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SYNTHESIS AND APPLICATION OF UV RAY'S PROTECTIVE MONO AZO ACID DYES ON WOOL, SILK AND NYLON

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Abstract- Health hazards due to exposure of skin to solar Ultraviolet radiation are increasing very rapidly due to environmental degradation or ozone layer depletion. It may be greatly reduced by minimizing the time exposure to UV rays. UV protection by fabrics has recently become the focus of great interest. A key element in achieving the goal of reduced UVR exposure is making proper UV protective goods with good UPF protection > 40. Keeping this in mind, the current research aimed at new area of research on synthesis of UVR protective functional dyes containing benzophenone based UV absorbers and its application on wool, silk and nylon.fabrics. All the wool, silk and nylon fabrics dyed with sythesised dyes shows less than 5% UVA and UVB transmission indicating good protection against UV radiation, Dyed fabric also exhibits good to excellent washing, rubbing and light fastness properties

Keywords- Mono azo acid dyes, 4-hydroxy benzophenone, 2, 4-dihydroxy benzophenone, 2 hydroxy-4 methoxy benzophenone, light fastness, UPF factor, UVA UVB blocking.

I. INTRODUCTION

Technical textiles are the fastest growing sector of the textile industry [1] Technical textiles account for over 40% of the total textile production in many developed countries. The current volume of the market worldwide for technical textiles is more than $60 billion [2,3]. Medical textiles plays very important role in application areas of technical textiles. The demand for medical textiles products is enormous both in developed and developing countries [4]. Protection against ultraviolet (UV) radiation is one of the most important need for skin diseases[5,6,7,8].

In the last decade growing awareness is seen concerning protective properties of textiles against UV radiation originating from sunlight [9]. Protection against UV radiation is usually controlled by applying sunscreen which contains a UV absorber composition [10]. The safest protection from UV radiation exposure is obtained by clothing and its protectiveness depends on fabric composition, fabric parameters like GSM and UV absorbing properties [11].

Benzophenone is an excellent UV absorber [12] , which prevents the photo degradation of many vinyl polymers [13]. Compounds 4-hydroxy benzophenone, 2, 4-dihydroxy benzophenone and 2-hydroxy-4-methoxy benzophenone bearing hydroxyl and Methoxy (as auxochrome) groups and a keto (chromophore) group. This compound has wide applications as a polymer additive[14]. In the literature few benzophenone based acid, reactive and disperse azo dyes are reported [9,13, 15,16, 17,18,19]

There has been a progressive increase in the incidence of skin cancers, particularly that of cutaneous melanomas over the last few decades [20]. Evidence from various disciplines has implicated ultraviolet radiation (UVR) from the sun as an important factor in causing skin cancer. UV radiation

(UV) is classified as a "complete carcinogen" because it is both a mutagen and a non-specific damaging agent and has properties of both a tumor initiator and a tumor promoter. In environmental abundance, UV is the most important modifiable risk factor for skin cancer and many other environmentally-influenced skin disorders [21]. Health risks associated with exposure to solar UVR may be greatly reduced by minimizing the time exposure. UV protection by fabrics has recently become the focus of great interest, particularly in connection with environmental degradation or ozone layer depletion. Clothing is perceived as a good means of sun protection, but not all apparel is sufficiently protective against UV radiation [22]. A key element in achieving the goal of reduced UVR exposure is making proper UV protective goods with good UPF protection > 40. These kinds of textiles are very much encouraged in high altitude countries for protection from skin related disease [23]

Keeping this in mind, the present study is an attempt to synthesis Novel azo acid dyes with built-in UV-absorber and its application on textile fabrics. The synthesized acid dyes are applied on wool, silk, and nylon respectively. The dyed fabrics are evaluated for ultraviolet protection factor(UPF), UV-A and UV-B transmission, photo-stability of the dyes and fastness properties including light fastness.

II. EXPERIMENTAL

A. Materials

4-hydroxy benzophenone, 2,4-dihydroxy benzophenone, 2-hydroxy-4-methoxy benzophenone, Orthanilic acid, Metanilic acid, 3-amino benzoic acid, 4- amino benzoic acid, sodium hydroxide, sodium nitrite , sodium carbonate, Dimethylformamide, Acetone, Methanol conc. H_2SO_4 and conc. HCl were purchased from S. D. Fine Chemicals Ltd, Mumbai, India. Lyogen WSN was procured from Archroma, Thane. All reagents were characterized by melting or boiling point and used without further purification. Solvents were used after distillation at their boiling point and drying according to standard processes. Ready for dyeing wool, silk and nylon (100%) substrate, woven wool fabric (weight 173 gm/m2, ends per inch 55 and picks per inch 48), woven silk fabric (weight 51 gm/m2, ends per inch 320 and picks per inch 146) and knitted nylon fabric (190 gm/m^2, courses/inch 60 and wales/inch 38) was purchased from Kiran Threads, Surat, India.

All the compounds were purified by recrystallization and confirmed by TLC silica plate. Thin layer chromatography (TLC) was performed using aluminium plates coated with silica gel 60 F254 supplied by Merck. Melting points were recorded on instrument from Sunder Industrial Product, Mumbai.

The UV-Vis spectrum of the synthesised azo dyes was recorded on Perkin Elmer UV-Vis spectrometer Lambda. The L* ,a*, b*, C*, hº, K/S, DEcmc, and %STR-WSUM of dyed fabrics were obtained using a X-rite Color i7, color eye reflection spectrophotometer (under D65 standard light source and 10° observer).

B. Synthesis of UV rays protective mono azo acid dyes

General procedure for preparation of Azo Dyes(6a-6d) (7a–7d) and (8a–8d)

To a 100 mL round bottom flask, metanilic acid/orthanilic acid (1.73 g, 0.01 mol) and Na_2CO_3 (0.53 gm, 0.005) dissolved in minimum quantity of water were added, then sodium nitrite (0.75g, 0.011 mol) dissolved in minimum amount of water was added to the round bottom flask. The solution was cooled to 0-5ºC with an ice bath. Then 2.5 ml hydrochloric acid was cooled to 0~5^{o}C and pored quickly to the round bottom flask. The nitrous acid was checked by using starch-iodide paper. When diazotization was complete, the excess nitrous acid was decomposed with urea.

