UV-Curable Coating Process on CMYK-Printed Duplex Paperboard, Part II: Effects of Nano-TiO_2 Modification

Mojtaba Soltani,[a,f]* Ali Asghar Rohani,[a] Omid Ramazani,[b] Hamid Reza Naji,[c] Abdul-Hamid Hazandy,[d] Lionel Simonot,[e] and Edi Suhaimi Bakar [f]

The influence of TiO_2 nano-particles (nano-TiO_2) was studied relative to the mechanical and optical properties of CMYK printed paperboard after coating with a UV-curable varnish. Commercial duplex paperboard (glazed grayback paperboard, 230 g/m^2) was printed with a CMYK offset printing process. Board samples were coated with a nano-TiO_2 modified UV-curable varnish at four treatment levels (0, 0.2, 0.5, and 1%) using an industrial screen-coating machine. The samples were then dried using a UV lamp in an industrial UV drying machine. Sample discoloration was measured spectrophotometrically using CIELab parameters (L^*, a^*, b^*, and ΔE) before and after coating. The whiteness, brightness, fold, and tear resistance of the ink films were also measured. The nano-treatment had a significant effect on the relative optical parameters, which resulted in increasing the lightness of the treated samples. Color change (ΔE) was recorded for all tested samples, and an unperceivable change was observed in case of the nano-treatment with 0.2% as the end value. The weakly perceivable changes were found in the cases of treatment with 0.5 and 1% nano-intensities. The nano-TiO_2 treatment significantly improved the fold and tear resistance of the samples.

Keywords: UV-curable coating; Nano-TiO_2; Offset CMYK inks; Color measurement; Duplex paperboard; Mechanical properties

*Contact information: a: Department of Wood and Paper Science and Technology, Islamic Azad University, Chalous Branch, P. O. Box 46615/397, Mazandaran, Iran; b: Department of Cellolose and Paper Technology, Shahid Beheshti University, Science and Research Park, Zirab campus, Zirab, Iran; c:Department of forest sciences, University of Ilam, Ilam, Iran.; d: Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, 43400 (UPM), Serdang, Selangor, Malaysia; e: Institut Pprime, Université de Poitiers, 86962 Chasseneuil- Futuroscope Cedex – France; f: Faculty of Forestry, Universiti Putra Malaysia, 43300 UPM Serdang, Selangor, Malaysia; * Corresponding author: soltani_iau@yahoo.com*

INTRODUCTION

Coating treatment is usually a widespread method in industries as well as the printing and packaging industries. It is used to enhance the optical properties and some mechanical properties such as abrasion and scratch resistance (Schwalm 2006; Vlad *et al.* 2009). UV-curable varnishes are commonly used to give a high gloss and rub-resistance to paperboard in the printing process (Karlović *et al.* 2010), However, reductions in the paperboard's folding and tear resistances are commonly associated with this coating process. On the other hand, the coating process can affect optical properties of printed inks in the CMYK offset process (Soltani *et al.* 2014). The CMYK color model (four color process printing) is a commercial printing process and means the four inks employed in a color printing, specifically cyan, magenta, yellow, and "key" (black) (Almutawa and Moon 1999; Bergman 2005).

Mechanical properties related to creasing and folding processes are crucial for the performance of a paperboard in the packaging industries. In the process of converting paperboards, making the corner is a critical phase. The straightness of a corner is also critical for the strength of the paperboard boxes. The corner must be sharp and form no cracks if folded by 90 degrees (Beldie 2001; Borbély 2010). Cracks on the fold-line in the paperboard box must be avoided, and this is a critical subject in box making processes (Beex and Peerlings 2009).

In some cases, UV-curable coatings have negative effects on mechanical behaviors, especially the brittleness of fold-lines. Increasing brittleness has resulted in some operational drawbacks including reducing foldability, breaking in the fold-line after a die-cutting process, and peeling in the coater, as well as limiting their aesthetic appeal (Coffin *et al.* 2011). In previous work by the authors (Soltani *et al.* 2014), it was found that the tear and fold resistances of printed paperboard were reduced through a coating process with the UV-cure coater.

