ethanol and catalyst, hydrochloric acid were purchased from Al Beruni, Pakistan.

Dyeing

Bleached cotton fabric samples of 7 gms were dyed (0.5% and 3% o.w.f) with reactive dyes (Drimarene Reactive Red-5B and Drimarene Reactive Blue-BR) on Rapid HT dyeing machine. Dyeing process was carried out at liquor to goods ratio of 20:1. At 60 °C dye, Sodium chloride (40 -60 g l^{-1}) and Drimagen E2R (0.5 – 2.0 g l^{-1}) were added and treated for 30 mins. Then, Soda Ash (10 -15 g l^{-1}) was added and again treated for further 30 mins. The fabric samples were then washed according to the method recommend by Clariant & Schönberger and Schäfer [9], and at last dried in an oven.

Sols Preparation & Application

The dyed fabric samples were then coated according to the recipe mentioned in Table 1. Firstly, sol-gel was prepared using Ultrasonic cleaner (FRT-200B) at room temperature for 30 mins. The sol-gel solution was then applied on fabric samples by dip-dry-cure process suggested in previous work [3]. The treated fabric samples were then stored in air tight polyethylene bags for two hours till they were tested.

TABLE I. Recipe with different concentration of Aerosil® 200 [3].

Chemical Used	RCP 1	RCP 2	RCP 3	RCP 4
Silica Nanoparticles Aerosil® 200	-	0.02%	0.1%	0.2%
Ethanol (ml)	96	96	96	96
Hydrochloric Acid (ml)	24	24	24	24
TEOS (ml)	20	20	20	20
TMOS (ml)	20	20	20	20
n-octyltriethoxysilane (ml)	4	4	4	4

MEASUREMENTS

Wash Durability

Before and after washing, the durability towards fabric repellency was assessed through water repellency test and water uptake values. However, washing of dyed fabric was carried out using standard test method [10]. This single washing treatment is equal to five home launderings.

Water Repellency

Water repellency of coated dyed fabric samples was assessed by Spray Rating test through standard [11]. The water repellency was assessed by using AATCC rating scale ranging from AATCC 50 (highly absorbent) to AATCC 100 (highly hydrophobic).

Water Uptake

Water uptake or rain test was assessed using American standard [12]. The coated fabric sample was placed (in clamped condition) on a known weight backing paper. The water was showered with impact (such as rain) and backing was weighed again and then % of weight uptake was calculated by using Eq. (1).

$$= \frac{Wt.after\ spray - Wt.before\ spray}{Weight\ before\ spray} 100 \qquad (1)$$

Lower the % age of water uptake, higher will be the resistance towards rain.

Surface Morphology

The dyed fabrics samples were examined before and after sol-gel coating of silica nanoparticle. SEM assessed the change in surface morphology with accelerating voltage of 10 kV and magnification of x700.

Color Strength (K/S)

$(K/S)_{\lambda max}$ value of dyed coated sample was assessed on an X-rite Color-Eye 7000A Spectrophotometer using Eq. (2).

$$\left(\frac{K}{S}\right)_{\lambda \max} = \frac{(1-R)^2}{2R} \quad (2)$$

Where; R = decimal fraction of the reflectance of the dyed fabric,
K = absorption co-efficient and
S = scattering co-efficient.

Color Difference, ΔE (CMC)

The dyed samples when coated with sol-gel coating having a transparent layer on it. The change in color due to coating was measured on an X-rite Color-Eye 7000A Spectrophotometer using Eq. (3).

$$\Delta E(CMC) = \sqrt{(\frac{\Delta L}{lSL})^2 + (\frac{\Delta C}{cSc})^2 + (\frac{\Delta H}{SH})^2} \quad (3)$$

Where; Δ*E* (CMC) is the total color difference with l:c ratio of 2:1, keeping commercial factor 1.2, Δ*L* = lightness difference, Δ*C* = difference in saturation or chroma difference, Δ*H* = hue difference, l = luminosity factor, c = chroma factor, SL = semi sphere of lightness, Sc = semi sphere of chroma and SH = semi sphere of hue.

