The effect of Inorganic Nanoparticles on Camouflage Properties of Cotton/Polyester Fabrics

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ABSTRACT
In order to make use of the reflectance behavior of woodland colors to produce dark brown in the UV-VIS-NIR bands, two colored pigments were used to print cotton/polyester (Co/PET) goods. Inorganic nanoparticles of TiO2, ZnO and Al2O3 were also loaded in the printing formulation. The reflectance profile of treated samples was studied using Jasco V-670 reflectance spectrophotometer. The effect of inorganic nanoparticles on rubbing, light and washing fastnesses as well as wettability and air permeability of printed samples were investigated. Tuning the reflectance curve of dark brown shade was successfully applied using colored pigments along with the nanoparticles. The results indicate that the presence of TiO2 and ZnO nanoparticles in load of 0.25-1 g/kg in printing pastes made significant changes in the behavior of IR band, though only a slight change in visible reflectance of printed fabrics was found. The samples containing nanoparticles showed great fastness levels in washing, rubbing and light fastness experiments and a considerable increase in wettability of printed fabrics. Furthermore, air permeability of printed fabrics containing nanoparticles was superior to samples printed without nanoparticles. Prog. Color Colorants Coat. 9 (2016), 29-40 © Institute for Color Science and Technology.

1. Introduction
Operational programs and supplying goals for armed systems become distinct through controlling, watching and organizing the location of enemy forces. It is then necessary for military groups and other things to be effectively concealed [1-4]. Camouflage and its usual methods is one of the ways to defend soldiers, weapons, equipment and systems. It is the most effective and usual non-agent defensive method in the classical military operations around the world. Camouflage is simply defined as a change in the shape of the forces and equipment to prevent enemies’ detection [4-8]. There are now new controlling devices in the electromagnetic spectrum in the battle field which are sensitive to NIR, FIR and Radar waves [6-8]. With the invention and production of devices such as photography and IR spectroscopy that can detect IR wavelength, it is easy to recognize objects even at night. Therefore, camouflage of personnel and

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equipment is necessary not only in visible areas, but also in higher bands [6-9].

Commonly, the hues of desert regions and vegetation are confined to bright stony, black stony, olive green, brown and deep green color, so it is necessary that IR reflectance values of formulation tune the IR reflectance of these shades in the background desert and plants [8]. A target is recognized through differences between the radiation effect and the local background (location of the thing). Raising distance between the observer and the target, variations are gradually concealed between colors as well as color and light [8, 9].

The probability of recognition depends on the colors and differences between backgrounds. Hence, the ability of concealment and camouflage in visible region and NIR largely depends on the surface colors of target, particularly distribution of reflection spectrum in these two areas [9]. It is then necessary for patterns to be coated or printed with some dyes or pigments having NIR reflectance to match the adjacent landscape [7-9]. Materials to camouflage textiles to be used in visible and NIR include conventional textile dyes such as vat [10-12], disperse [13], sulfur and acid dyes [14] and pigments [15-21]. Acid dyes have been used to camouflage nylon fibers [21] and disperse dyes on polyester samples [22].

Some researchers have reported on the production of camouflage fabrics by loading carbon black and titanium dioxide particles onto the printing formulation for matching khaki, olive green and brown colors in the visible and near-infrared bands [16-20]. NIR reflective pigments are one of the camouflage materials that are used for military applications. These pigments are in two types, i.e. organic and inorganic. Organic pigments that are NIR reflective can be coated on fabrics to provide NIR camouflage. Metal oxides are a class of inorganic pigments that have reflection in NIR waveband. These pigments absorb visible wave band and reflect NIR portion of electromagnetic spectrum. Nanoparticles of metal oxides are one of the important classes of inorganic pigments. These nanoparticles have high surface area. Nano TiO2 and ZnO are among the metal oxides which are used as pigments, adsorbents, and catalytic supports on fabrics [23, 24].

Most of colored pigments for printing of camouflage textiles have not appropriate reflection in the VIS-NIR bands and can't be used independently for this purpose. The novelty of our study is that to obtain camouflage properties, some nanoparticles with different particle size and refractive index to the printing paste was used.