Papermaking has, in effect, been practicing nanotechnology for a long time (Reitzer 2007). In recent years, there has been a great increase in the variety of additives used in papermaking and also the coating processes. Nanoparticulate additives are used, for instance, to improve printability, to increase surface strength, as crosslinking agents, for antistatic effects, as flame retardant treatments, as anti-slip coating materials, as microbiocides, and as miscellaneous chemicals for repelling or attracting various substances (Hajas *et al.* 2005; Mohiedin *et al.* 2010; Kharisov and Kharisova 2010; Shen *et al.* 2010). The use of nanoparticles is a convenient way to enhance the coatings properties, as their aspect ratio is high and their efficiency also can be high (Cristea *et al.* 2011). For stabilization of color under indoor conditions, nanoparticles can be dispersed in a continuous medium down to a primary particle size well below 50 nm. Such nanoparticles can be used in various coating applications without the need for additives (Hajas *et al.* 2005). Recently, inorganic nano-materials such as nano-TiO_2 and nano-ZnO have received much attention since their application was found to improve the optical properties and endowed other special functions to coatings (Shi *et al.* 2008; Sow *et al.* 2010, 2011).

The present work considered the use of nano-TiO_2 to enhance the properties of paper, wood, and other lignocellulosic materials (Blanchard and Blanchet 2011; Sun *et al.* 2010; Wang *et al.* 2012). The goal was to evaluate the effects of nano-TiO_2 in the coating formulation on the optical and mechanical properties of UV-curable coated-printed paperboard.

EXPERIMENTAL

Materials and Methods

Commercial glazed duplex paperboards were printed using a CMYK offset method (based on the paint-pattern shown in Fig. 1) and coated with a commercial UV-curable glossy varnish. The processes are described in Part 1 of this series (Soltani *et al.* 2014).

Fig. 1. Printing-test pattern by CMYK printing method

The materials, machines, and methods used in the printing and coating processes are described in Table 1. The Nano-TiO_2 specifications are described in Table 2.

Table 1. Materials, Machine, and Method Specifications in Printing and Coating Processes

Paperboard	Ink	Print Process and Machine	Coater	Coating Method and Machine
230 g/m^2, Grayback, Hansol, Korea	Standard CMYK ink - Heidelberg, Germany	CMYK offset printing method - GTO machine, Heidelberg, Germany	UV-Lacquer, FG.01, Laner, Turkey	Screen coating method - TMC machine - China

Table 2. Properties of Nano-TiO_2 Particles

Type	A.P.S (nm)	Purity (%)	S.S.A (m^2/gr)	Brand	M.P (%)
Anatase, Powder	30-50	99.8	80	Lotus, Iran	0, 0.2, 0.5, 1

A.P.S, average particle size; S.S.A, specific surface area; M.P, mix proportion.

After printing, the printed paperboard was room-conditioned at 22 °C ± 3 °C and 65% relative humidity (RH) for 24 hours.

The coating was then applied using a commercial UV-curable glossy varnish (UV-LACQUER). Prior to coating, lacquer was mixed with ethyl alcohol (50:50 ratio) to dilute the coater solution. Nano-TiO_2 particles were added at four levels (0%, 0.2%, 0.5%, and 1%) with the coater. In the mixing procedure, ethyl alcohol and nano-TiO_2 were first mixed together (nano particles dissolved in the alcohol), then the solution was added with the coater to provide the final lacquer for the printed sides of the paperboards along the machine direction. Finally, the coated printed paperboard was room-conditioned (Butkinaree *et al.* 2008).

Each measurement was carried out in exactly the same direction. There were five treatment groups, as listed in Table 3.

Table 3. Treatment Groups

Testing Groups	Un-Coated	Printed	Coated			
			Un-Treated	Nano-Treated (%)		
				0.2	0.5	1
Un.C	√	√	√	---	---	---
C-Un.T	---	√	√	---	---	---
C-N.T-0.2	---	√	---	√	---	---
C-N.T-0.5	---	√	---	---	√	---
C-N.T-1	---	√	---	---	---	√

Un.C, un-coated; C-Un.T, coated un-treated; C-N.T-0.2, coated nano-TiO_2 treated 0.2 %; C-N.T-0.5, coated nano-TiO_2 treated 0.5 %; C-N.T-1, coated nano-TiO_2 treated 1 %.