Rubbing and Washing Fastness

Dyed sol-gel treated samples are required to assess their washing and rubbing fastness properties. It is because hydrophobic layer may be affected due to crocking and washing treatment. Stability of treated samples to crocking was measured by AATCC test method [13] and to washing was measured by AATCC standard [10]. The rubbing fastness was assessed on crock meter whereas washing fastness test was carried out on Rapid HT dyeing machine.

RESULTS AND DISCUSSIONS

Water Repellency (Before Washing)

Results of water repellency test of un-coated and coated samples with silica nanoparticles and dyed with Drimarene Reactive Red-5B and Drimarene Reactive Blue-BR (0.5% and 3% o.w.f) are shown in *Figure 1(a-b).* It has been observed that water repellency increased with the concentration of silica nanoparticles. Highest value of water repellency has been achieved for both dyes at 0.5% shade and 0.2% o.w.b (weight of bath) of silica is AATCC 90, which means good repellency. Whereas, at 3% shade of both dyes, the maximum repellency observed is AATCC 95 at 0.2% o.w.b of silica. In most of the recipes TEOS has given high repellency value on AATCC scale than TMOS, because TEOS has long carbon chain than TMOS attached with cotton structure as shown in *Figure 2* and *Figure 3.* It is also observed that silane cross-linker form covalent bonds with cellulose, hence increases the durability of treated samples.

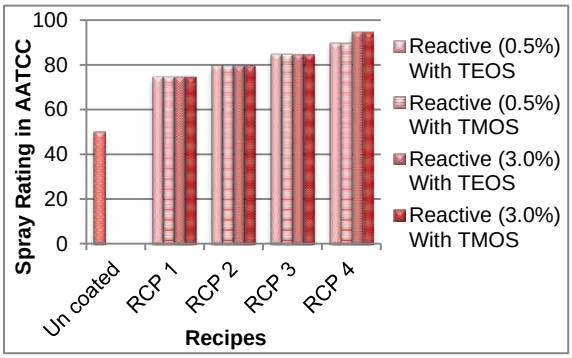

FIGURE 1. (a) Spray rating of Drimarene Reactive Red-5B 0.5% & 3% o.w.f dyed sample before washing.

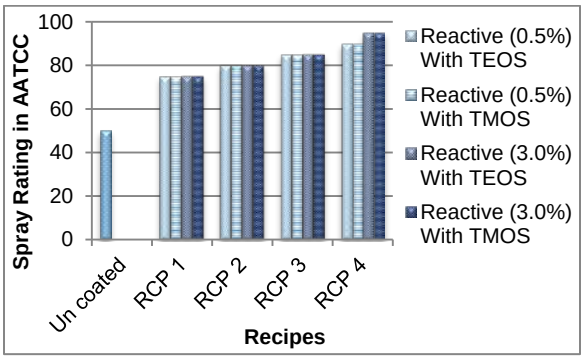

FIGURE 1(b). Spray rating of Drimarene Reactive Blue-BR 0.5% & 3% o.w.f dyed sample before washing.

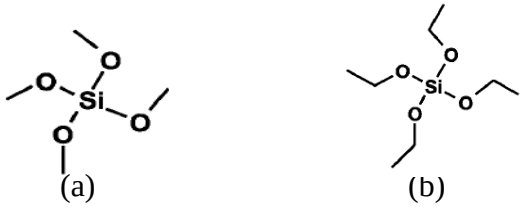

FIGURE 2. (a) Tetramethoxysilane (TMOS) and (b) Tetraethoxysilane (TEOS).

