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 synthesised 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 (ultraviolet protection factor) 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 nitrite, sodium carbonate, Dimethylformamide, Acetone, Methanol 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 process. 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/m2, 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 synthesized azo dyes was recorded on Perkin Elmer UV-Vis spectrometer Lambda. The L*, a*, b*, C*, h°, 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, metaanilic acid/orthanilic acid (1.73 g, 0.01 mol) and Na2CO3 (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 0–5°C with an ice bath. Then 2.5 ml hydrochloric acid was cooled to 0–5°C and poured 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, Na2CO3 (1.059g, 0.01) and NaOH (0.4gm, 0.01 mol) was dissolved in 50 mL H2O 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°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 synthesised 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

![Synthesis scheme of benzophenone based acid dyes](image)

Figure 1: Synthesis scheme of benzophenone based acid dyes (6a-6d) (7a-7d) and (8a-8d)
Table 1. Properties of Synthesised Acid dyes

| Dye No. | Dye                        | Compound Structure                              | Molecular Formula | Yield (%) | Elemental analysis     | M.P. (°C) | Wavelength (in Methanol) | Colour |
|---------|---------------------------|-------------------------------------------------|-------------------|-----------|-------------------------|-----------|--------------------------|--------|
| Dye 1  | Orthanilic acid/2,4-diOH Benzophenone (7a) | ![Compound Structure](image1) | C$_{19}$H$_{14}$N$_2$O$_6$S | 82.15     | C, 57.28; H, 3.54; N, 7.03; O, 24.10; S, 8.05 | 226  | 290/360nm                | ![Color](image2) |
| Dye 2  | Orthanilic acid/4-OH Benzophenone (6a) | ![Compound Structure](image3) | C$_{19}$H$_{14}$N$_2$O$_5$S | 73.17     | C, 59.68; H, 3.69; N, 7.33; O, 20.92; S, 8.39 | 213  | 295/375 nm               | ![Color](image4) |
| Dye 3  | Orthanilic acid/2-OH,4-OCH$_3$ Benzophenone (8a) | ![Compound Structure](image5) | C$_{20}$H$_{16}$N$_2$O$_6$S | 79.54     | C, 58.25; H, 3.91; N, 6.79; O, 23.28; S, 7.77 | 185  | 325/445 nm               | ![Color](image6) |
| Dye 4  | Metaniolic acid/2,4-diOH Benzophenone (7b) | ![Compound Structure](image7) | C$_{19}$H$_{14}$N$_2$O$_6$S | 88.99     | C, 57.28; H, 3.54; N, 7.03; O, 24.10; S, 8.05 | 206  | 290/405 nm               | ![Color](image8) |
| Dye | Structure | Formula | Solubility | C, H, N, O, S (%) | Temp (°C) | Wavelength (nm) |
|-----|-----------|---------|------------|----------------|----------|----------------|
| 5   | ![Structure 6b](image) | C$_{19}$H$_{14}$N$_2$O$_5$S | 77.85 | C, 59.68; H, 3.69; N, 7.33; O, 20.92; S, 8.39 | 225 | 295/370 |
| 6   | ![Structure 8b](image) | C$_{20}$H$_{16}$N$_2$O$_6$S | 79.36 | C, 58.25; H, 3.91; N, 6.79; O, 23.28; S, 7.77 | 215 | 335/360 |
| 7   | ![Structure 7c](image) | C$_{20}$H$_{14}$N$_2$O$_5$ | 71.61 | C, 66.30; H, 3.89; N, 7.73; O, 22.08 | 135°C-140 | 290/360 |
| 8   | ![Structure 6c](image) | C$_{20}$H$_{14}$N$_2$O$_4$ | 86.95 | C, 69.36; H, 4.07; N, 8.09; O, 18.48 | 100-115 | 295/360 |
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 °C, maintained at this temperature for 1 hour, and then cooled to 50 °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

| Sr. No. | Sample Name | % Shade | Wool UPF | T(UV-A) | T(UV-B) | Silk UPF | T(UV-A) | T(UV-B) | Nylon 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       | Dye 1       | 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       | Dye 2       | 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       | Dye 3       | 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       | Dye 4       | 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      | Dye 5       | 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    |
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 dyed 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 synthesised 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 dyed 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 synthesised 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**

| 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| 5.04  | 164.82    |
|                     | After Exposure | 86.73 | -0.96  | 21.73  | 21.76| 92.54| 0.779| 2.84  | 94.06     |
| 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|       |           |
| 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 |       |           |
## 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*   | h*   | 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      |
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     |
Undyed and Dyed wool fabrics are exposed to UV radiation for 100 hours. Colour parameters such as L*a*b*, c*h* and 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%.

| Sample Description | UV Exposure | L* | a* | b* | C*  | h* | K/S   | DEcmc | %STR-WSUM |
|--------------------|-------------|----|----|----|-----|----|-------|-------|-----------|
| Nylon Dye 71%      | 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 72%      | 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 81%      | 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 82%      | 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 91%      | 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 92%      | 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 101%     | 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 102%     | 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 111%     | 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 112%     | 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 121%     | 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 122%     | 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     |
E. Fastness properties of Wool

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

F. Fastness properties of Silk

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

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

| Testing | % Shade | Washing Fastness | Light Fastness | Rubbing Fastness |
|---------|---------|------------------|----------------|------------------|
|         |         | Change in shade  | Staining on Nylon | Staining on Cotton | Dry Rub | Wet Rub |
| Sr. No. | Sample Name |                  |                |                  |          |         |
| 1       | Dye 1    | 1%               | 4-5            | 4-5              | 6        | 5        |
|         |          | 2%               | 4-5            | 4-5              | 6        | 5        |
| 2       | Dye 2    | 1%               | 4-5            | 4-5              | 4-5      | 5        |
|         |          | 2%               | 4              | 4                | 3        | 4-5      |
| 3       | Dye 3    | 1%               | 4-5            | 4-5              | 3-4      | 4-5      |
|         |          | 2%               | 4              | 4                | 5        | 3-4      |
| 4       | Dye 4    | 1%               | 5              | 5                | 6-7      | 5        |
|         |          | 2%               | 5              | 5                | 7        | 5        |
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 synthesized using simple diazo-coupling process. All the wool, silk and nylon fabrics dyed with synthesized dyes shows less than 5% UVA and UVB transmission indicating good protection against UV radiation. Synthesized dyes also exhibits good to excellent washing, rubbing and light fastness properties when applied on wool, silk and nylon.

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