The statistical analyses for the mean differences in all treatments were tested using the Statistical Package for Social Science (SPSS® statistics processor, version 15) for Windows. The data were subjected to an analysis of variance (ANOVA) to examine the variability in the various properties. The Duncan multiple range test was used to separate the means of the various parameters at a 5 % probability.

SEM-EDX Analysis

An electron microscopy in combination with energy dispersive analysis of X-rays (SEM-EDX) was the method of choice for examining the distribution of nano-TiO_2 by using of a Jeol, JSM-6400 scanning electron microscope under an accelerating voltage of 10-15 kV. Prior to the SEM examination all the surfaces were sputtered with gold.

Tear and Fold Resistance

The fold- and tear measurements were carried out in accordance with the TAPPI Standards (T511-om-02 and T414-om-98, respectively). More information was described in Part 1 of this series (Soltani *et al.* 2014).

Colorimetric Properties

The reflectance spectra were measured in the 350 to 950 nm range with a spectrometer (QE65000 Ocean Optics™) by using an integrating sphere in the configuration 8°/diffuse with the specular component excluded (SCE) (see Appendix 1). This mode is adapted for shiny and high gloss surfaces such as the coated papers of this study where only the diffuse reflectance modifications are quantified (Schanda 2007).

The CIELab (L^*, a^*, and b^*) colorimetric coordinates were computed from the measured spectra in accordance with the TAPPI Standard (T524-om-02) and assuming an illuminant D65 and the standard observer 2°, CIE1931. Here, L^* refers to the lightness (from 0 to 100), a^* refers to the redness (typically from -60/green to 60/red), and b^* refers to the yellowness (typically from – 60/blue to 60/yellow) of the specimens. The differences in the lightness (ΔL^*) and chroma coordinates (Δa^* and Δb^*) between the uncoated and coated specimens were calculated using the following equations:

$$\Delta L^* = L^*_{C} - L^*_{Un} \qquad (1)$$

$$\Delta a^* = a^*_C - a^*_{Un} \quad (2)$$

$$\Delta b^* = b^*_C - b^*_{Un} \quad (3)$$

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (4)$$

In the foregoing equations, L^*_c, a^*_c, and b^*_c are L^*, a^*, and b^* values of the coated specimens, and L^*_{Un}, a^*_{Un}, and b^*_{Un} are L^*, a^*, and b^* values of the uncoated specimens, respectively.

The brightness and whiteness of the paper specimens were also measured according to TAPPI Standards (T452-om-92 and T462-om-05, respectively).

RESULTS AND DISCUSSION

SEM-EDX

The microanalysis concerning the structure and elemental composition of printed-coated paperboard, before and after TiO_2 nano-treatment was studied (Fig. 2).

