MODULATION OF WATER BASED COMMERCIAL VARNISH BY ADDING ZnO AND SiO_2 NANOPARTICLES TO ENHANCE PROTECTIVE FUNCTION ON PRINTED PACKAGING

Tomislav Cigula, Tomislav Hudika, Marina Vukoje

University of Zagreb, Faculty of Graphic Arts, Zagreb, Croatia

Original scientific paper
doi: 10.5281/zenodo.5256586
thudika@grf.hr

Abstract: *The packaging sector of graphic industry is continuosly growing and developing in terms of packaging function, used materials and production technology. The aim of this paper was to evaluate modification of commercial water-based varnish by determining its protective properties regarding colour degradation as well as barrier properties. For that purpose a set of composite coatings of different composition was prepared and applied onto cardboard prints. The prepared samples were characterized by measuring CIE L*a*b*, colour density and water vapour transfer rate before and after accelerated ageing. Results showed that applying prepared nanocomposite coatings do not cause significant colour change (max.* dE_{2000} *= 2.84) but do increase the tone value at 80% nominal value for almost 5%. Furthermore, barrier to the water vapour is increased by adding nanoparticles. Adding ZnO into the composite decreases yellow fading because of accelerated ageing. This research proved the positive influence of added nanoparticles into the commercial varnish by increasing its protective role in print's ageing and barrier properties while just slightly changing the primary colour apearence.*

Keywords: cardboard packaging, functional coatings, nanoparticles, zinc oxide, silicon dioxide

1 INTRODUCTION

The printing industry, closely the packaging sector reached 917.1 billion US in the 2019 (Smyth, 2017) Entire sector is projected to experience a steady growth of 2.8% and reach 1.05 trillion US dollars by 2024 (Leblanc, 2019). The main idea of packaging is to preserve the product from any form of damage while remaining aesthetic throughout the product’s life cycle (Primary, Secondary & Tertiary Packaging | Saxon Packaging, no date). Today, market demands and competitiveness, as well as customer habits, require packaging to be innovative in its various segments - from design, materials choice, functionality, environmental sustainability and most of all, quality of the end-product. One of the most common quality factors are the prints colour consistency and structural stability when exposed to environmental factors such as the sunlight, heat, moisture, pollutant gases, grease, etc. which can considerably influence the quality (Aydemir and Yenidoğan, 2018). Moreover, there is an increasing effort to replace unsustainable and non-degradable polymeric materials with natural ones, mostly those based on paper and cardboard. But paper and cardboard themselves do not have mechanical properties that can match the properties of polymeric materials. However, by applying different coatings or varnishes these drawbacks can be overcome. In addition, most packaging materials can after printing be coated with a varnish that has both protective and decorative means (Kipphan, 2001). It is beneficial when coating has versatile protective gain i.e., to protect printed surface from colour degradation, to enhance the barrier properties, etc (Kipphan, 2001). To upgrade existing varnish benefits, it is possible to introduce certain compounds in the mixture, which are known to have desired protective potential. Those kinds of compounds are mostly nanosized (<100 nm) and can be homogenized in the commercial varnishes (Schoff, 2014). Several research have been conducted with commercial varnish and nanosized particles, where nano sized compounds have enhanced some features of the varnish (Salla, Pandey, and Srinivas, 2012; Hudika et al., 2020). Moreover, nano sized compounds were also studied in the mixture with bio polymer PCL, where again, nanoparticles did show beneficial properties (Cigula et al., 2020). Most research conducted up to now, are mostly focused on the application of nanomodified biodegradable coatings in packaging and printing applications. Although such coatings significantly improve the functionality and properties of packaging materials and stability of prints, their application requires additional units (devices), i.e. additional investment costs. by modification of existing varnishes by nanoparticles, easier use, especially for small and medium printers, would be allowed. Therefore, the aim of this research is to modify commercial water-based varnish and determine its protective properties regarding colour degradation as well as barrier properties. In other hand, the proposed nanocomposite coating should not cause colour change of the original print.

2 MATERIAL AND METHODS

Offset prints on cardboard were prepared for the purpose of this research. The cardboard used was coated with gloss finish (UPM Finesse gloss paper 300g/m^2) and printed using quickset process inks (Novavit Supreme Bio, Flintgroup). Printing was conducted on a sheedfer offset printing press KBA Rapida 105 in compliance with Fogra PSO 2016, i.e. ISO 12647-2:2013 (ISO, 2013).