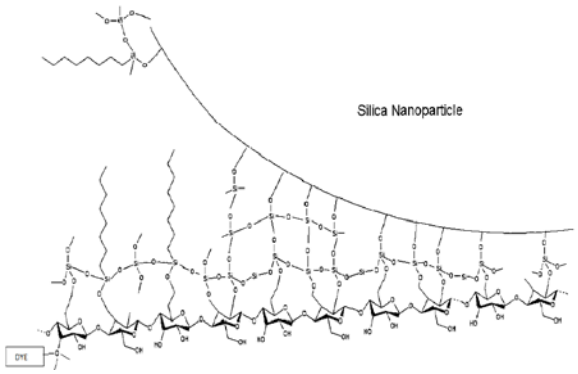

FIGURE 3. Proposed surface chemistry of reactive dyed cotton fabric when treated with silica nanoparticles and mixed silanes. "(Roe, 2009) also suggested almost same schematic for un-dyed cotton fabric" [3]

Water Uptake (before washing)

The water uptake values calculated using equation (1) are shown in *Figure 4* (a-b), lower uptake value means high repellency towards water [8]. The water uptake value of un-coated dyed sample was 130%, while coated dyed samples treated with RCP 4 with TEOS gives maximum repellency value towards water (only 6.8% uptake).

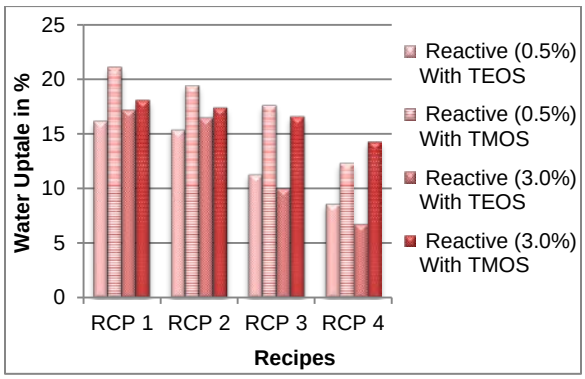

FIGURE 4(a). Water Uptake values of dyed fabric with Drimarene Reactive Red-5B (0.5% & 3% owf) before washing.

Figure 4 (b) shows that the water uptake values are gradually decreased (RCP 2 – RCP 4) with the % w.o.b (weight of bath) of silica nanoparticles. The minimum uptake value (10%) has been observed when fabric samples were coated with 0.2% silica (TEOS cross-linking agent) and dyed with Drimarene Reactive Blue-BR (RCP 4). When comparing the cross-linking agent, again TEOS gives much better repellency than the TMOS it may be due to its structure.

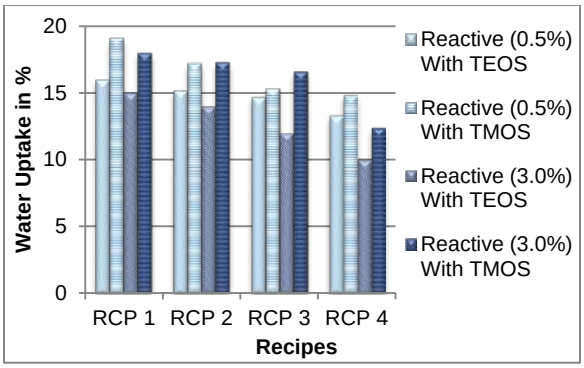

FIGURE 4(b). Water Uptake values of fabric dyed with Dimarene Reactive Blue-BR (0.5% & 3% o.w.f) before washing.

Water Repellency (After Washing)

After washing, the durability toward water repellency was assessed through spray rating tester by AATCC standard [10]. *Figure 5 (a-b)* illustrates the results of spray rating values after five wash cycles. It has been observed that fabric samples coated with silica nanoparticles have highest repellency values AATCC 85 after washing. This indicate that silica coatings are durable to some extent, the repellency rating of coated samples dyed with drimarene Red 5B declined from RCP1 to RCP 4 (6.6 to 5.5 %) in 0.5% shade and from (12.5% to 15.7%) in 3.0% shade (*Figure 5a*). The coated fabric samples still have water repellency but the spray rating values are decreasing in all samples as compared to unwashed samples (*Figure 1 a-b*).