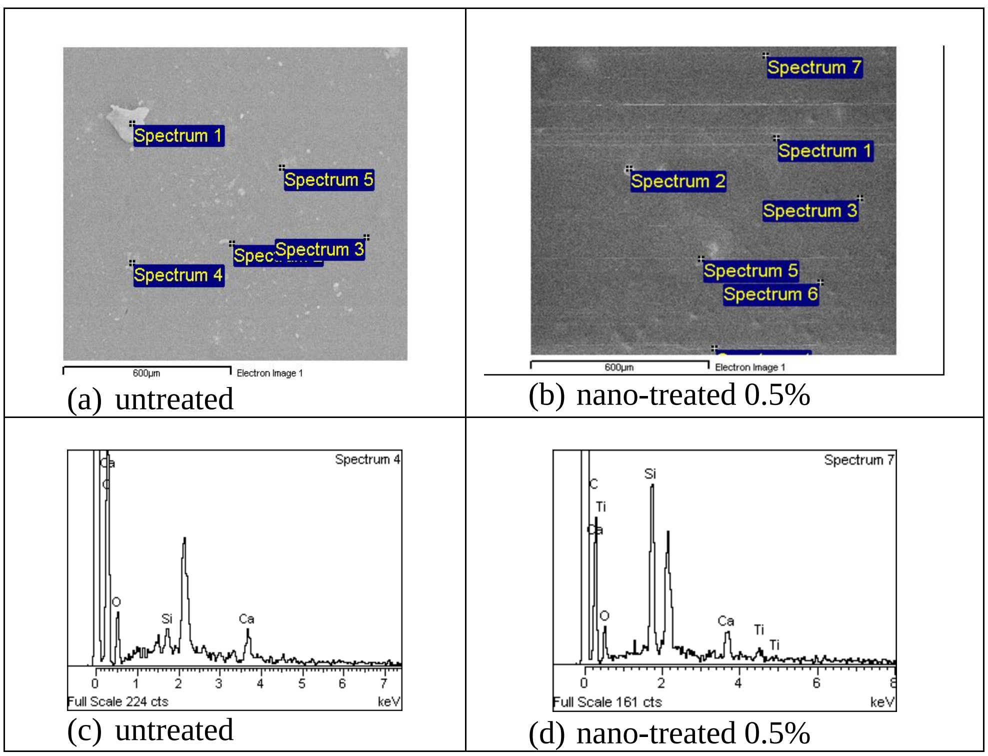

Fig. 2. SEM-EDX analysis of the printed coated paperboard

The EDX spectrum shows the characteristic peaks for Ti at 0.2, 4.5, and 5 keV as depicted in Fig. 2d. This explicitly indicated the presence of TiO_2 nanoparticles on the surface of the nano-treated sample.

Tear and Fold Resistances

The mechanical properties related to the tear and fold resistances, as important factors in the packaging process, are affected by UV-curable coatings (Beldie 2001; Soltani *et al.* 2014), where it may be modified by the use of nanoparticles. The application of the nano-TiO_2 resulted in significant changes in the fold and tear values (Fig. 3).

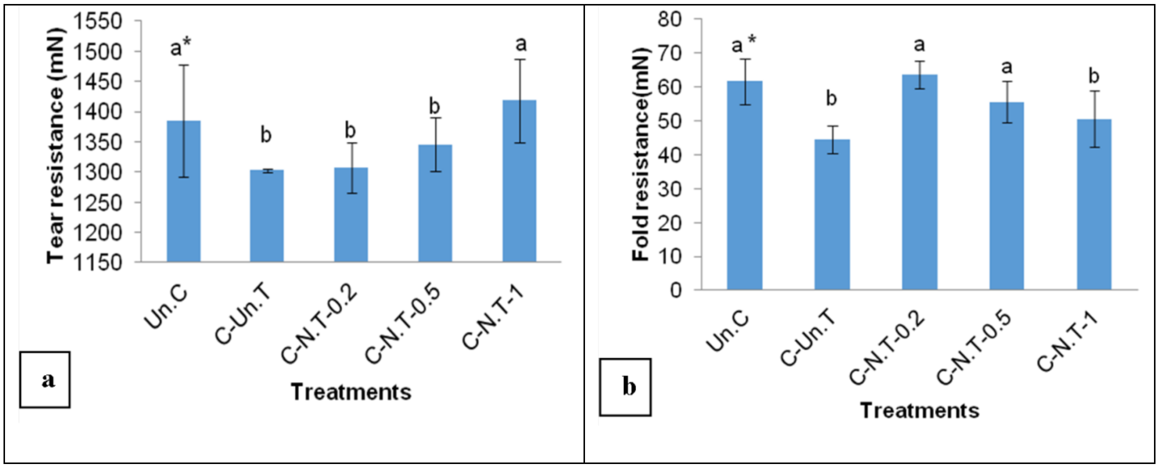

Fig. 3. The effects of UV-curable coater and nano-TiO_2 on the fold and tear resistances of CMYK printed coated paperboard (* The letters indicate the Duncan classification.)

