Simultaneous Disperse Printing and UV-Protection of Wool/Polyester blended Fabric

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Abstract:
A new approach for enhancing disperse printability and UV-protection functionality of wool/polyester blended fabric (50/50) was carried out through incorporation of 4-hydroxybenzophenone, as UV-absorber, or ZnO-NP's, as UV-blocker, into the disperse printing formulation [$\beta$CD (10g/Kg), Na-alginate (500g/Kg), Citric acid (10g/Kg), DMDHEU (10g/Kg), PEG-600 (20g/Kg), and Disperse dye (20g/Kg)]. The obtained results show that the enhancement in UV-protection capacity follows the decreasing order ZnO-NP's > 4-hydroxybenzophenone keeping other parameters constant. The opposite holds true for the depth of disperse printings. The improvement of UV-protection ability depends on the loaded UV-protecting agent onto the fabric surface; along with the positive impact of the used disperse dye on absorbing and/or blocking of the harmful UV-B radiation. The durability of imparted UV-protection property is still high even after 15 washing cycles.

Keywords:
- wool/polyester blended disperse printing
- UV-protection
- Nanosized material
- UV-absorber or blocker

1- Introduction
UVR is an electromagnetic radiation between the wavelength 150-400 nm. The UVR is divided into UV-A (315-400 nm), UV-B (280-315 nm) which burns and skin cancer, and UV-C (100-280 nm). This type is completely absorbed by the oxygen and ozone from the atmosphere and does not reach the Earth's surface (1,2,3). Therefore, in recent years, researchers have devoted efforts to add or improve the properties of protection against the harmful UVR and their negative impact such as damage, skin photo cancer...etc by using UV-absorber such as derivatives of o–hydroxybenzophenones, o–hydroxyphenyl triazoles, o–hydroxy phenyl hydrazines (4-8) and/or inorganic UV-blockers like ZnO nanoparticles (8-12) and TiO$_2$ nanoparticles (12-16, 8).

The extent of UV-protection is governed by type of fibre, fabric construction, used coloring agents as well as finishing treatments (8)

The goal of this research is to develop a simultaneous process for upgrading the disperse printability and UV-blocking functionality of wool/polyester blend via incorporation of 4-hydroxybenzophenone, as UV-absorber, or ZnO-NP's, as UV-blocker, into the disperse printing formulation [$\beta$CD, Na-alginate, Citric acid, DMDHEU, PEG-600, and Disperse dye].

2- Experimental
2.1. Materials
The fabric used in this study was mill-scoured, and semi-bleached polyester/wool (50/50, 230g/m$^2$) blend.

Cavasol® W7 [beta cyclodextrin with seven glucose units, Wacker, Germany], Dialgin® LV-100 [Na-alginate of low viscosity, BF-Goodrich Diamalt, GmbH, Germany], , and Arkofix® NDF liquid C [low formaldehyde-reactant resin based on modified N-methylol dihydroxyethylene urea, Clariant], were of commercial grade. In addition, commercial disperse dyes namely Disperse Blue 183, and Disperse Red 74 Sinochem Ningbo, China, were used in this study. ZnO-nanoparticles [50% wt. % in water, particle size < 35nm, avg., Aldrich], 4-hydroxybenzophenone [analytical grade, Aldrich], and other laboratory, grade chemicals such as citric acid and PEG-600 were employed.

2. Methods
2.2.1. Functional finishing and printing in one step
The polyester/wool fabric samples were anti-UV finishing and disperse printing using the flat screen technique and the following print paste formulations:

<table>
<thead>
<tr>
<th>Components</th>
<th>g/kg paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>a- Disperse dye</td>
<td>20</td>
</tr>
<tr>
<td>Na-alginate (10%)</td>
<td>500</td>
</tr>
<tr>
<td>Citric acid</td>
<td>10</td>
</tr>
<tr>
<td>DMDHEU (35%)</td>
<td>10</td>
</tr>
<tr>
<td>$\beta$CD (Cavasol® W7)</td>
<td>10</td>
</tr>
<tr>
<td>PEG-600</td>
<td>20</td>
</tr>
<tr>
<td>(without using carrier)</td>
<td></td>
</tr>
<tr>
<td>b- UV-protector</td>
<td></td>
</tr>
<tr>
<td>4- Hydroxybenzophenone</td>
<td>0-20</td>
</tr>
<tr>
<td>Or ZnO-NP's (&lt; 35nm)</td>
<td>0-20</td>
</tr>
<tr>
<td>c- H$_2$O</td>
<td>X</td>
</tr>
<tr>
<td>Total</td>
<td>1000g</td>
</tr>
</tbody>
</table>

Printed fabric samples were then dried at 85°C for
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5 min and steam fixed at 110°C for 20 min using Ariolt® CSL-Steamer-Italy, rinsed thoroughly, soaped for 15 min at 60°C in the presence of 2g/L Leomin® W (nonionic wetting agent and detergent-BASF), then thoroughly rinsed and finally dried at 85°C for 5 min.

