



Functionalization of linen/cotton pigment prints using inorganic nano structure materials



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ABSTRACT

The present work opens up a novel strategy for the development of new multifunctional cellulosic pigment prints. The developed process aims at modifying the solvent-free pigment printing formulations via inclusion of certain inorganic nano materials namely silver (Ag-NPs), zinc oxide (ZnO-NPs), zirconium oxide (ZrO₂-NPs) or titanium dioxide (TiO₂-NPs) at 20 g/kg paste followed by screen printing and microwave fixation. The imparted functional properties together with the depth of the obtained prints are governed by the type of nano additives, type of binder and the pigment colorant. The imparted antibacterial and/or UV protection properties to the pigment prints were retained with an acceptable level (>70%) of durability even after 20 washing cycles. The presence of nano materials on the surface of the obtained pigment prints was confirmed using SEM images and EDX spectra.

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1. Introduction

Cellulose is the most abundant natural polymer of glucose available today worldwide. The abundant hydroxyl groups on each anhydroglucose unit allow extensive inter/intra molecular hydrogen bonding thereby enhancing the strength of the cellulose structure as well as offer an active sites for chemical modification and coloration. Cotton fibers are the purest form of cellulose ($\approx 90\%$ α -cellulose). Cotton cellulose offers better overall quality. Cotton fibers combine durability with attractive qualities and comfort (Choudhury, 2006; Koh, 2011). Flax or linen is the best among the bast fibers. Flax fiber is very compact and its strength makes it superior to cotton for certain applications. It is smoother than cotton and provides excellent summer suiting due to its good heat conductivity. Its chemical properties are similar to those of cotton. On the other hand, blending of similar or dissimilar textile fibers is carried out to: overcome the drawbacks of the used fiber components, achieve economic advantages, upgrade the performance and quality properties as well as to develop innovative textile products to meet the consumer demands (Ibrahim, 2011).

Printing process is a localized application of dyes or pigments in thickened form to a substrate to create an attractive design with well defined boundaries. Textile printing process can give a

quick response to changes in fashion, design, color trends and consumer demands thereby making just in-time processing feasible. In the textile industry, more than 50% of all printed substrates are cellulosic fabrics. Pigment printing dominates certain market and accounts for nearly 50% of printing production worldwide most probably due to its simplicity, low cost, minimum requirement for wet-processing as well as its applicability to a wide range of textile types. A typical pigment printing paste contains: pigment colorant, thickener, binder, cross-linker, handle modifier, surfactant and catalyst. Pigment printing stages are preparation of printing paste, printing of the fabric followed by drying and fixation. The development of textile printing has forced today's the researchers, designers, artists and industrialists to use latest technological innovations to move forward in the field of creation and production of innovative textile prints taking into consideration esthetic and production quality, functionality, environmental awareness, health and safety legislations, more design variety on shorter time and shorter production cycles (Dedhia & Shah, 2010; Giesen & Eisenlohr, 1994; Ibrahim, El-Zairy, Zaky, & Borham, 2005; Neral, Sostar-Turk, & Voncina, 2006; Park, 2010; Yaman, Ozdogan, & Seventekin, 2012).

On the other hand, functional finishes play a vital role for quality and value improvement of textiles and garments. Increasing consumer demands for innovative textile products and attitude toward hygiene and active lifestyle have created a rapidly increasing market for a wide range of antibacterial and UV-protection textiles, which in turn have stimulated intensive research and development efforts (Cakir, Budama, Topel, & Hoda, 2012; Cerkez, Kocer,

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Worley, Broughton, & Huang, 2012; Emam et al., 2013; Hashem, Ibrahim, El-Sayed, & El-Husseiny Sh Elanany, 2009; Hashemikia & Montazer, 2012; Hong & Sun, 2011; Ibrahim, Abdalla, El-Zairy, & Khalil, 2013; Ibrahim, Abo-Shosha, Gaffar, Elshafei, & Abdel-Fatah, 2006; Ibrahim, Amr, Eid, Mohamed, & Fahmy, 2012; Ibrahim, Eid, & El-Batel, 2012; Ibrahim, Eid, & El-Zariy, 2011; Ibrahim, Eid, Hashem, Refai, & El-Hossamy, 2010; Ibrahim, Eid, Youssef, El-Sayed, & Salah, 2012; Ibrahim, El-Zairy, Abdalla, & Khalil, 2013; Ibrahim, El-Zairy, El-Zairy, Eid, & Ghazal, 2011; Ibrahim, El-Zairy, El-Zairy, & Ghazal, 2013; Ibrahim, El-Zairy, & Eid, 2010; Ibrahim, Gouda, Hussein, El-Gammal, & Mahrous, 2009; Ibrahim, Gouda, & Zairy, 2008; Ibrahim, Mahrous, El-Gamal, Gouda, & Hussein, 2010; Ibrahim, Refaie, & Ahmed, 2010; Ibrahim, Refaie, Youssef, & Ahmed, 2005; Kathirvelu, D'souza, & Dhurai, 2008, 2009; Papaspyrde, Pavlidou, & Vouylouka, 2009; Sundaresan, Sivakumar, Vigneswaran, & Ramachandran, 2011). Additionally, the use of nanotechnology, as one of the key technologies of the 21st century, in the textile industry for medical, hygienic, and technical textiles has increased dramatically. The application of nano particles, especially nano-metals and metal oxides, to impart finished fabrics with a wide-range of functional performances has been the object of several studies (Dastjerdi & Montazer, 2010; Hebeish & Ibrahim, 2007; Simoncic & Tomsic, 2010; Wong, Yuen, Leung, Ku, & Lam, 2006).