A mixture of, Na_2CO_3(1.059g, 0.01)and NaOH (0.4gm, 0.01 mol) was dissolved in 50 mL H_2O and stirred till dissolution, then 0.01 mol benzophenone was added in the solution and stirred till it gets completely dissolved. The mixture temperature was cooled to 0~5^{o}C. The above diazonium salt solution of was slowly added drop wise to the coupling component during 0.5h, at the same time, the pH value

was kept between 8.5~9. The reaction mixture was stirred for 2 h, the pH value of the mixture was adjusted to 2~3 by the 10% (wt/wt) aqueous solution of HCl, filtered, and the yellow filter cake was purified by DMF-ether to give dye1-6. Dye 7-12 was also sythesised by the same procedure.

C. The synthetic scheme for the preparation of dyes 6a-e, 7a-e and 8a-e is shown in Scheme 1

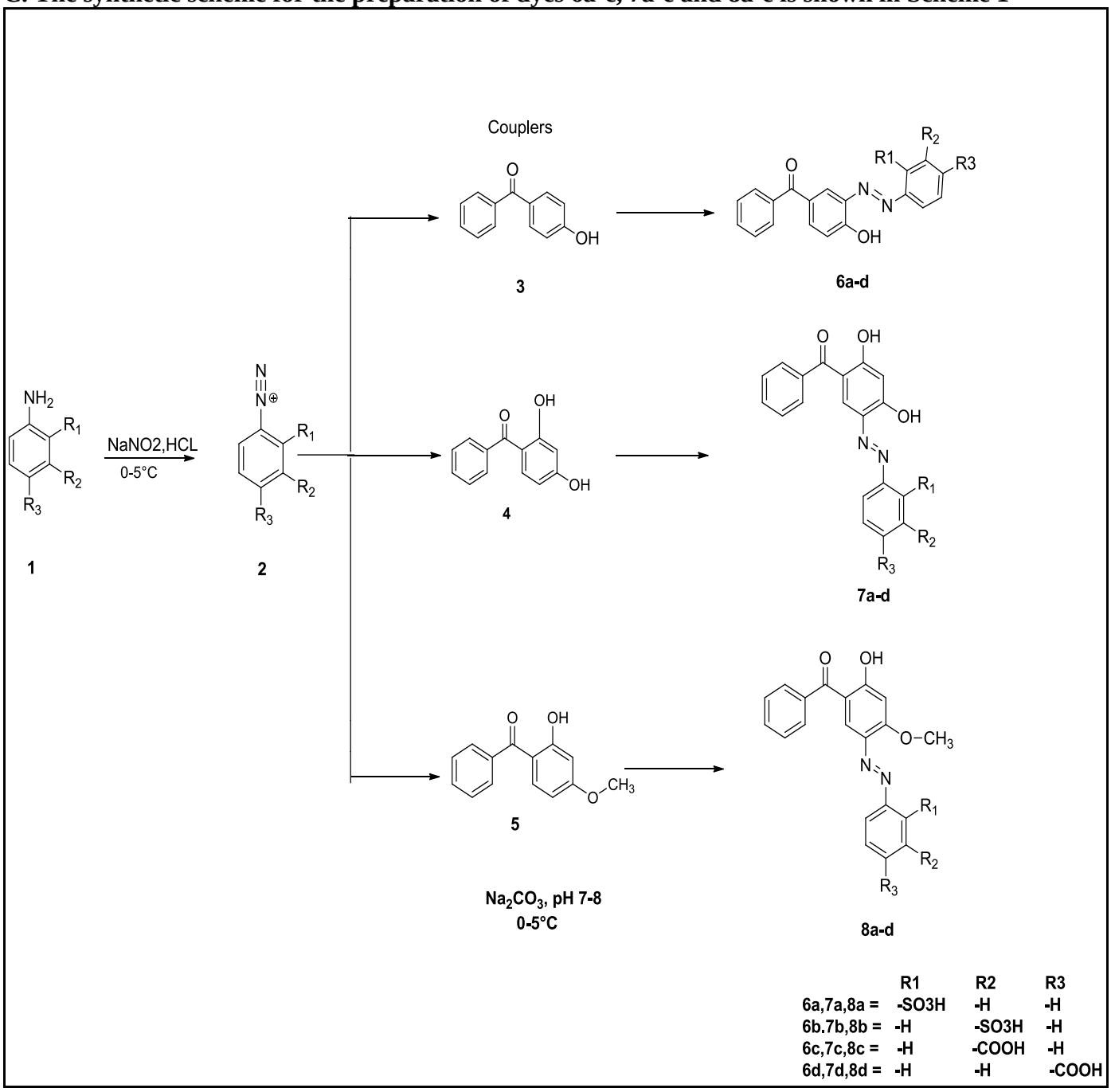
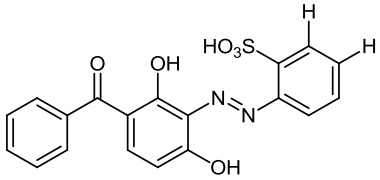
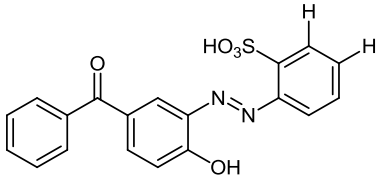
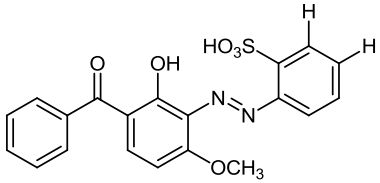
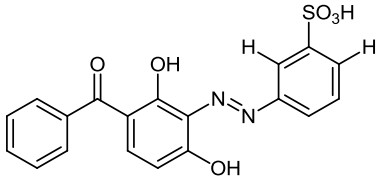
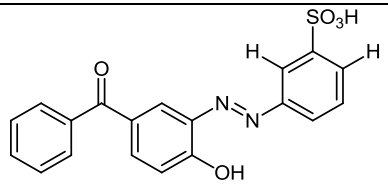
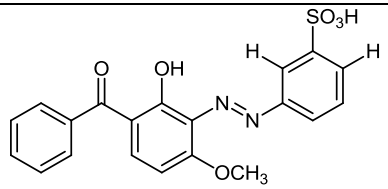
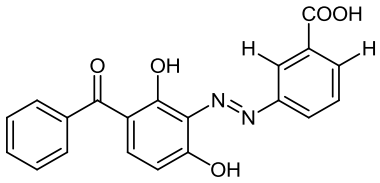
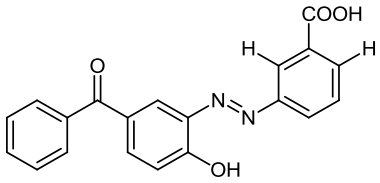
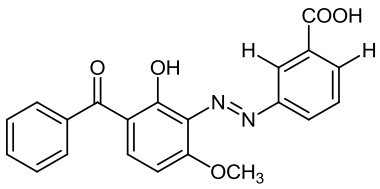
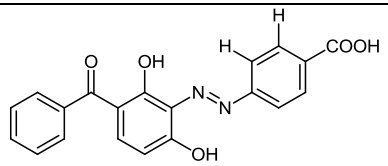
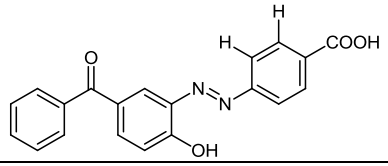
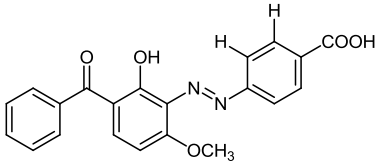