Significant reductions in tear and fold resistances were demonstrated between the uncoated (Un.C) and un-treated coated (C-Un.T) paperboards, thus revealing the effect of the coating application (Fig. 3). The results indicate an increasing trend by adding different nanoparticle amounts, especially on the tear factor. The nanoparticle-modified coating increased the tear resistance; the maximum tear resistance was observed in the case of the 1% nano treatment (C-N.T-1) (Fig. 3a). Conversely, the fold resistance was decreased after coating (C-Un.T), but modification of the coating by addition of nano-particulate TiO_2 increased the fold resistance (Fig. 3b). The Duncan classification indicated that the uncoated sample and the nanoparticle-modified coated sample (0.2 and 0.5 intensities) were in a category with maximum amount of the fold resistance (Fig. 3b). Therefore, the level of 0.2 percent nano-TiO_2 was judged to be the best treatment in terms of the fold resistance index.

A UV-curable coating enhances the paperboard resistance to rubbing and scratching, but it increases the stiffness and brittleness of the paper (Coffin *et al.* 2011). The findings described above may have been due to an increase in composite stiffness in un-treated samples, resulting in reduced flexibility of the paperboard. This makes it somewhat brittle (Beldie 2001; Coffin *et al.* 2011). However, an improving trend in the mechanical properties resulted from the effects of nano-TiO_2, which resulted in a reduction in the stiffness of the composite. This was obtained by increasing the flexibility value (Fig. 3).

Colorimetry

CIELab color parameters

Significant changes were observed in the optical parameters of the CMYK printed paperboard after the nano-TiO_2 treatment (Fig. 4).

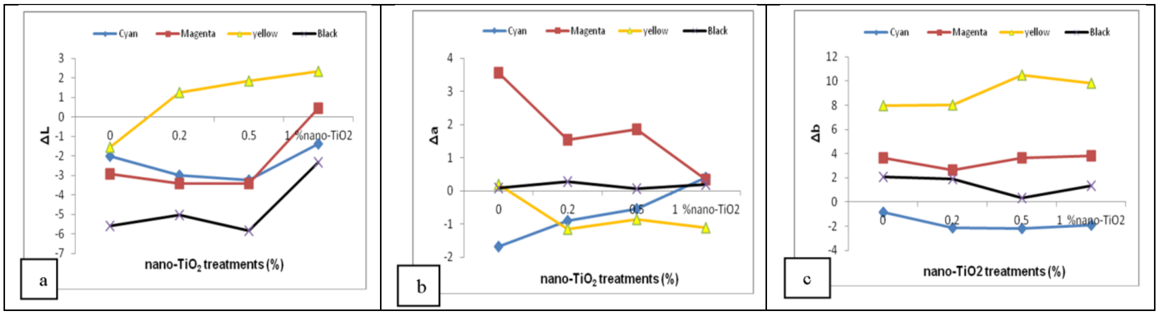

Fig. 4. The effects of nano-TiO_2 on the differences of color parameters of CMYK inks on the printed coated paperboard (Eqs. 1 to 3)

The authors' previous study indicated that the coating process increased the darkness of CMYK ink films (Soltani *et al.* 2014). The application of nano-TiO_2 resulted in different changes in the ΔL values with the inks. For yellow ink, the lightness increased with increasing content of nanoparticles, as depicted in Fig. 4a. However, there were no significant differences in untreated 0%, 0.2%, and 0.5% of nano-TiO_2 content, especially for cyan and magenta ink films. Meanwhile, the nanoparticle level of 1% significantly increased the lightness of all ink films. The tint-reducing power of TiO_2 may be described as the ability to lighten the ink films in nano-treated samples (Braun *et al.* 1992).