This paper tends to create a suitable camouflage covering on cotton/polyester (Co/PET) fabrics in visible and IR areas. First camouflage covering in brown color according to the standards of military clothes of the forest regions was printed on the fabrics by certain selected colored pigments and different inorganic nanoparticles. Then, the sample reflectance in UV-VIS-NIR region was measured. Washing, light and rubbing fastness as well as the wettability, air permeability of the treated samples are also evaluated carefully.

2. Experimental

2.1. Materials and Methods

Co/PET (50/50) fabric with plain weaveed sample (180 g/m²) and 31 ends cm⁻¹ and 18 picks cm⁻¹ (Yazd Baf Co., Ltd, Iran) was applied as the substrate to consider the reflectance curve of diverse printing formulations. Fabrics print was prepared by a mixture of several pigments and metal oxide nanoparticles such as TiO₂, ZnO and Al₂O₃ to produce specific dark brown shade which is used in concealment patterns of a woodland camouflage cloth used as the reference. Table 1 shows the selected pigments and metal oxide nanoparticles used in print pastes to cover up purposes in UV-VIS-NIR bands.

The samples were printed with a conventional pigment printing method, using a stock paste of synthetic thickeners. A vinyl-acrylic binder was used in the formulation of stock paste. All samples were printed by a flat screen. Formulation of printing paste is presented in Table 2. To obtain a homogeneous printing paste, the materials were mixed well with a mechanical stirrer 2000 rpm for 15 minutes. Treated fabrics were simultaneously dried and cured in a laboratory stenter at 160 °C for 3 min. Printing formulations containing colored pigments were regulated to imitate UV-VIS-NIR reflectance performance of dark brown shade in the woodland region. Anatase TiO₂ (<26 nm), ZnO (<30 nm) and Al₂O₃ nanoparticles (<80 nm) were also loaded (0.25-1 g/kg) to explore their effect on the reflectance profile of fabrics.
2.2. Scanning Electron Microscope (SEM) Images

The surface morphology of the Co/PET fabrics before and after printing was studied using scanning electron microscope (SEM, Mira 3-XMU).

2.3. Measurement of Color Characteristics

Reflectance curves of each printed fabric were measured in the UV-Vis-IR wavelengths using a Jasco V-670 reflectance spectrophotometer in 190–2700 nm band width. Observation geometry in the above spectrophotometer was set to d/0. The reflectance behavior of samples was studied in comparison to the reflection performance of the reference fabric.

Reflectance of samples was measured in three different points of samples and their average value is reported.

Color values of printed samples in the visible area were evaluated under D65/10 illuminant/observer using an X-rite SP62 reflectance spectrophotometer. The CIE L*a*b* 1976 colorimetric space was used to assemble all color data points. Color difference (ΔE) was determined using Eq. (1):

\[ ΔE = \sqrt{ΔL^*^2 + Δa^*^2 + Δb^*^2} \]  \hspace{1cm} (1)

Which explains the differences in lightness ΔL*, redness–greenness Δa* and yellowness–blueness Δb* between any two positions.

Table 1: Applied pigments in the printing formulation.

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>Manufacturing factory</th>
<th>C.I.No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bercolin Brown CR</td>
<td>Bersa Turkey</td>
<td>-</td>
</tr>
<tr>
<td>Bercolin Yellow BG</td>
<td>Bersa Turkey</td>
<td>-</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>P-25 degussa</td>
<td>C.I. Pigment White 6</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>Nanomavadiranian</td>
<td>C.I. Pigment White 4</td>
</tr>
<tr>
<td>Aluminium oxide</td>
<td>Notrino</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2: Used materials in the printing formulation.

<table>
<thead>
<tr>
<th>Material</th>
<th>g/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bercolin Brown CR</td>
<td>32.5</td>
</tr>
<tr>
<td>Bercolin Yellow BG</td>
<td>40.2</td>
</tr>
<tr>
<td>synthetic thickeners</td>
<td>836.5</td>
</tr>
<tr>
<td>vinyl-acrylic binder</td>
<td>90.8</td>
</tr>
<tr>
<td>Total</td>
<td>1000</td>
</tr>
</tbody>
</table>
2.4. Wettability Time
The wetting time of printed samples was estimated using a drop test as characterized in ASTM D4772-09e1. According to the method, a 3×3 cm² square is selected as the sample. The sample is set in a hoop and it should be free from wrinkles. A water drop with height of 9.5 mm falls on to the sample and the time taken to sink below the sample surface as wetting time is measured. For each sample, the test was performed 10 times and then the average value is reported.