Figure 1:Synthesis scheme of benzophenone based acid dyes(6a-6d) (7a-7d) and (8a-8d)

Table 1. Properties of Sythesised Acid dyes

Dye No.	Dye	Compound Structure	Molecular Formula	Yield (%)	Elemental analysis (%)		M.P. (^{0}C)	Wavelength (in Methanol)	Colour
					Calculated	Found			
Dye 1	Orthanilic acid/2,4-diOH Benzophenone **(7a)**		$C_{19}H_{14}N_2O_6S$	82.15	C, 57.28; H, 3.54 ;N, 7.03; O, 24.10; S, 8.05	C,57.31; H, 3.55; N, 7.03	226	290/360nm	
Dye 2	Orthanilic acid /4-OH Benzophenone **(6a)**		$C_{19}H_{14}N_2O_5S$	73.17	C,59.68. H, 3.69; N, 7.33, O, 20.92; S, 8.39	C 59.69; H, 3.68: N, 1.34	213	295/375 nm	
Dye 3	Orthanilic acid /2-OH,4-OCH_3 Benzophenone **(8a)**		$C_{20}H_{16}N_2O_6S$	79.54	C, 58.25; H, 3.91; N,6.79; O, 23.28; S, 7.77	C,58.28; H, 3.90; N, 6.78	185	325/445 nm	
Dye 4	Metanilic acid/2,4-diOH Benzophenone **(7b)**		$C_{19}H_{14}N_2O_6S$	88.99	C, 57.28; H, 3.54; N, 7.03; O, 24.10; S, 8.05	C,57.26; H, 3.55; N, 7.04	206	290/405 nm	

Dye 5	Metanilic acid /4-OH Benzophenone **(6b)**		$C_{19}H_{14}N_2O_5S$	77.85	C, 59.68; H, 3.69; N, 7.33; O, 20.92; S, 8.39	C,59.71; H, 3.68; N, 7.34	225	295/370 nm	
Dye 6	Metanilic acid /2-OH,4-OCH_3 Benzophenone **(8b)**		$C_{20}H_{16}N_2O_6S$	79.36	C, 58.25; H, 3.91; N, 6.79; O, 23.28; S, 7.77	C,58.27; H, 3.92; N, 6.78	215	335/360 nm	
Dye 7	3 amino benzoic acid/2,4-diOH Benzophenone **(7c)**		$C_{20}H_{14}N_2O_5$	71.61	C, 66.30; H, 3.89; N, 7.73; O, 22.08	C,66.32; H, 3.88; N, 7.74	135 - 140	290/360 nm	
Dye 8	3 amino benzoic acid /4-OH Benzophenone **(6 c)**		$C_{20}H_{14}N_2O_4$	86.95	C,69.36; H, 4.07; N, 8.09; O, 18.48	C,69.37; H, 4.08; N, 8.08	100-115	295/360 nm	

Dye 9	3 amino benzoic acid /2-OH,4-OCH_3 Benzophenone **(8 c)**		$C_{21}H_{16}N_2O_5$	74.07	C, 67.02; H, 4.28; N, 7.44; O, 21.26	C,67.05; H, 4.28; N, 7.45	125	330/360 nm	
Dye 10	4 amino benzoic acid /2,4-diOH Benzophenone **(7d)**		$C_{20}H_{14}N_2O_5$	81.84	C, 66.30; H, 3.89; N, 7.73; O, 22.08	C,66.31; H, 3.88; N, 7.74	115	290/360 nm	
Dye 11	4 amino benzoic acid / 4-OH Benzophenone **(6d)**		$C_{20}H_{14}N_2O_4$	70.93	C, 69.36; H, 4.07; N, 8.09; O, 18.48	C,69.40; H, 4.08; N, 8.08	135 - 140	295/360 nm	
Dye 12	4 amino benzoic acid /2-OH,4-OCH_3 Benzophenone **(8d)**		$C_{21}H_{16}N_2O_5$	81.48	C, 67.02; H, 4.28; N, 7.44; O, 21.26	C,67.05; H, 4.29; N, 7.43	118	345/360 nm	

C. General Procedure of Dyeing Wool Silk and Nylon

Dyeing of Wool, silk, nylon fabric was carried out in a laboratory dyeing machine (R.B.E. Electronics) with a material to liquor ratio of 1:20 and depth of the shade was 1% and 2% (calculated on weight of the fabric). The dyeing bath was adjusted at pH 4 to 5 by using acetic acid in water and Lyogen WSN is used as levelling agent. Wool, silk and nylon fabrics were dyed using the above dye solution. Dyeing was started at room temperature and temperature was raised to 100 $^{\circ}$C, maintained at this temperature for 1 hour, and then cooled to 50 $^{\circ}$C**.** At the end of the dyeing process, dyed samples were rinsed with warm and cold water and then air dried.