2.2.2. Testing

The depth of the obtained disperse prints, expressed as K/S, was measured at the wavelength of the maximum absorbance using an automatic-filter spectrophotometer, and calculated by the Kubelka Munk equation (Judd & Wyszeck, 1975)(17):

\[ K/S = \frac{(1-R)^3}{2R} \]

where K, S, and R are the absorption coefficient, the scattering sufficient and the reflectance at the wavelength of maximum absorbance of the used dye respectively.

Fastness properties to washing, crocking, perspiration and light of printed fabric samples were evaluated according to AATCC test methods: (61-1972), (8-1972), (15-1973) and (16A-1972) respectively.

UV-protection factor (UPF) was evaluated according to AS/NZS 4399-1996 standard.

3. Results and Discussion

For simultaneous disperse printing and anti-UV protection wool/polyester, both β-CD and 4-hydroxybenzophenone, as UV-absorber, or ZnO-NP's, as UV-blocker were included into finishing/printing paste followed by steam fixation. Factors affecting the simultaneous step such as β-CD content as well as type and concentration of UV-absorber, were studied.

3.1. β-CD content

Fig.1. reveals that i) the increase in β-CD up to 10g/kg improves the K/S values (18), ii) further increase in β-CD concentration leads to a marginal decrease depth of produced printings, and iii) increasing K/S value of printed wool/polyester samples is attributed to the positive role of loading βCD moieties onto the printed substrates via covalent bonds thereby creating hydrophobic cavities onto/within the fabric which, in turn facilitates and dye fixation (19).

The most probable mechanism of the interactions among DMDHEU, citric acid, βCD, disperse dye and the substrate during the steam fixation step is given below (18, 20).

Additionally, the increase in β-CD content i.e. beyond 10 g/Kg results in decreasing the depth of produced colour, which is ascribed to increased printing paste viscosity, side reactions with β-CD in addition of partial hydrolysis of the β-CD, which impedes the movement and hinders mobility of disperse dye molecules, thereby decreasing the depth of obtained disperse prints (21, 22).
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3.2. Anti-UV additive

Fig. 2 (a). shows that the effect of type and concentration of the added 4-hydroxybenzophenone, as UV-absorber, or ZnO-NP's, as UV-blocker on depth of printed fabric. It demonstrates that i) increasing the concentration 5g/Kg in the disperse printing paste along with other ingredients results in increasing the depth of the printed substrate. ii) increasing the concentration beyond 5g/Kg is accompanied by a slight decrease in depth of shade as a direct consequence of blocking and/or a decrease in number of dye sits on fabric thereby minimizing the transfer of disperse dye from printing paste film to fabric surface during fixation step, i.e. lower K/S values, and iii) improvement in K/S values followed the decreasing order: ZnO-NP's > 4-hydroxybenzophenone (4).

Fig. 2 (b). shows the variation in UV-protection factor as a function of 4-hydroxybenzophenone and ZnO-NP's concentration. Fig. 2(b) reveals that, i) inclusion of a benzophenone moiety, by loading 4-hydroxybenzophenone on/within the blended fabric, 5g/kg, brings about a remarkable improvement UV-protection values. Significant UPF values of 4-hydroxybenzophenone treated samples is a direct consequence of their higher UV-B absorption capacity as well as ability to dissipate energy via the structure change from keto to enol form as follows (23):

![Chemical structure](image)

and ii) increasing the nano ZnO-Sol up 5g/kg in printing formulation is accompanied by a remarkable increase in the UPF value, and indicates that the obtained printings have excellent UV-protection ability. The imparted UV-protection functionality to the disperse printed samples reflects the positive influence of nano-sized ZnO on improving the UV-blocking functionality most probably due to their increased surface area along with intense absorption in the UV-region (24-27, 4). Moreover, the improvement in the UV-blocking activity of the printed fabrics, is governed by: the absorption capacity of the ZnO-NPs-loaded substrate in the UV-region of 280-400nm (25, 28). The enhancement in UPF values of the produced disperse prints, as a function of kind of additive, follows the decreasing order: ZnO-NP's > 4-hydroxybenzophenone >> none.