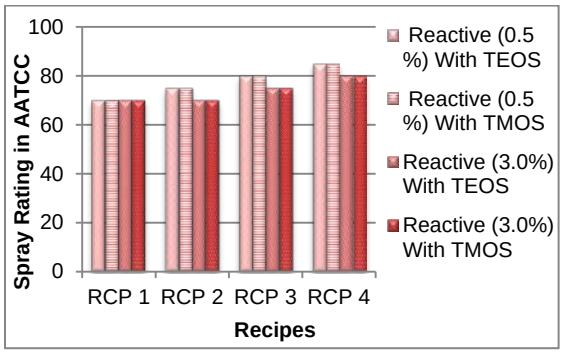

FIGURE 5(a). Spray rating value of Drimarene Reactive Red 5B dyed samples after 5 wash cycles.

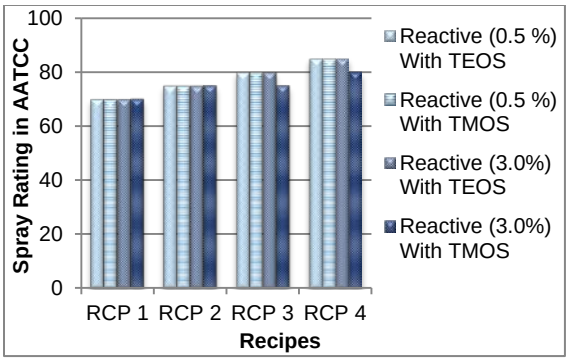

FIGURE 5(b). Spray rating of Drimarene Reactive Blue-BR dyed samples after 5 wash cycles.

Similar declining trend has been observed with Drimarene Reactive Blue-BR. Drimarene Reactive Blue-BR (3.0% shade) cross-linked with TEOS shows less decline in repellency after 5 washes as compare to Drimarene Reactive Red 5B 3.0% w.o.f. Cotton fabric cross-linked with TEOS sustains wash cycles more firmly. The gradual reduction in repellency was seen after each wash cycle. This reduction was high in first washing as compared to other washes.

Water Uptake (After Washing)

Results of wash durability to water resistance are given in *Figure 6(a)* dyed with Drimarene Reactive Red-5B and *Figure. 6(b)* dyed with Drimarene Reactive Blue-BR. Findings show similar trend of declination as discussed in preceding section, the resistance to water uptake value has been reduced markedly after five wash cycles but as compared to without silica coated samples, silica nanoparticles coated samples show good resistance to water. Again TEOS cross-linker shows better performance than TMOS cross-linker.

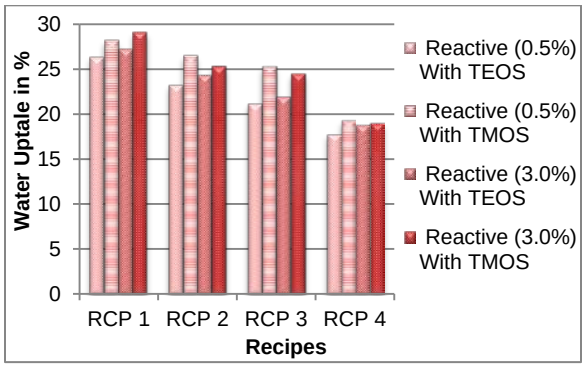

FIGURE 6(a). Water uptake values of Drimarene Reactive Red-5B dyed samples after 5 wash cycles.

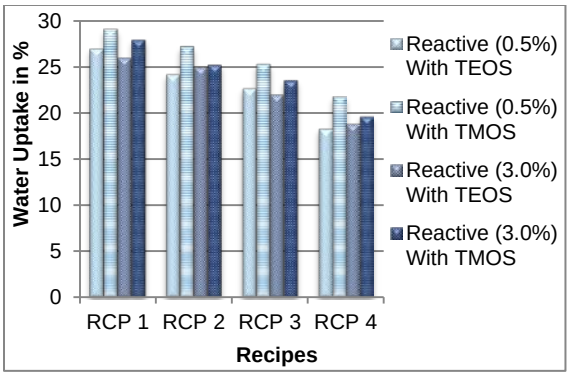

FIGURE 6(b). Water uptake values of Drimarene Reactive blue-BR dyed samples after 5 wash cycles.