III. TESTING

A. Determination of UPF Factor (UPF and UV transmission)

The transmission of ultraviolet radiation (UV-R) through a specimen is measured on a spectrophotometer (Labsphere UPF TesterV-2000F Fabric Analyzer). Percentage UVA and UVB transmission were measured and the UPF is calculated according to AATCC Test Method 183-2010. The ultraviolet protection factor (UPF) is computed as the ratio of the erythemally weighted ultraviolet radiation (UV-R) irradiance at the detector with no specimen to the erythemally weighted UV-R irradiance at the detector with a specimen present. UPF rating, %UV A blocking and %UV B blocking are recorded.

B. UV Light exposure and colour fading measurement

UV light exposure and color fading measurement is study carried out using customized method based on AATCC 186. Samples were exposed for 100 hrs at. 60˚C temp. at irradiance of 0.77Watt/m2. Colour difference between unexposed and exposed samples and colour strength after 100hrs of exposure is measured on reflectance spectrophotometer (Color i7, X-rite)

C. Fastness Property

Light fastness of the dyed samples was tested on Xenon arc lamp apparatus by ISO 105- BO2 method. Washing Fastness of dyed samples was tested on Washometer (from SDL Atlas) by the ISO 105- C10- C(3) method. The shade change, together with staining of adjacent fabrics, was rated according to appropriate grey scales. Rubbing fastness of the fabric is tested on MAG rubbing tester by ISO 105 X12:2016(E) method including both dry and wet rubbing. Staining of cotton rubbing cloth is assessed with the grey scale for staining under suitable illuminant.

IV. RESULTS & DISCUSSIONS

A. UV protective properties of undyed and dyed wool, silk and nylon fabric

Table 2. UPF, T(UVA), T(UVB) properties of undyed and dyed wool, silk and nylon fabric

Sr. No.	Sample Name	% Shade	Wool			Silk			Nylon		
			UPF	T(UV-A)	T(UV-B)	UPF	T(UV-A)	T(UV-B)	UPF	T(UV-A)	T(UV-B)
1	Undyed		56	5.76	0.96	8	19.04	6.79	45	8.32	1.25
2	Dye 1	1%	382	0.37	0.25	46	3.52	1.78	1391	0.09	0.06
3		2%	540	0.42	0.36	60	2.30	1.57	1651	0.11	0.05
4	Dye 2	1%	299	0.34	0.33	30	3.43	3.40	594	0.16	0.15
5		2%	343	0.32	0.28	34	3.37	2.66	870	0.18	0.08
6	Dye 3	1%	311	0.38	0.31	32	3.85	2.52	1462	0.07	0.07
7		2%	393	0.27	0.26	46	2.54	1.90	1565	0.07	0.06
8	Dye 4	1%	314	0.40	0.36	36	4.31	2.21	1768	0.09	0.05
9		2%	371	0.36	0.26	43	3.24	2.12	1895	0.07	0.05
10	Dye 5	1%	297	0.40	0.32	29	4.09	2.66	1798	0.05	0.05
11		2%	326	0.33	0.31	41	2.70	2.07	1983	0.05	0.05
12	Dye 6	1%	324	0.45	0.28	29	5.63	2.50	1426	0.12	0.07

13		2%	350	0.39	0.27	36	5.38	2.20	1771	0.06	0.06
14	Dye 7	1%	446	0.24	0.21	37	4.92	2.13	1592	0.15	0.06
15		2%	471	0.14	0.17	62	2.81	1.42	1937	0.05	0.05
16	Dye 8	1%	353	0.40	0.27	31	3.86	2.70	1529	0.10	0.06
17		2%	369	0.31	0.22	48	2.60	1.80	1978	0.05	0.05
18	Dye 9	1%	300	0.41	0.30	29	4.97	2.50	1849	0.05	0.05
19		2%	395	0.28	0.25	38	3.91	2.06	1997	0.05	0.05
20	Dye 10	1%	455	0.25	0.18	36	4.82	2.04	1345	0.17	0.06
21		2%	576	0.23	0.15	51	3.38	1.57	1888	0.08	0.05
22	Dye 11	1%	234	0.42	0.37	27	4.71	2.80	1778	0.07	0.05
23		2%	353	0.40	0.27	39	3.40	1.99	1963	0.05	0.05
24	Dye 12	1%	422	0.26	0.22	37	2.72	2.22	1890	0.05	0.05
25		2%	565	0.19	0.18	59	1.68	1.59	2000	0.05	0.05

The ultraviolet protection capability of the undyed and dyed wool is evaluated according to AATCC 183-2010. Ultraviolet protection factor (UPF), UVA transmission and UVB transmission of undyed and dyed wool, silk and nylon fabrics are mentioned in table no. 2. UPF of undyed wool fabric is 56, whereas wool fabric dyed with synthesised dyes with 1% and 2% shade shows UPF above 234 and above 326 respectively. and the and the highest UPF obtained is for dye 10, which is 455 foe 1% shade and 576 for 2% shade, indicating excellent ultraviolet protection. Generally, the UV protective property of the fabrics is evaluated as good when the ultraviolet transmittance is less than 5%. Undyed wool fabric shows 5.76% and 0.90% UVA and UVB transmission respectively. Wool fabric dyed with all the sythesised dyes (benzophenone as coupler) shows UV (A) transmission below 0.45 and UV (B) transmission below 0.37. UPF of undyed silk fabric is 8, silk fabric dyed with 1% and 2% shade shows UPF in the range of 27-46 and 34-62 respectively, indicating very good ultraviolet protection. Out of 12 synthesised dyes 8 dyes shows UPF above 30 indicating excellent protection against UV Rays. Undyed silk shows 19.05 % UV-A Transmission and 6.79% UV-B transmission. Silk fabric dyed with sythesised dyes shows UV (A) transmission in the range of 1.68-5.63% and UV (B) transmission in the range of 1.42-3.40%. UPF of undyed nylon fabric is 45, nylon fabric dyed with 1% and 2% shade shows UPF in the range of 594-1890 and 870-2000 indicating excellent Ultraviolet ray's protection. Out of 12 synthesised dyes 11 dyes shows UPF above 1000 indicating excellent protection against UV Rays on nylon fabric. Undyed nylon shows 8.32% UV-A Transmission and 1.25% UV-B transmission. Nylon fabric dyed with sythesised dyes (benzophenone as coupler) shows UV (A) transmission in the range of 0.05-0.18% and UV (B) transmission in the range of 0.05-0.15%.