2.5. Air Permeability
Air permeability of samples was investigated using a Shirley air permeability tester according to ISO 9237, 1995. As specified in the standard test method, the samples were prepared with the size of 5×5 cm² and the pressure of machine was set at 15 mmHg.

2.6. Rubbing, Washing, and Light Fastnesses
Washing fastness of fabrics was evaluated according to ISO 105 C06 (1994). The printed fabrics in washing solution containing 5g/l non-ionic detergent (Acta wash, Arak, Iran), 2g/l sodium carbonate and 10 still bullets for 30 min at 95°C with L:R=1:50.

Based on AATCC 8-2005 for color fastness to rubbing, a colored test sample is rubbed with white crock test cloth under ten orders. To evaluate light fastness with ISO 105 B02 (1989) method, treated fabrics were exposed to high power light for 72h in a SDL-Atlas light fastness.

3. Results and discussion
3.1. SEM Analysis of Printed Fabrics
Figure 1 indicates SEM images of blank and brown printed fabrics containing TiO₂, ZnO and Al₂O₃ nanoparticles.

Figure 1: SEM images of different fabric surface (a) blank, (b) dark brown printed fabric with ZnO nanoparticles, (c) dark brown printed fabric with TiO₂, (d) dark brown printed fabric with Al₂O₃ nanoparticles.
It can be seen that the untreated fiber (blank sample) has smooth surface. Printing on fabrics formed thin homogeneous and fairly well dispersed films on the surface and between the fiber edges containing binder, nanoparticles and colored pigments.

3.2. Color Value Measurement

In order to verify the effect of visible camouflage, we measured the chromatic values ($L^*$, $a^*$ and $b^*$) of printed fabrics and then calculated the color differences between printed fabrics and reference sample. According to results shown in Table 3, the presence of nanoparticles in the printing formulation resulted in significant changes in color difference of samples in visible band. It was also revealed that the color difference between samples decreases by increasing the amount of inorganic nanoparticles. Samples containing $\text{Al}_2\text{O}_3$ have the lowest color difference. It is most probably owing to the size of $\text{Al}_2\text{O}_3$ nanoparticles which is larger than the others, so reduces the emissions. It was indicated that the printed samples containing ZnO and TiO$_2$ nanoparticles has color difference more than other samples. Color differences of printed samples with ZnO nanoparticles decreased with increasing their concentration, because by increasing of the quantity of nanoparticles, reduce the light emission and so the reflectance increase.

As it is clearly indicated in the table, the presence of nanoparticles in printing paste could decrease the lightness ($L^*$) of samples compared with the samples printed in the absence of nanoparticles. When the color difference of printed sample was less than of reference fabric, camouflage ability of the samples in the visible band is better.

### Table 3: Color characteristics of printed fabrics with various concentrations of TiO$_2$, ZnO and Al$_2$O$_3$ nanoparticles.