3.3. UV-protective and printing properties

Effect of using 4-hydroxybenzophenone as UV-absorber or ZnO-NP's as UV-blocker on the printing and UV-protection properties of wool/polyester fabric samples using different disperse dyes along with β-CD in the printing paste are shown in Table 1. The data so obtained show an increase in K/S, fastness properties and the UV-protection capacity of the obtained
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Printings. Fastness properties of the obtained prints, using the nominated functional additives, were very good to excellent, irrespective of the used disperse dye. The increase in the obtained printing and protecting properties is governed by kind of disperse dye and type of the UV-protecting agent whether its UV-absorber or blocker. On the other hand the improvement in the UV-protection ability is determined by type of the functional additive, and follows the descending order: ZnO-NPs > 4-hydroxybenzophenone >> none. Wool/polyester prints have remarkable UV-protection functionality even after 15 washing cycles.

![Graphs showing UV-protection properties](image)

**Fig. 2. Effect of anti-UV type and concentration on K/S (a) and UPF (b) of the functionalized disperse prints**

Disperse Printing formulation: Disperse dye (20g/Kg); Sodium alginate (10%) (500g/Kg); citric acid (10g/Kg); ArkoFax® NDF (10g/Kg); β-CD (0-20g/Kg); PEG-600 (20g/Kg); UV-protector (0-20 g/Kg)

Drying followed by steam fixation at 120 °C/20min.

**Table 1. Effect of UV-protective/ printing properties of printed wool/polyester blended fabric using different disperse dyes along with β-CD in the printing paste.**

<table>
<thead>
<tr>
<th>Dye Stuff</th>
<th>UV-Protector</th>
<th>K/S</th>
<th>Incr. in K/S (%)</th>
<th>WF</th>
<th>RF</th>
<th>PF</th>
<th>LF</th>
<th>UPF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alt</td>
<td>C</td>
<td>Dry</td>
<td>Wet</td>
<td>Acidic</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alt</td>
<td>C</td>
<td>Alt</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>20.25</td>
<td>4</td>
<td>3-4</td>
<td>4</td>
<td>3-4</td>
<td>4</td>
<td>3-4</td>
<td>4</td>
</tr>
<tr>
<td>Disperse Blue 83</td>
<td>29.72</td>
<td>46.76</td>
<td>4-5</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>4-Hydroxybenzophenone (5g/Kg)</td>
<td>27.81</td>
<td>37.33</td>
<td>4-5</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>ZnO-NPs</td>
<td></td>
<td></td>
<td></td>
<td>Alt</td>
<td>C</td>
<td>Alt</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>None</td>
<td>5.14</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Disperse Red 74</td>
<td>9.56</td>
<td>85.99</td>
<td>3-4</td>
<td>4</td>
<td>3-4</td>
<td>4</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>4-Hydroxybenzophenone (5g/Kg)</td>
<td>8.03</td>
<td>56.22</td>
<td>4-5</td>
<td>4</td>
<td>3-4</td>
<td>4</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>ZnO-NPs</td>
<td></td>
<td></td>
<td></td>
<td>Alt</td>
<td>C</td>
<td>Alt</td>
<td>C</td>
<td></td>
</tr>
</tbody>
</table>

Disperse Printing: Disperse dye (20g/Kg); Sodium alginate (10%) (500g/Kg); citric acid (10g/Kg); ArkoFax® NDF (10g/Kg); β-CD (0-20g/Kg); PEG-600 (20g/Kg); UV-protector (5 g/kg); Drying followed by steam fixation at 120 °C/20min. K/S: color depth; WF: wash fastness; RF: rubbing fastness; PF: perspiration fastness; LF: light fastness; Alt: alteration; C: staining on cotton; UPF: ultraviolet protection factor; Values in brackets represent durability to wash after 15 laundering cycles.

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Conclusions

- Functionalized wool/polyester disperse prints were obtained by individual inclusion of 4-hydroxybenzophenone (5g/Kg) or ZnO-NP's (5g/Kg) along with β-CD (10g/Kg), Sodium alginate (500g/Kg), Disperse dye (20g/Kg), citric acid (10g/Kg), DMDHEU (10g/Kg) and PEG-600 (20g/Kg) in print formulation, followed by printing and steam fixing at 120°C/20min.
- The enhancement in UPF values of the produced disperse prints, as a UV-protecting agent, follows the descending order: ZnO-NP's > 4-hydroxybenzophenone >> none.
- Fastness properties of obtained prints using nominated functional additives, were very good to excellent.
- The printed fabric still had an excellent UV-protection functions even after 15 washing cycles.
- Finally, the suggested one step method can be adapted on industrial scale.

4- References

20. Ibrahim, N. A., El-Zairy, E. M. R., El-Zairy,