B. Colour Parameters of undyed and dyed Wool fabric after 100hrs UV Exposure

Table 3. Colour parameters of undyed and dyed wool fabric

Sample Description	UV Exposure	L*	a*	b*	C*	h°	K/S	DEcmc	%STR-WSUM
Undyed Wool	Before Exposure	87.83	-0.27	14.21	14.22	91.09	0.377		
	After Exposure	86.73	-0.96	21.73	21.76	92.54	0.779	5.42	164.82
Wool Dye 1 1%	Before Exposure	74.43	13.77	50.28	52.14	74.68	5.930		
	After Exposure	74.47	9.80	48.30	49.28	78.53	5.754	2.84	94.06
Wool Dye 1 2%	Before Exposure	68.30	17.68	54.50	57.30	72.02	10.753		

	After Exposure	66.77	15.19	47.71	50.07	72.34	8.232	2.73	85.92
Wool Dye 2 1%	Before Exposure	47.15	26.63	51.39	57.88	62.61	22.127		
	After Exposure	51.80	23.87	52.34	57.53	65.49	17.149	3.07	77.50
Wool Dye 2 2%	Before Exposure	40.22	30.05	42.46	52.02	54.71	24.957		
	After Exposure	47.10	30.25	51.31	59.56	59.47	21.433	6.71	80.97
Wool Dye 3 1%	Before Exposure	73.60	18.34	63.06	65.67	73.78	8.806		
	After Exposure	74.89	15.60	55.38	57.53	74.27	6.037	2.88	68.81
Wool Dye 3 2%	Before Exposure	70.02	23.15	70.71	74.40	71.87	14.764		
	After Exposure	70.97	21.04	63.88	67.26	71.77	10.900	2.38	70.82
Wool Dye 4 1%	Before Exposure	76.45	11.76	52.57	53.86	77.39	7.856		
	After Exposure	75.07	10.74	48.34	49.52	77.47	5.401	1.72	89.79
Wool Dye 4 2%	Before Exposure	71.49	17.20	58.79	61.26	73.69	14.041		
	After Exposure	69.54	16.13	54.06	56.41	73.38	10.548	1.90	91.25
Wool Dye 5 1%	Before Exposure	59.30	20.13	63.30	66.71	72.44	20.270		
	After Exposure	60.48	20.77	63.21	66.53	71.81	15.930	0.72	78.58
Wool Dye 5 2%	Before Exposure	50.87	23.23	57.97	62.45	68.17	25.413		
	After Exposure	51.98	23.55	58.70	63.25	68.14	24.306	0.58	94.00
Wool Dye 6 1%	Before Exposure	77.22	10.85	68.57	69.42	81.01	5.169		
	After Exposure	77.97	9.26	54.26	55.05	80.32	2.558	4.89	54.78
Wool Dye 6 2%	Before Exposure	74.07	16.30	76.53	78.25	77.98	9.152		
	After Exposure	74.93	14.53	65.19	66.79	77.44	4.972	3.73	58.02

Sample Description	**UV Exposure**	**L***	**a***	**b***	**C***	**h°**	**K/S**	**DEcmc**	**%STR-WSUM**
Wool Dye 7 1%	Before Exposure	74.43	9.37	38.25	39.38	76.24	3.026		
	After Exposure	74.78	7.83	35.09	35.95	77.43	2.726	1.64	88.21
Wool Dye 7 2%	Before Exposure	69.09	11.05	41.60	43.04	75.13	4.893		
	After Exposure	68.71	10.24	38.03	39.38	74.93	4.447	1.54	91.33
Wool Dye 8 1%	Before Exposure	59.27	19.72	62.97	65.99	72.62	19.516		
	After Exposure	58.54	19.71	61.44	64.53	72.22	18.496	0.68	94.77
Wool Dye 8 2%	Before Exposure	50.16	22.26	56.41	60.64	68.46	25.416	0.70	
	After Exposure	49.58	22.69	55.48	59.94	67.75	24.131	0.70	94.94
Wool Dye 9 1%	Before Exposure	76.91	10.32	40.02	41.33	75.54	2.496		
	After Exposure	78.55	8.03	38.64	39.46	78.25	2.418	1.91	86.23
Wool Dye 9 2%	Before Exposure	55.60	21.04	58.53	62.20	70.23	20.388		
	After Exposure	56.15	20.44	57.23	60.77	70.35	18.965	0.57	90.13
Wool Dye 10 1%	Before Exposure	63.42	18.46	61.46	64.18	73.29	14.186		
	After Exposure	64.09	18.26	61.70	64.34	73.51	14.401	0.33	96.93
Wool Dye 10 2%	Before Exposure	67.19	13.38	46.26	48.16	73.87	7.876		
	After Exposure	66.79	11.18	39.92	41.45	74.36	5.875	2.68	81.53
Wool Dye 11 1%	Before Exposure	53.87	30.01	64.22	70.89	64.96	23.604		
	After Exposure	54.48	28.88	60.70	67.14	64.71	18.613	1.31	78.63
Wool Dye 11 2%	Before Exposure	48.51	30.61	57.68	65.30	62.04	26.777		