The values of Δa indicated a significant change in the magenta, yellow, and cyan ink films after use of the coating with the nano-TiO_2. In contrast, the nano-treated coating process showed an insignificant change for the Δa value of the black ink. In other words, the redness of the yellow and magenta inks were decreased; however, the cyan was increased by increasing the nano-TiO_2 intensity (Fig. 4b). The yellowness of the printed paperboard and effects of nano-treatment were compared with the Δb^* of the treated and untreated paperboards (Fig. 4c). The increase of Δb of yellow ink clearly indicated a significant increase of yellowness in the samples with increasing nanoparticle content; there were no significant differences between untreated (0 %) and nano-treated samples in other ink films. The results indicated that the nano-TiO_2 did not influence the yellowness of most of the inks in CMYK ink films. For the total color difference (ΔE) calculations, we choose the corresponding coated (without treatment) sample as reference to highlight the color changes specifically due to the nano-TiO_2 treatment (Fig. 5).

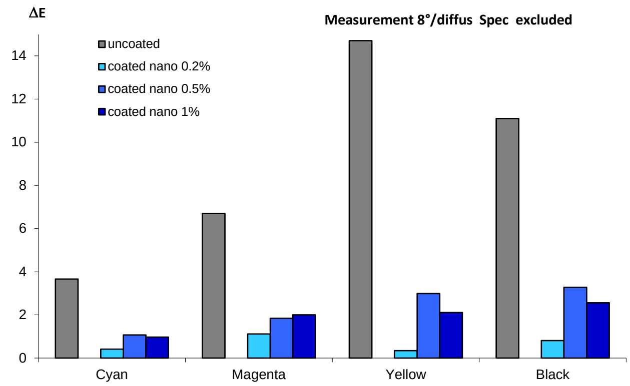

Fig. 5. The effects of nano-TiO_2 on total Color changes (ΔE). The coated without treatment samples were used as reference.

The results indicated that the coating (without treatment) greatly influenced the color perception. It should be noted that the highest stability was observed for cyan (ΔE<4) and the least was seen in the other inks ΔE>6 (Fig. 5) (Havlínová *et al.* 2002; Soltani *et al.* 2014). The treatment with nano-TiO_2 induced weak color changes, almost unperceivable by the eye (ΔE <1) in the case of the treatment with 0.2% and weakly perceivable (ΔE<3.5) in the case of treatment with 0.5 and 1% (Fig. 5) (Molkrzycki and Total 2011).

Whiteness and brightness

The whiteness index of the samples indicated that the coating process can noticeably improve cyan ink reflection, but the whiteness of the other CMYK inks was decreased after the coating process (Un.C compared to others in Fig. 6). The brightness of the CMYK inks was also decreased by the coating process (Fig. 6).

There were no significant differences between different levels of nano-TiO_2 treatment on the whiteness and brightness values of the coated paperboard, as shown in Fig. 6.

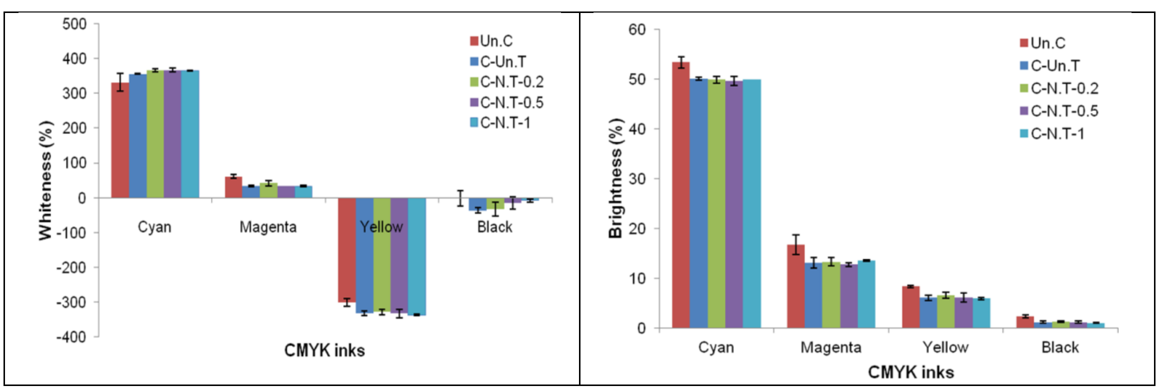

Fig. 6. The effects of UV-coating and nano-TiO_2 on whiteness and brightness of the CMYK printed coated paperboard

CONCLUSIONS

The UV-curable coating process was applied to printed paperboard to modify some mechanical drawbacks and enhance the optical stability. The nano-TiO_2 was used as a coater modifier.