With the above in mind, the main task of the present work is to find out the proper pigment printing formulations for attaining functionalized Linen/cotton pigment prints using certain inorganic nano-materials.

2. Experimental

2.1. Materials

Plain wave mill-scoured and bleached linen/cotton blend (65/35, 180 g/m²) was used throughout the study.

Printofix® Binder MTB-01 liquid (acrylate based copolymer, anionic, Clariant), GBinder® FMD (based on polyacrylate, anionic, BASF GB Chem., Egypt) Printofix® Binder 86 (acrylate based copolymer dispersion, Clariant), Alcoprint® PB-55 (aqueous dispersion of self-crosslinking butadiene copolymer, Ciba), Printofix® Thickener 160 EG liquid (synthetic thickening agent based on ammonium polyacrylate, Clariant), GBresin® CPN (based on hydroxymethylated 4,5 dihydroxyethylene urea, BASF/GB Chem., Egypt), and Durex® Silicone-1020 (based on modified polysiloxane microemulsion, Texchem, Egypt), Unisperse® Blue G pigment (Ciba), Unisperse® Red G pigment (Ciba), Imperon® Gold Gelb K-RN pigment (Dystar), Printofix® Blue R2H pigment (Clariant), Printofix® Yellow HRNC pigment (Clariant) and Imperon® Royal Blue SP pigment (Dystar), were of commercial grade.

Nano-sized ZnO (50 wt.% in water, particle size <35 nm avg.), ZrO₂ (10 wt.% in water, particle size <100 nm), and nano sized-Ag (0.02 mg/L, particle size 40 nm) were purchased from Sigma Aldrich.

All other chemicals used during this study such as Titanium tetrakispropoxide (analytical grade, Sigma), while ammonium persulphate [(NH₄)₂S₂O₈], nitric acid and 2-propanol were of laboratory reagent grade.

2.2. Methods

2.2.1. TiO₂ sol-gel preparation

TiO₂-nanoparticles were prepared as previously reported (Bozzi, Yuranova, & Kiwi, 2005) using titanium tetrakispropoxide precursor with 2-propanol and nitric acid particle size <10 nm (Ibrahim, Amr, et al., 2012).

2.2.2. All-in printing method

Guide formulation for all-in aqueous pigment printing using flat screen technique follows:

Printing paste components	g/kg paste
Pigment	20
Thickener	20
Binder	100
Crosslinker	20
Softener	10
(NH ₄) ₂ S ₂ O ₈	2
Nano-material	20
Water	808
Total	1000

Printed fabric samples were then simultaneously dried and fixed in a commercial microwave oven at power of 386 W/5 min.

2.3. Measurements

The color strength (K/S) values of the obtained pigment prints were determined from the reflectance measurements using the Kubelka Munk equation (Judd & Wyszeck, 1975):

$$K/S = \frac{(1 - R)^2}{2R},$$

where K/S is the ratio of absorption and scattering coefficient, *R* is the reflectance at the wave length of maximum absorbance of the used pigment colorants.

Fastness properties to washing, rubbing and light of the obtained pigment prints were determined according to AATCC Test Methods (61-1972), (8-1972), and (16A-1972), respectively.

Antibacterial activity assessment against G+ve bacteria (*Staphylococcus aureus*) and G-ve bacteria (*Escherichia coli*) was evaluated qualitatively according to AATCC Test Method (147-1988), and expressed as zone of growth inhibition (mm).

UV-protection factor (UPF) was assessed according to the Australian/New Zealand Standard Method 135-2000. According to the Australian classification scheme, fabrics can be rated as providing good protection, very good protection, and excellent protection if their UPF values range from is 15 to 24, 25 to 39, and above 40, respectively (Ibrahim, Refaie, et al., 2010).

Scanning electron microscope (SEM) images of the untreated and printed fabric samples were obtained with a JEOL, JXL 840A electron probe microanalyser, equipped with energy disperse X-ray (EDX) spectroscopy for the composition analysis.

The metal content of the obtained pigment prints was determined by a flame atomic absorption spectrophotometer GBC-Avanta, Australia.

Durability to washing was evaluated according to ASTM Standard Test Method (D737-96).

3. Results and discussion

The main task of the current work is to introduce a facile novel one-step procedure for producing linen/cotton pigment prints with demanded functional performances via individual inclusion of Ag-, ZnO-, ZrO₂- and TiO₂-nanoparticles (NPs) into the pigment paste formulation. Results obtained along with appropriate discussion follow.

3.1. Effect of TiO₂-NPs concentration

Fig. 1a shows that, within the range examined, increasing the TiO₂-NPs from zero up to 20 g/kg paste followed by screen printing and microwave fixation at 386 W for 5 min results in a significant improvement in the depth of the obtained pigment prints,

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