Nanocomposites were prepared by dispersing two nanoscale compounds, ZnO (Alfa Aesar NanoArc) and SiO_2 (Aerosil 200 Fumed Silica) in a commercial water-based varnish (TerraWet High Gloss Coating G9/285, ACTEGA,). The two sets of nanocomposites (WD+SiO_2 and WD+ZnO) were prepared by adding nanoparticles in designated weight ratios 0.1%, 0.5%, 1%. The third set (WD+SiO_2+ZnO) was prepared by adding both nanoparticles by fixing concentration of SiO_2 to 0.5% and altering ZnO weight ratio (0.1%, 0.25% and 0.5%). Smaller maximal concentration of ZnO in third set is due to the increased viscosity of nanocomposite.

The homogenization of nanoparticles into water-based varnish (WD) was conducted using ultrasound dispenser Hirrlscher UP100H for 30 minutes at 100% amplitude and 100% power. During homogenization process, the containers were cooled in a bath with water at 7 °C. The prepared nanocomposites were applied onto the printed samples using K202 Control Coated in controlled conditions defined by the ISO 187:1990 using coating bar 1 leading to the wet coating thickness of approx. 6 µm (RK Printcoat instruments, no date). After drying, samples were characterized and exposed to an artificial ageing process in the Cofomegra Solarbox 1500e Xenon Test chamber for 30 hours at 550 W/m^2, temperature of 50 °C and by using indoor filter (Solarbox, nd).

The prepared samples were analysed by determining ink density and colour coordinates in all three stages (original prints, coated samples and aged samples) The measurements were performed by Techkon SpectroDens spectrophotometer (Techkon GmbH, no date). The setting for the colorimetric measurements were illuminant D50, standardized observer 2°, no polarization filter, filter M1 and calibrated on absolute white. Instrument setting for the density measurements were density statues E, illuminant D50, no polarization filter and calibrated on paper sample (for all measurements calibration was set to printed sample) (ISO, 2013).

In addition to detect change of the barrier properties, water vapour transmission rate (WVTR) was determined. WVTR was determined using gravimetric cup method (water method). In this type of test the sample acts as a water-vapor barrier where water is inside of the glass container and this represents 100% humidity on the test start (ASTM E96/GB 1037, 2013). In this research, amount of the water was 75 mL while samples were at the distance of approx. 10 mm from the water surface. Samples were weighted at 0 h, 24 h, 48 h and 72 h. This way, the given results represent the weight change of the lost water in a given time interval. The WVTR was calculated using equation (1). The results are presented in g/day*m^2:

$$WVTR = \frac{\Delta m}{\Delta t * A} \qquad (1)$$

where Δm is the change in the glass container mass in grams, Δt is the time between sample weighing given in days and A is the area of the sample in m^2.

The samples were in a surrounding with temperature of 22 ± 1 °C and RH of 60 ± 2 %.

3 RESULTS AND DISCUSSION

3. 1 Colorimetric characterization

To determine the influence of the coating process on the colour perception, colour difference (dE_{2000}) was calculated from measured L*a*b* values (Sharma, Wu, and Dalal, 2005) (Mokrzycki and Tatol, 2011). In Table 1 it can be seen the colour difference of primary colours (black(K), cyan (C), magenta (M) and yellow (Y)) between uncoated and sample coated by nanocomposites including SiO^2 (WD+SiO_2) or ZnO (WD+ZnO) nanoparticles.

Table 1: Colour difference (dE_{2000}) between uncoated and samples coated with WD+SiO_2 and WD+ZnO

w (nanoparticle) / %	***0.1***		***0.5***		***1.0***	
sample	*WD+SiO_2*	*WD+ZnO*	*WD+SiO_2*	*WD+ZnO*	*WD+SiO_2*	*WD+ZnO*
paper	*0.60*	*1.81*	*0.54*	*0.65*	*0.57*	*0.81*
K	*2.00*	*2.10*	*1.80*	*2.84*	*1.31*	*2.15*
C	*0.43*	*0.69*	*0.27*	*0.40*	*0.35*	*0.44*
M	*0.81*	*0.74*	*0.75*	*0.65*	*0.83*	*0.86*
Y	*0.79*	*0.27*	*0.58*	*0.40*	*0.32*	*0.58*

The coating process does not significantly affect the colour reproduction of primary colours. Higher differences can be seen at K, due to the darkening of the print after coating process (CIE L* of the uncoated print is approx. 20 while CIE L* of coated samples are approx. 17).