Based on a recent study (Soltani *et al.* 2014), application of a UV-curable coating decreased fold and tear resistance and caused some drawbacks such as changing the reflection of inks from light to dark, yellowing the coated printed paperboard, and reducing the whiteness and brightness. This study set out to modify these properties using TiO_2 nano particles in the coating formulation. The findings are as follows:

1. The UV-curable coating with addition of nano-particulate TiO_2 exhibited better fold and tear resistances, compared to the untreated samples. The nano-TiO_2 improved the mechanical properties of the coated printed paperboard and modified the properties of the UV-curable coating.
2. For most of the CMYK ink films, the lightness notably increased, the redness differentially changed (based on different inks), and there was no significant change to yellowness, after treatment by the nano-TiO_2.
3. The nano-treatment did not significantly affect whiteness and brightness of the printed coated paperboard.
4. In contrast, the variations in total color difference showed an unperceivable color change in case of the nano-treatment with 0.2%, and weackly perceivable in the case of treatment with 0.5 and 1%.
5. The effects of the different levels of nano-TiO_2 indicated that the low level (0.2 %) of nano-particulate treatment can effectively improve the properties of UV-curable coated printed paperboard.

REFERENCES CITED

Almutawa, S., and Moon, Y. (1999). "The development of a connectionist expert system for compensation of color deviation in offset lithographic printing," *Artificial Intelligence in Engineering* 13, 427-434. DOI: 10.1016/S0954-1810(99)00019-9

Beex, L. A. A., and Peerlings, R. H. J. (2009). "An experimental and computational study of laminated paperboard creasing and folding," *International Journal of Solids and Structures* 46(24), 4192-4207. DOI: 10.1016/j.ijsolstr.2009.08.012

Beldie, L. (2001). *Mechanics of Paperboard Packages: Performance at Short Term Static Loading*. Lund University, Sweden.

Bergman, L. (2005). *Using Multicoloured Halftone Screens for Offset Print Quality Monitoring*, Halmstad University, Sweden.

Blanchard, V., and Blanchet, P. (2011). "Color stability for wood products during use: Effects of inorganic nanoparticles," *BioResources* 6, 1219-1229.

Bohlin, E. (2010). *Optics of Coated Paperboard: Aspects of Surface Treatment on Porous Structures*, Karlstad University, Sweden.