Surface Morphology

The effect of sol-gel technique on cotton fabric samples are shown in *Figure 7 (a-b).* The coated fabric samples have irregular surface behavior as compared to uncoated samples. It is observed that increase of water repellency with silica concentration is due to the deposition of silica nanoparticles as shown in *Figure 7 (b).* The surface roughness provides the lotus effect, which resist the penetration of water and reduces the reflectance of light hence increases the color strength values.

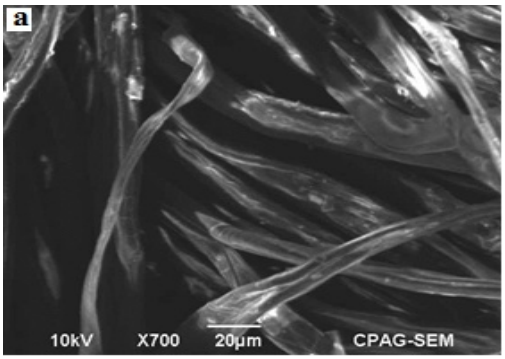

FIGURE 7(a) before coating of silica nanoparticles.

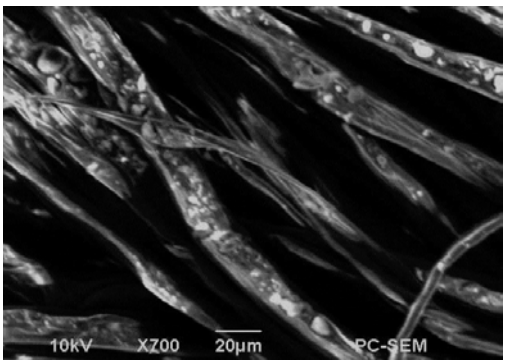

FIGURE 7(b) after coating of silica nanoparticles.

Color Strength $(K/S)_{\lambda max}$

The color strength values of 0.5% and 3% o.w.f of fabric samples dyed with Drimarene Reactive Red-5B and Drimarene Reactive Blue-BR are shown in *Figure 8 (a- b).* When comparing the color strength value of uncoated fabric to the coated fabric samples the $(K/S)_{\lambda max}$ values are increasing up to RCP 3 samples and then decreasing. It is because as the surface roughness trap the incident light, hence, reduces the reflectance value of dyed samples.

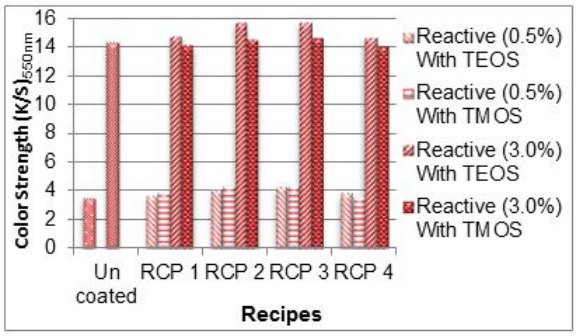

FIGURE 8 (a). $(K/S)_{550nm}$ of Drimarene Reactive Red-5B 0.5% & 3% o.w.f.

In case of RCP 4 the maximum quantity of silica was used, as it is white in color and hence, affect the color yield of dyed samples. TEOS gives high (15.79) $(K/S)_{550nm}$ values as compared to TMOS in 3% o.w.f while vice versa trend is observed in 0.5% o.w.f except RCP4 sample. Therefore it is observed that surface shade can be affected by using silica nanoparticles.

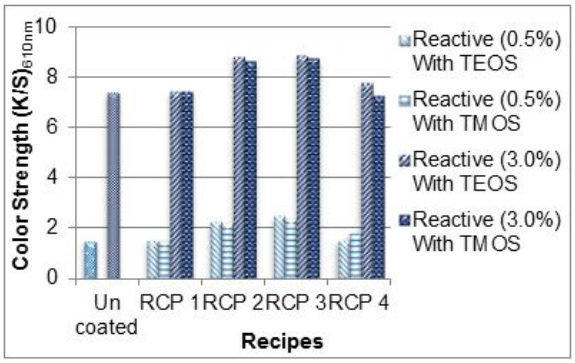

FIGURE 8 (b). $(K/S)_{610nm}$ of Drimarene Reactive Blue BR 0.5% & 3% o.w.f.