<table>
<thead>
<tr>
<th>Printed fabrics</th>
<th>ZnO g/kg</th>
<th>Al$_2$O$_3$ g/kg</th>
<th>TiO$_2$ g/kg</th>
<th>Color characteristic</th>
<th>Color Diff. $\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference fabric without nanoparticle</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>33.36</td>
<td>7.96</td>
</tr>
<tr>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>15.92</td>
<td>34.12</td>
<td>7.68</td>
</tr>
<tr>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>16.33</td>
<td>34.84</td>
<td>7.62</td>
</tr>
<tr>
<td>0.75</td>
<td>-</td>
<td>-</td>
<td>16.06</td>
<td>32.92</td>
<td>7.63</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>16.46</td>
<td>34.09</td>
<td>7.23</td>
</tr>
<tr>
<td>-</td>
<td>0.25</td>
<td>-</td>
<td>13.41</td>
<td>33.17</td>
<td>7.12</td>
</tr>
<tr>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>14.79</td>
<td>33.79</td>
<td>7.13</td>
</tr>
<tr>
<td>-</td>
<td>0.75</td>
<td>-</td>
<td>15.79</td>
<td>33.98</td>
<td>7.42</td>
</tr>
<tr>
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<td>1</td>
<td>-</td>
<td>33.78</td>
<td>7.06</td>
<td>14.12</td>
</tr>
<tr>
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<td>-</td>
<td>0.25</td>
<td>13.41</td>
<td>33.17</td>
<td>7.12</td>
</tr>
<tr>
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<td>-</td>
<td>0.5</td>
<td>13.15</td>
<td>33.46</td>
<td>7.34</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>0.75</td>
<td>15.08</td>
<td>34.14</td>
<td>7.14</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1</td>
<td>15.37</td>
<td>34.26</td>
<td>7.35</td>
</tr>
</tbody>
</table>
3.3. UV-Vis-IR reflection of printed fabric

Figures 2 indicates the reflection behavior of Co/PET fabrics which are printed to attain dark brown hue of the woodland regions with different amounts of mineral nanoparticle. It presents the reflection profile of dark brown treated samples containing various quantities of ZnO nanoparticles. The reflectance value of samples in IR band increases but with increasing ZnO, reflectance of samples was reduced about 5%. According to Figure 2, it can be found that the sample without nanoparticles had reflection close to the reference sample. Moreover quantities of ZnO nanoparticles in printing paste could reduce the reflectance in IR band totally only at 0.75g/kg ZnO presence.

Figure 3 shows the UV-VIS-NIR reflectance profile for samples with TiO$_2$ nanoparticles added to printing past. It is obvious from Figure 2 that by adding nanoparticles, no changes could be seen in reflection in visible area but only in IR region. According to Figure 3, at first by adding 0.25g/kg nanoparticles, sample reflection decreased significantly in IR area. But, by increasing the amount of nanoparticles, sample reflection decreased, and in 1g/kg of TiO$_2$, reflection became more than reference sample in visible area.

![Figure 2: UV-VIS-NIR reflectance curve of dark brown printed fabrics via different quantities of ZnO nanoparticles.](image-url)
Figure 3: UV-VIS-NIR reflectance curve of dark brown printed fabrics via different quantities of TiO$_2$ nanoparticles.

Figure 4 shows the reflectance profile of samples with Al$_2$O$_3$ nanoparticles in their printing past. It is shown that sample reflectance had little changes in visible but generally decreased in IR area. Raising load of nanoparticles in printing past did not change amount of reduction significantly. No significant relationship was also observed between increasing amount of nanoparticles and sample reflectance behavior.

The particle size of a metal oxide affects its color influencing reflectance properties. Due to high surface areas, metal oxide nanoparticles are also useful for coatings. According to K-M theory, the distribution of nanoparticles in printing paste plays a key role in light reflection. According to the properties of nanoparticles used in printing paste, since TiO$_2$ diameter is smaller than the two others, it has more reflection. But for Al$_2$O$_3$, which has the largest diameter, less reflection occurs. When the concentration of mineral pigments in colored films increases, the distance among the particles also decreases. According to the results shown in Figures 2 to 4, introducing TiO$_2$ to the printing paste causes more superficial reflection than printed fabrics without TiO$_2$ pigment. Therefore, the penetration depth of light decreases and results in absorption reduction. As a result, reflection increases and this is in complete accord with K-M theory.

3.4. Wetting time of Printed samples

Figure 5 indicates the effect of nanoparticles on wettability of fabrics. The wettability was calculated on printed areas. Each reported wetting time measurement is an average of five assessments on each specimen. Considering the wetting time of nanoparticles-free fabric (30.83s), the wetting time of printed fabrics containing nanoparticles increased.
Figure 4: UV-VIS-NIR reflectance curve of dark brown printed fabrics via different quantities of Al$_2$O$_3$ nanoparticles.