Table 2: Colour difference (dE_{2000}) between uncoated and sample coated with WD+0.5% SiO_2+ZnO

w (ZnO) / %	0.1	0.25	0.5
paper	0.81	0.52	0.69
K	2.15	2.36	1.75
C	0.44	0.39	0.19
M	0.86	1.30	1.32
Y	0.58	0.56	0.54

Observing Table 2 it can be noticed that adding two types of nanoparticles into the WD will not cause significant colour differences of prints. The difference is slightly higher on M due to the increase of the CIE b* coordinate (original print has CIE b* = -2.02 while sample coated with w(SiO2) = 0.5% and w(ZnO) = 0.5% has CIE b* = 0.62).

The varnishing often causes yellowing of the print which in colour coordinates reflects as a b* coordinate increase (Simonot and Elias, 2004).

3. 2 Densitometry of the prints

Density measurements were performed on the patches of different nominal tone values (0 – 100%) and afterward tone values (TV) were calculated using Murray-Davies formula (Lychock, 1995).

To enable better assessment of coating influence, in Table 3 and tone value differences are presented, where positive values mean that TV of coated sample is higher than one on the uncoated sample.

The TV difference is highest on yellow halftones (Y) in the mid-range with highest difference on sample coated with WD+ZnO, W(ZnO) = 0.1 %. The lowest influence is noticed at magenta (M).

The results of calculated TV differences indicate that coating of the samples could lead to darkening of the halftone images. Furthermore, having in mind tolerances set by the standard, these differences of round 5% cause new process setting (ISO, 2013).

Table 3: TV difference between coated and uncoated samples on TV patch with nominal value of 40 and 50 %

w (nanoparticle) / %	***0.1***		***0.5***		***1.0***	
sample	*WD+SiO_2*	*WD+ZnO*	*WD+SiO_2*	*WD+ZnO*	*WD+SiO_2*	*WD+ZnO*
K40	*4.01*	*4.98*	*3.83*	*3.43*	*5.15*	*3.56*
K80	*1.34*	*1.31*	*1.54*	*0.56*	*1.57*	*0.88*
C40	*4.18*	*5.11*	*2.97*	*2.87*	*3.06*	*3.92*
C80	*0.96*	*1.03*	*1.17*	*1.08*	*1.56*	*1.30*
M40	*3.09*	*5.03*	*4.16*	*4.15*	*3.31*	*3.88*
M80	*1.87*	*1.25*	*1.05*	*0.47*	*1.10*	*1.02*
Y40	*4.17*	*5.47*	*4.50*	*5.15*	*5.26*	*4.26*
Y80	*1.65*	*1.53*	*1,24*	*1.34*	*1.46*	*1.21*

Table 4: TV difference between coated and uncoated samples on TV patch with nominal value of 40 and 50 %

w (ZnO) / %	***0.1***	***0.25***	***0.5***
K40	*3.928008*	*4.75*	*5.02104*
K80	*1.559564*	*1.334319*	*1.802298*
C40	*4.20198*	*6.240383*	*5.09207*
C80	*1.240181*	*1.116752*	*1.278077*
M40	*3.026352*	*6.20354*	*5.183982*
M80	*0.475654*	*1.586287*	*1.480573*
Y40	*3.245057*	*6.196283*	*5.2874*
Y80	*0.531726*	*1.605734*	*1.495779*

Although coating with nanocomposites including only one nanoparticle, SiO_2 or ZnO, the coating with nanocomposite including both nanoparticles in proposed concentrations of w(SiO_2) = 0.5% and w(ZnO) = 0.25 and 0.5% lead to a significant increase of the TV, i.e. darkening of the halftone images. These results are in line with results of the colour difference (Table 2).

3. 3 Barrier behaviour of coated samples

Figure shows WVTR of investigated samples. As mentioned before, SiO_2 is a nanoparticle which should increase the barrier properties to the water vapour and therefore, measurement of WVTR od samples coated with nanocomposite including ZnO was performed only on sample with w(ZnO) = 0.5%.

KD and WD in Figure are samples without coating (KD) and sample varnished with plain WD (without adding nanoparticles), respectively.

As it can be noticed from the Figure 1 adding nanoparticles significantly decreases WVTR, i.e. increases barrier behaviour. The increase in the w(SiO_2)

causes decrease of the WVTR. The lowest WVTR was measured on sample with both particles included (w(SiO_2) = 0.5% and w(ZnO) = 0.5%).