Assessment of Color Difference (ΔE)

The deviation of color values to the standard fabric (uncoated fabric samples) is shown in *Figure 9 (a-b).* The dyed fabric sample coated with RCP 3 having highest color strength values among other RCPs and also highest color difference values. However, in RCP 4 samples were coated much higher silica concentration to RCP 3 but it gives lower values of $(K/S)_{\lambda max}$ with both Drimarene Reactive Red 5B and Drimarene Reactive Blue BR because high silica concentration affect the surface morphology of fiber [14], make the fabric surface irregular. Surface color shade may be affected with sol-get treatment [7].

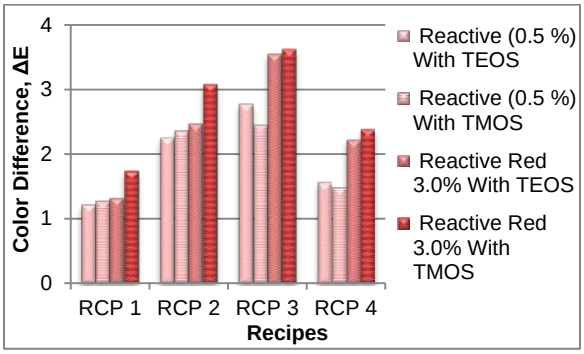

FIGURE 9(a). ΔE values of fabric sample dyed with Drimarene Reactive Red-5B 0.5% & 3% o.w.f.

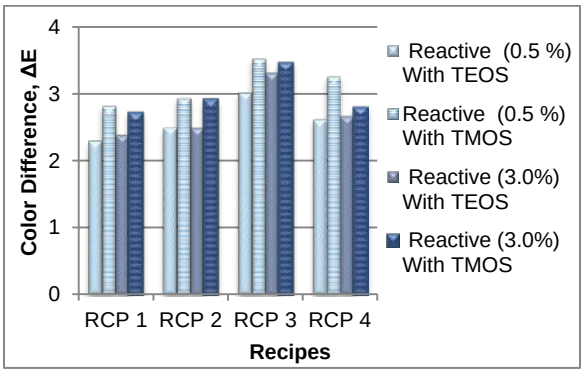

FIGURE 9 (b). ΔE values of fabric sample dyed with Drimarene Reactive Blue-BR 0.5% & 3% o.w.f.

Similar trend is observed in *Figure 9 (b)* TEOS treated fabric samples provide less color difference ranging from 2.2 -3.32 and for TMOS treated fabric samples difference values are 2.3 – 3.47, when compared with uncoated fabric.

Rubbing Fastness

Post treatment enhances the rubbing fastness properties of cotton material. As shown in *Table II* and *Table III*, cross-linker, TMOS have high resistance to crocking than the fabric sample coated with TEOS cross-linker in both shades (0.5% and 3.0% o.w.f). Drimarene Reactive Red 0.5 % has dry rubbing value ranging from 3 to 5 before and after

treatment respectively. Dyed sample with 3.0% o.w.f has lower rating than the sample dyed with 0.5% o.w.f. Moreover, excellent fastness (5) rating is achieved when fabric is dyed with Drimarene Blue BR at 0.5% o.w.f and very good (4) at 3 % o.w.f. It is because high number of dye molecules on the surface of the fabric has high potential to rub-off easily. As the fabric sample is hydrophobic in nature, the wet rubbing fastness shows more resistance to crocking as compared to dry rubbing fastness.

TABLE II. Rubbing fastness of Drimarene Reactive Red- 5B after sol-gel coating.