	After Exposure	47.87	29.89	55.89	63.38	61.86	25.824	0.75	96.19
Wool Dye 12 1%	Before Exposure	81.04	5.90	46.21	46.59	82.72	2.675		
	After Exposure	80.74	5.30	44.18	44.50	83.16	2.788	0.89	95.97
Wool Dye 12 2%	Before Exposure	79.19	8.12	50.27	50.92	80.83	3.616		
	After Exposure	79.19	6.30	46.68	47.10	82.31	3.190	1.74	87.35

C. Colour Parameters of undyed and dyed Silk fabric after 100hrs UV Exposure

Table 4. Colour parameters of undyed and dyed silk fabric

Sample Description	UV Exposure	L*	a*	b*	C*	hº	K/S	DEcmc	%STR-WSUM
Untreated Silk	Before Exposure	94.58	-0.29	5.11	5.12	93.23	0.054		
	After Exposure	89.08	0.61	18.52	18.53	88.12	0.427	14.39	678.11
Silk Dye 1 1%	Before Exposure	85.97	1.86	40.64	40.68	87.38	2.260		
	After Exposure	83.17	3.88	32.53	32.76	83.20	1.398	4.06	86.05
Silk Dye 1 2%	Before Exposure	83.08	4.64	49.60	49.81	84.66	4.738		
	After Exposure	79.42	7.18	39.53	40.18	79.70	2.641	4.82	81.43
Silk Dye 2 1%	Before Exposure	72.93	12.98	71.92	73.08	79.77	14.303		
	After Exposure	71.57	14.13	68.11	69.56	78.28	10.923	2.77	76.00
Silk Dye 2 2%	Before Exposure	62.21	20.16	68.34	71.25	73.57	20.337		
	After Exposure	64.34	18.07	69.42	71.14	75.41	16.296	2.15	80.12
Silk Dye 3 1%	Before Exposure	86.43	3.98	40.80	40.99	84.43	2.075		
	After Exposure	85.29	4.28	35.39	35.65	83.11	1.464	2.41	86.88
Silk Dye 3 2%	Before Exposure	83.35	7.87	48.62	49.25	80.81	3.748		
	After Exposure	82.22	7.48	43.65	44.29	80.28	2.798	2.02	88.68
Silk Dye 4 1%	Before Exposure	86.10	3.04	43.42	43.52	85.99	1.958		
	After Exposure	84.47	4.37	37.00	37.26	83.26	1.463	3.02	87.28
Silk Dye 4 2%	Before Exposure	84.56	5.67	45.83	46.18	82.94	3.851		
	After Exposure	81.79	6.47	41.22	41.72	81.08	2.720	2.32	97.11
Silk Dye 5 1%	Before Exposure	78.26	16.18	72.78	74.55	77.47	5.733		
	After Exposure	78.69	15.13	57.51	59.29	74.56	3.946	3.53	68.82
Silk Dye 5 2%	Before Exposure	73.81	22.68	81.69	84.78	74.48	11.690		
	After Exposure	73.89	21.17	78.22	70.99	72.67	9.101	3.57	77.85
Silk Dye 6 1%	Before Exposure	66.36	24.09	72.83	76.71	71.70	13.118		
	After Exposure	65.02	24.09	62.79	66.79	68.85	11.570	4.07	88.19
Silk Dye 6 2%	Before Exposure	57.76	28.87	69.35	75.12	67.40	21.780		
	After Exposure	55.57	29.49	64.78	71.18	65.52	20.941	2.37	96.27
Sample Description	**UV Exposure**	**L***	**a***	**b***	**C***	**hº**	**K/S**	**DEcmc**	**%STR-WSUM**
Silk Dye 7 1%	Before Exposure	84.22	5.16	28.90	29.35	79.87	0.991		
	After Exposure	83.64	4.79	26.02	26.46	79.57	0.928	1.48	94.50
Silk Dye 7 2%	Before Exposure	80.23	7.50	32.89	33.73	77.16	1.591		
	After Exposure	80.38	7.17	29.10	29.97	76.16	1.319	1.84	86.26
Silk Dye 8 1%	Before Exposure	66.50	16.34	66.28	68.26	76.15	14.980		

	After Exposure	69.05	15.37	70.36	72.02	77.68	13.82	2.06	92.25
Silk Dye 8 2%	Before Exposure	59.05	20.84	65.55	68.78	72.36	21.113		
	After Exposure	60.60	19.26	67.47	70.16	74.07	19.250	1.63	91.17
Silk Dye 9 1%	Before Exposure	85.49	3.66	33.43	33.63	83.75	1.375		
	After Exposure	86.07	4.73	34.86	35.18	82.28	1.198	1.05	87.12
Silk Dye 9 2%	Before Exposure	82.62	7.84	38.21	39.01	78.41	1.724		
	After Exposure	84.94	4.45	39.14	39.39	83.51	1.747	3.07	89.14
Silk Dye 10 1%	Before Exposure	82.47	5.10	33.91	34.29	81.45	1.688		
	After Exposure	82.56	5.59	29.93	30.45	79.42	1.234	2.05	83.72
Silk Dye 10 2%	Before Exposure	78.06	7.72	37.31	38.10	78.31	2.548		
	After Exposure	78.68	7.44	31.89	32.74	76.87	1.743	2.50	77.52
Silk Dye 11 1%	Before Exposure	74.00	26.50	50.25	56.81	62.19	2.424		
	After Exposure	76.79	21.93	39.21	43.99	63.06	1.914	3.98	78.96
Silk Dye 11 2%	Before Exposure	72.89	26.89	51.17	57.81	62.28	3.538		
	After Exposure	73.31	28.51	50.03	56.98	61.67	3.267	0.59	92.34
Silk Dye 12 1%	Before Exposure	86.05	2.67	35.77	35.87	85.73	1.477		
	After Exposure	88.02	2.11	36.33	36.39	86.67	1.329	0.87	89.97
Silk Dye 12 2%	Before Exposure	87.55	1.95	38.86	38.91	87.12	1.685		
	After Exposure	84.57	3.48	35.40	35.57	84.39	1.550	2.26	91.98