Borbély, Á. (2010). "Evaluation of offset prints on recycled carton substrates," *Óbuda University e-Bulletin* 1, 11-16.
Braun, J. H., Baidins, A., and Marganski, R. E. (1992). "TiO_2 pigment technology: A review," *Progress in Organic Coatings* 20, 105-138. DOI: 10.1016/0033-0655(92)80001-D
Butkinaree, S., Jinkarn, T., and Yoksan, R. (2008). "Effect of biodegradable coating on barrier properties of paperboard food packaging," *Journal of Metals, Materials and Minerals* 18, 219-222.
Coffin, D. W., Gustafsson, P.-J., Hägglund, R., Kulachenko, A., Mäkelä, P., *et al.* (2011). *Mechanics of Paper Products*, Walter de Gruyter.
Cristea, M. V., Riedl, B., and Blanchet, P. (2011). "Effect of addition of nanosized UV absorbers on the physico-mechanical and thermal properties of an exterior waterborne stain for wood," *Progress in Organic Coatings* 72(4), 755-762. DOI: 10.1016/j.porgcoat.2011.08.007
Efi™. Delta E, Delta H, Delta T: What Does It Mean? http://w3.efi.com/about-efi/overview.
Hajas, J., Lenz, P., and Schulte, K. (2005). "Enhancing mechanical properties of UV-curing wood varnishes by synergistic combinations of silicones and nano-alumina particles," Proc. RadTech Europe Conference and Exhibition, Barcelona, SP, October, 2005.
Havlínová, B., Babiakova, D., Brezova, V., Ďurovič, M., Novotna, M., and Belányi, F. (2002). "The stability of offset inks on paper upon ageing," *Dyes and Pigments* 54, 173-88. DOI: 10.1016/S0143-7208(02)00045-1
Karlović, I., Novaković, D., and Novotny, E. (2010). "The influence of surface topography of UV coated and printed cardboard on the print gloss," *Journal of Graphic Engineering and Design* 1, 23-31.
Kharisov, B. I., and Kharissova, O. V. (2010). "Advances in nanotechnology in paper processing," *International Journal of Green Nanotechnology: Materials Science & Engineering* 2(1), M1-M8. DOI: 10.1080/19430841.2010.488204
Molkrzycki, W. S., and Total, M. (2011). "Color difference ΔE – A survey," *Machine Graphic and Vision* 20(4), 33-411.
Reitzer, R. (2007). "Technology roadmap: Applications of nanotechnology in the paper industry," University of Jyväskylä: Jyväskylä, Finland.
Schanda, J. (2007). *Colorimetry: Understanding the CIE System*, John Wiley & Sons. DOI: 10.1002/9780470175637
Schwalm, R. (2006). *UV Coatings: Basics, Recent Developments and New Applications*, Elsevier.
Shen, J., Song, Z., Qian, X., Yang, F., and Kong, F. (2010). "Nanofillers for papermaking wet end applications," *BioResources* 5(3), 1328-1331.
Shi, H., Liu, F., Yang, L., and Han, E. (2008). "Characterization of protective performance of epoxy reinforced with nanometer-sized TiO_2 and SiO_2," *Progress in Organic Coatings* 62, 359-68. DOI: 10.1016/j.porgcoat.2007.11.003
Soltani, M., Veisi, R., Rohani, A. A., Ramzani, O., Naji, H. R., and Sohaimi Bakar, E. (2014). "UV-curable coating process on CMYK-printed duplex paperboard, Part I: Mechanical and optical properties," *BioResources* 9(1), 86-92.

Sow, C., Riedl, B., and Blanchet, P. (2010). "Kinetic studies of UV-waterborne nanocomposite formulations with nanoalumina and nanosilica," *Progress in Organic Coatings* 67, 188-194. DOI: 10.1016/j.porgcoat.2009.10.002

Sow, C., Riedl, B., and Blanchet, P. (2011). "UV-waterborne polyurethane-acrylate nanocomposite coatings containing alumina and silica nanoparticles for wood: Mechanical, optical, and thermal properties assessment," *Journal of Coatings Technology and Research* 8, 211-221. DOI: 10.1007/s11998-010-9298-6

Sun, Q., Yu, H., Liu, Y., Li, J., Lu, Y., and Hunt, J. F. (2010). "Improvement of water resistance and dimensional stability of wood through titanium dioxide coating," *Holzforschung* 64(6), 757-761. DOI: 10.1515/hf.2010.114

Vlad, M., Riedl, B., and Blanchet, P. (2009). "Anti-UV waterborne nanocomposite coatings for exterior wood," *International Conference on Nanotechnology for the Forest Products Industry*, Alberta, June 2009.

Wang, X., Liu, J., and Chai, Y. (2012). "Thermal, mechanical, and moisture absorption properties of wood-TiO_2 composites properties prepared by a sol-gel process," *BioResources* 7(1), 893-901.

Article submitted: April 22, 2015; Peer review completed: November 18, 2015; Revised version received and accepted: December 15, 2015; Published: January 11, 2015.
DOI: 10.15376/biores.11.1.1930-1940

APPENDIX 1

The light reflection giving rise to the perception of gloss is directed reflection called specular (Bohlin 2010). In the CIE colorimetry, the integrating spheres have played a major role in color quality control system. The integrating spheres have two alternative geometric configurations named Specular Component Excluded (SCX or SCE) and Specular Component Included (SCI) whether a gloss trap is used or not. Most of the instruments use an angle close to the perpendicular, usually 8°, to give the capability of including or excluding the specular reflectance while measuring (Schanda 2007).