	Reactive Red 0.5 %				**Reactive Red 3.0 %**			
Dry/Wet	D^*	W^+	D^*	W^+	D^*	W^+	D*	W^+
Un-coated	3/4	3			3	2/3		
Cross-Linker	TE		TM		TE		TM	
RCP 1	5	4/5	5	5	3/4	3/4	3/4	4
RCP 2	4/5	5	5	5	3/3	3/4	3/4	4
RCP 3	4/5	5	5	5	3/4	3/4	3/4	4
RCP 4	5	5	5	5	3/4	3/4	3/4	4

D^* = Dry and W^+ = wet
TE = tetraethoxysilane (TEOS)
TM = teramethoxysilane (TMOS)

TABLE III. Rubbing fastness of Drimarene Reactive Blue-BR after sol-gel coating.

	Reactive Blue 0.5 %				**Reactive Blue 3.0 %**			
Dry/Wet	D^*	W^+	D^*	W^+	D^*	W^+	D^*	W^+
Un coated	3/4	3			3	2/3		
Cross Linker	TE		TM		TE		TM	
RCP 1	5	4/5	5	5	3/4	3/4	3/4	4
RCP 2	4/5	5	5	5	3	3/4	3/4	4
RCP 3	4/5	5	5	5	3/4	3/4	3/4	4
RCP 4	5	5	5	5	3/4	3/4	3/4	4

Washing Fastness

The wash fastness of reactive dyed sample is already good because reactive dye is attached with cellulose by covalent bonds. The sol-gel coatings having cross linker, which further cross-linked with cellulose as shown in *Figure 3* also slightly improved the washing fastness of hydrophobic cotton material. There is no significant effect of silica nanoparticles seen on washing fastness of fabric sample dyed with Drimarene Reactive Red-5B, whereas slightly improvement in washing rating of Drimarene Reactive Blue-BR is observed when silica nanoparticles were 0.2% (w.o.b) as given in *Table IV.*

TABLE IV. Washing fastness of Drimarene Reactive after sol-gel coating.

	Red-5B (0.5 %)		**Red-5B (3 %)**		**Blue-BR (0.5%)**		**Blue-BR (3%)**	
Un-coated	4/5		4/5		4		4	
Cross-Linker	TE	TM	TE	TM	TE	TM	TE	TM
RCP 1	4/5	4/5	4/5	4/5	4	4	4	4
RCP 2	4/5	4/5	4/5	4/5	4	4	4	4
RCP 3	4/5	4/5	4/5	4/5	4	4	4	4
RCP 4	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5

CONCLUSION

Durable hydrophobicity was achieved on cotton reactive dyed sample through non-fluorine sol-gel route with silica nanoparticles. Highest value of spray rating AATCC 80 is achieved without silica in sol-gel coatings. The highest value with silica nanoparticles is obtained in case of Drimaren Reactive Red-5B and Drimaren Reactive Blue-BR i.e. AATCC 95 at RCP 4 on 3.0% w.o.f. least water uptake 6.8% was observed in Drimaren Reactive Red-5B in 3% shade with TEOS as cross-linker. A maximum value of AATCC 85 was achieved after five washes, it shows that fabric coated with sol-gel technique still have potential to repel water. $(K/S)_{\lambda max,}$ color strength value has been improved by increasing quantity of silica nanoparticles up to 0.1% w.o.b, afterward it is reduced, it is due the white color of silica nanoparticles, which affect the color depth value of dyed samples .Color difference of nanosol coated dyed sample was assessed to clarify the effect of sol-gel coating on dyed samples. The lowest value of ΔE 1.23 with Drimaren Reactive Red-5B is achieved. While highest value seems in Drimaren Reactive Blue-BR RCP 3 sample with TMOS cross-linker 3.47. This shows that where the color is the sole requirement, silica with sol-gel treatment should be avoided. Dry and wet rubbing fastness is increased but wet rubbing increased more as fabric become hydrophobic in nature. The washing fastness rating slightly increased with Drimaren Reactive Blue-BR but it remains same with Drimaren Reactive Red-5B after coating of dyed fabric. Hence the sol-gel coating on reactive dyed samples shows higher repellency value after five washes slightly affect the color strength value of dyed samples treated with RCP 3 and RCP 4.

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