D. Colour Parameters of undyed and dyed Nylon fabric after 100hrs UV Exposure

Table 5. Colour parameters of undyed and dyed nylon fabric

Sample Description	UV Exposure	L*	a*	b*	C*	h°	K/S	DEcmc	%STR-WSUM
Untreated	Before Exposure	93.56	-0.53	3.59	3.63	98.34	0.052		
	After Exposure	92.32	-0.30	4.10	4.11	94.14	0.059	0.80	141.42
Nylon Dye 1 1%	Before Exposure	80.22	10.75	54.05	55.11	78.75	6.301		
	After Exposure	80.20	10.80	49.04	50.21	77.58	4.684	1.98	81.08
Nylon Dye 1 2%	Before Exposure	78.23	10.72	64.23	65.12	80.53	12.785		
	After Exposure	77.84	11.03	60.82	61.82	79.72	10.048	1.29	86.30
Nylon Dye 2 1%	Before Exposure	49.81	29.67	59.71	66.68	63.58	28.490		
	After Exposure	59.88	25.11	56.25	61.26	64.45	21.117	4.08	74.12
Nylon Dye 2 2%	Before Exposure	53.80	40.88	68.67	79.91	59.23	30.594		
	After Exposure	57.56	36.95	65.80	75.46	60.68	18.667	2.72	60.26
Nylon Dye 3 1%	Before Exposure	77.49	15.43	64.40	66.23	76.53	9.291		
	After Exposure	78.34	15.00	61.80	63.60	76.35	8.059	0.97	85.63
Nylon Dye 3 2%	Before Exposure	76.37	19.20	72.01	74.52	75.07	16.203		
	After Exposure	76.34	17.78	69.03	71.29	75.55	14.729	1.14	89.46
Nylon Dye 4 1%	Before Exposure	83.70	7.84	58.67	59.19	82.39	8.302		
	After Exposure	82.43	7.67	55.17	55.70	82.09	6.687	1.36	91.46
Nylon Dye 4 2%	Before Exposure	79.29	13.44	66.66	68.00	78.60	15.873		
	After Exposure	78.98	14.40	65.54	67.20	77.63	14.090	0.81	95.30
Nylon Dye 5 1%	Before Exposure	50.25	28.93	62.38	68.76	65.12	30.317		
	After Exposure	50.25	29.25	61.55	68.14	64.59	29.589	0.55	95.29

Nylon Dye 5 2%	Before Exposure	47.15	28.82	57.53	64.35	63.39	30.774		
	After Exposure	47.12	28.64	56.83	63.64	63.25	29.533	0.28	96.17
Nylon Dye 6 1%	Before Exposure	82.35	8.70	74.18	74.69	83.31	4.752		
	After Exposure	83.02	8.05	62.94	63.46	82.72	2.750	3.72	60.62
Nylon Dye 6 2%	Before Exposure	79.56	14.69	84.82	86.08	80.18	9.439		
	After Exposure	78.85	12.71	74.90	75.98	80.37	6.108	3.15	67.43

Sample Description	UV Exposure	L*	a*	b*	C*	hº	K/S	DEcmc	%STR-WSUM
Nylon Dye 7 1%	Before Exposure	78.17	10.56	41.62	42.93	75.77	3.000		
	After Exposure	80.05	9.97	36.71	41.80	74.49	2.213	3.72	73.76
Nylon Dye 7 2%	Before Exposure	69.32	14.92	46.14	48.49	72.08	5.654		
	After Exposure	74.34	12.42	38.62	44.24	72.28	4.176	3.97	73.85
Nylon Dye 8 1%	Before Exposure	64.70	22.05	61.41	65.25	70.25	12.132		
	After Exposure	70.93	21.07	49.45	51.88	70.37	7.081	8.49	58.36
Nylon Dye 8 2%	Before Exposure	58.20	26.06	61.66	66.94	67.09	20.178		
	After Exposure	62.63	22.25	55.60	59.27	68.39	14.427	5.47	71.49
Nylon Dye 9 1%	Before Exposure	78.60	11.28	49.22	50.50	77.09	3.423		
	After Exposure	80.78	9.03	41.75	42.72	77.79	2.474	3.16	65.62
Nylon Dye 9 2%	Before Exposure	73.81	14.97	52.26	54.36	74.01	4.986		
	After Exposure	76.81	12.03	44.96	46.54	75.02	3.500	3.22	63.20
Nylon Dye 10 1%	Before Exposure	50.71	20.85	59.56	63.11	70.71	29.89		
	After Exposure	51.32	21.36	61.45	65.11	70.13	28.11	0.67	94.04
Nylon Dye 10 2%	Before Exposure	46.04	22.18	54.18	58.54	67.73	30.514		
	After Exposure	46.76	21.32	55.31	60.64	67.02	28.494	0.98	93.34
Nylon Dye 11 1%	Before Exposure	63.39	30.26	67.90	74.34	65.98	13.823		
	After Exposure	65.99	27.51	55.85	62.87	61.75	11.050	3.65	79.93
Nylon Dye 11 2%	Before Exposure	65.90	34.44	66.64	75.02	62.67	16.263		
	After Exposure	66.19	32.93	58.57	69.75	59.34	12.709	4.17	78.14
Nylon Dye 12 1%	Before Exposure	79.13	14.67	58.36	60.17	75.89	5.814		
	After Exposure	81.72	10.79	49.03	50.21	77.59	3.510	3.88	58.82
Nylon Dye 12 2%	Before Exposure	81.01	13.36	57.11	58.65	76.84	5.190		
	After Exposure	81.91	11.70	50.13	51.48	76.86	3.639	2.63	72.07

Undyed and Dyed wool fabrics are exposed to UV radiation for 100 hours. Colour parameters such as L a b c h, K/S of unexposed and exposed fabrics are measured on reflectance spectrophotometer (i7, X-rite), Colour Strength after exposure and colour difference between unexposed and exposed sample is also measured. The results are mentioned in table no. 3-5. From the result, it is observed that after 100 hrs UV exposure most of the wool fabric dyed with synthesized dyes retain colour strength in the range of 54.78 – 96.93%, dyed silk fabric retain colour strength in the range of 68.82 – 97.11% whereas nylon fabric dyed with synthesized dyes retain colour strength in the range of 58.36 – 96.17%.