According to Figure 5, the wetting time of printed samples containing TiO$_2$ was improved from 50.6 to beyond 67.6s and for Al$_2$O$_3$, it changed from 37 to 58.7 s whilst for samples with ZnO nanoparticles it varied from 45.5 to 34.7s. So, the presence of TiO$_2$ and Al$_2$O$_3$ in printing paste increased the wetting time compared to the fabric without nanoparticles. According to the results and properties of nanoparticles, it can be
concluded that these nanoparticles increase contacting angle of drop with surface, hence, increasing the spreading time of the drop on the surface. In other words, these nanoparticles make roughness on the surface which decreases the superficial tension of the surface. Also raising the quantity of nanoparticles increased the absorption time. But, the absorption time decreased as the amount of ZnO nanoparticles in the printed samples increased.

A variation in wettability is an expression of the formation of nano-sized films on the surface of the fabric. This results in increments in covalent bonding between the uncondensed hydroxyl groups of inorganic pigments and the hydroxyl groups of Co/PET fabrics. Indeed, the observed wettability decline by rising the concentration of nanoparticles is in conformation with [25, 26].

3.5. Air Permeability of Printed Samples

Figure 6 indicates the alteration of air permeability of fabrics treated with distinct quantities of various nanoparticles. According to the trends shown in Figure 6 and in comparison with the sample that is free of inorganic nanoparticles, it can be noted that the overall air permeability of the samples is acceptable results. According to Figure 6, we can say that the air permeability of printed samples increases with the nanoparticles concentration in printing paste. It was also observed that samples containing TiO2 nanoparticles have higher permeability values as compared to other samples.

3.6. Color Fastness of Printed Fabrics

Table 4 shows optical stability of printed samples by different loads of nanoparticles. All the printed samples have high light stability which may be due to the structure of organic pigments used in printing dough. It also depends on the mineral nanoparticles, as nanoparticles prevent light from penetrating into deeper layers of covering films. Table 4 shows the washing and rubbing fastness properties of printed fabrics. Wash fastness ratings for all printed fabrics were 4–5. The results show that increasing the mineral nanoparticles concentration to three to four times results in adverse effect on color fastness. Thus it can be concluded that there is adequate linking between the fiber and pigments even at low concentration.

![Figure 6: The alteration of air permeability in printed fabrics with different concentrations of nanoparticles.](image-url)
Table 4: Washing, rubbing and light fastness of printed samples containing different quantities of nanoparticles

<table>
<thead>
<tr>
<th>Light fastness</th>
<th>Rubbing fastness</th>
<th>Washing fastness</th>
<th>Printed fabrics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>wet</td>
<td>STN*</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>4</td>
<td>5</td>
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</tr>
<tr>
<td>8</td>
<td>4</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>

*STN: staining on nylon, STC: staining on cotton

4. Conclusions
In this study, cotton/polyester fabrics with pigment printing formulation containing different concentrations of TiO2, ZnO and Al2O3 nanoparticles on the reflectance behavior of samples was investigated. Although adding nanoparticles caused changes of reflection in IR area, little changes were shown in the reflection of samples in UV-Visible areas. It can be concluded that adding ZnO and TiO2 nanoparticles to the load of 0.25-1g/kg could decrease reflection in IR area clearly in lower values, which was followed by an improving upshot in higher concentration of nanoparticles. The results are consistent with the KM theory, however, by changing the amount of Al2O3 nanoparticles in printing paste, the amounts of reduction did not change significantly. Also, no relationship was found between increasing
amounts of nanoparticle reflectance behavior of sample. Color difference of samples containing nanoparticles in visible area did not result in the same behavior in the IR region. By adding the amount of inorganic nanoparticles, the color difference between samples increased. The color difference of those samples with ZnO and TiO₂ nanoparticles was more than other samples. In other words, ZnO and TiO₂ nanoparticles leave an effect more than Al₂O₃ nanoparticle on the color difference of samples.

Increasing TiO₂, ZnO and Al₂O₃ nanoparticles did not considerably influence the washing, rubbing, and light fastnesses of the treated samples, and all samples were obviously good. Moreover, air permeability and wettability of printed fabrics was evaluated good.

5. References