E. Fastness properties of Wool

Table 6. Washing, light and rubbing fastness of undyed and dyed wool fabric

Testing		% Shade	Washing Fastness			Light Fastness	Rubbing Fastness	
Sr. No.	Sample Name		Change in shade	Staining on Wool	Staining on Cotton		Dry Rub	Wet Rub
1	Dye 1	1%	4-5	5	4-5	6	5	5
		2%	4-5	4-5	4-5	6	4-5	4-5
2	Dye 2	1%	5	5	5	4-5	5	4
		2%	4-5	5	4-5	5	5	4-5
3	Dye 3	1%	4	4-5	4	6	5	4-5
		2%	3-4	3-4	3-4	6	5	4-5
4	Dye 4	1%	4-5	4	4-5	6	5	4-5
		2%	5	5	5	7	5	4-5
5	Dye 5	1%	4-5	4	4-5	5	5	4-5
		2%	5	5	5	4-5	4-5	4
6	Dye 6	1%	4	4-5	3-4	6	5	4-5
		2%	5	5	5	5-6	5	4-5
7	Dye 7	1%	4-5	4-5	5	6	5	5
		2%	4-5	5	4-5	6	4	4
8	Dye 8	1%	4-5	4-5	4	4-5	4 5	4
		2%	5	5	5	4	3-4	3
9	Dye 9	1%	4-5	4-5	4-5	5-6	4	4
		2%	5	5	5	5-6	3-4	3-4
10	Dye 10	1%	4-5	4-5	4	6	4-5	4-5
		2%	5	5	5	5-6	4	4
11	Dye 11	1%	4	4-5	4	6	3	3
		2%	4-5	4	5	5	3-4	3-4
12	Dye 12	1%	4-5	5	3-4	7	4	4
		2%	4-5	5	4-5	6	4-5	4-5

F. Fastness properties of Silk

Table 7. Washing, light and rubbing fastness of undyed and dyed silk fabric

Testing		% Shade	Washing Fastness			Light Fastness	Rubbing Fastness	
Sr. No.	Sample Name		Change in shade	Staining on Silk	Staining on Cotton		Dry Rub	Wet Rub
1	Dye 1	1%	5	5	5	6	5	4-5

		2%	5	5	5	6	5	4-5
2	Dye 2	1%	5	5	5	5	5	4-5
		2%	4-5	4-5	4-5	4-5	5	4-5
3	Dye 3	1%	5	5	5	7	5	4-5
		2%	4-5	4-5	5	7	5	5
4	Dye 4	1%	5	5	5	7	5	5
		2%	5	5	5	6	5	5
5	Dye 5	1%	5	5	5	5-6	5	5
		2%	5	5	5	5-6	5	4-5
6	Dye 6	1%	5	5	5	6	5	5
		2%	5	5	5	5	5	5
7	Dye 7	1%	5	5	5	6	5	5
		2%	4-5	4-5	4-5	5	5	5
8	Dye 8	1%	5	5	5	5-6	5	5
		2%	5	5	5	5-6	3-4	4
9	Dye 9	1%	5	5	5	6	4-5	4-5
		2%	4-5	5	4-5	6	4	4
10	Dye 10	1%	5	5	5	6	5	5
		2%	4-5	4-5	4-5	6	4-5	4-5
11	Dye 11	1%	4-5	4-5	4-5	4-5	3-4	4
		2%	4	4	4-5	5	4	3-4
12	Dye 12	1%	5	5	5	7	4-5	5
		2%	4-5	4-5	4	7	4-5	4

G. Fastness properties of Nylon

Table 8. Washing, light and rubbing fastness of undyed and dyed nylon fabric

Testing		**% Shade**	**Washing Fastness**			**Light Fastness**	**Rubbing Fastness**	
Sr. No.	**Sample Name**		Change in shade	Staining on Nylon	Staining on Cotton		Dry Rub	Wet Rub
1	Dye 1	1%	4-5	4-5	4	6	5	5
		2%	4-5	4-5	4-5	6	5	4-5
2	Dye 2	1%	4-5	4-5	4	4-5	5	5
		2%	4	4	3	5	4-5	4
3	Dye 3	1%	4-5	4-5	3-4	6	5	5
		2%	4	4	4-5	6	5	5
4	Dye 4	1%	5	5	5	6-7	5	5
		2%	5	5	5	7	5	5

5	Dye 5	1%	4-5	4	4	5	5	5
		2%	4-5	5	4-5	4-5	4-5	5
6	Dye 6	1%	4-5	4-5	4-5	4-5	5	5
		2%	5	5	5	5-6	5	5
7	Dye 7	1%	3-4	3-4	3-4	5-6	5	5
		2%	4-5	5	5	5	5	5
8	Dye 8	1%	4-5	4	4-5	5	5	5
		2%	4	3-4	3-4	5	5	5
9	Dye 9	1%	3-4	3-4	3-4	5	3-4	4-5
		2%	5	5	5	4-5	3	4
10	Dye 10	1%	3-4	3-4	3-4	5	4-5	5
		2%	5	5	5	5	4-5	5
11	Dye 11	1%	5	5	4-5	5-6	3	3
		2%	5	5	5	5	4-5	4
12	Dye 12	1%	5	5	5	6	4-5	4
		2%	4	4	3-4	6	4	4

From table no 6-8 it is observed that wool, silk and nylon fabric dyed with newly synthesized acid dyes exhibited good to excellent fastness to washing, light and rubbing.

V. CONCLUSION

The UV rays protective dyes based on 4-hydroxy benzophenone, 2,4-di hydroxy benzophenone and 2-hydroxy-4-methoxy benzophenone are sythesised using simple diazo-coupling process. All the wool, silk and nylon fabrics dyed with sythesised dyes shows less than 5% UVA and UVB transmission indicating good protection against UV radiation, Sythesised dyes also exhibits good to excellent washing, rubbing and light fastness properties when applied on wool, silk and nylon.

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