By adding only the ZnO nanoparticles in the WD, the lowest decrease of VWTR was noticed due to its partly ionic and a partly covalent character, i.e. due to molecularly and dissociative adsorption of water onto ZnO.

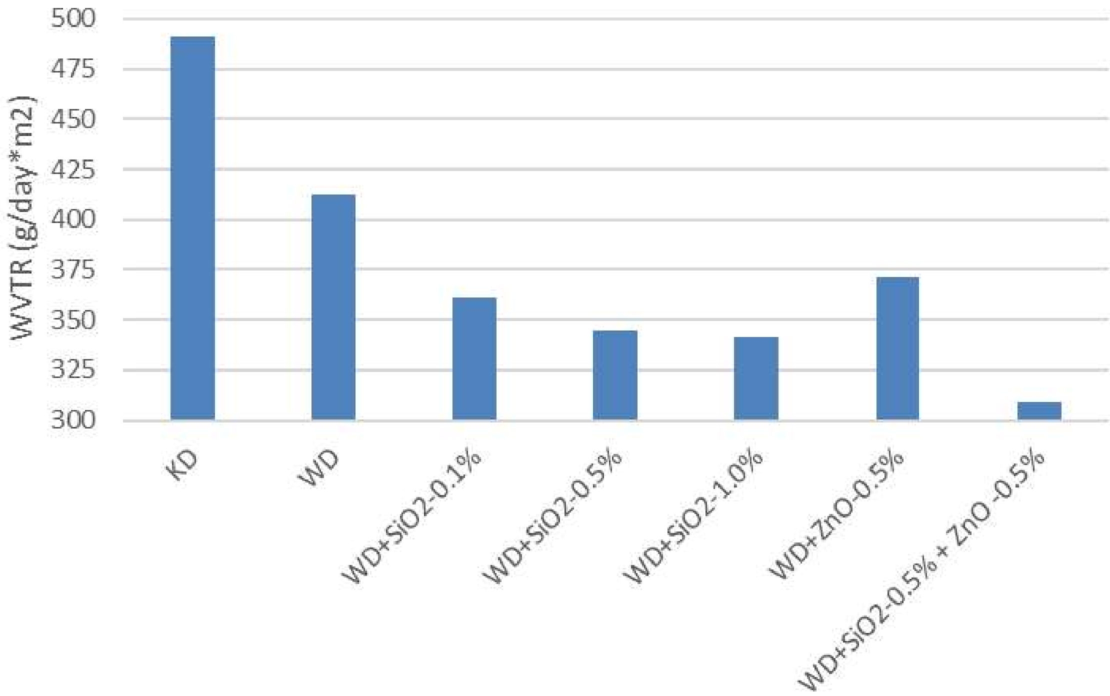
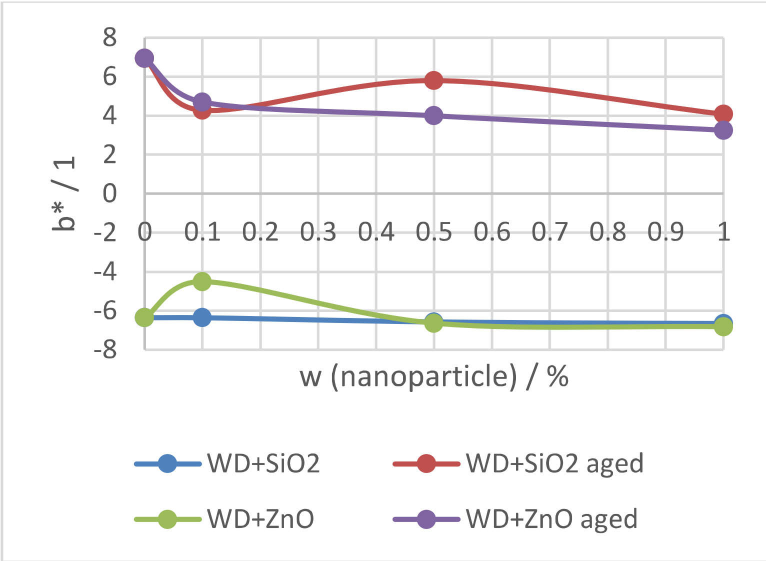


Figure 1: WVTR of investigated samples

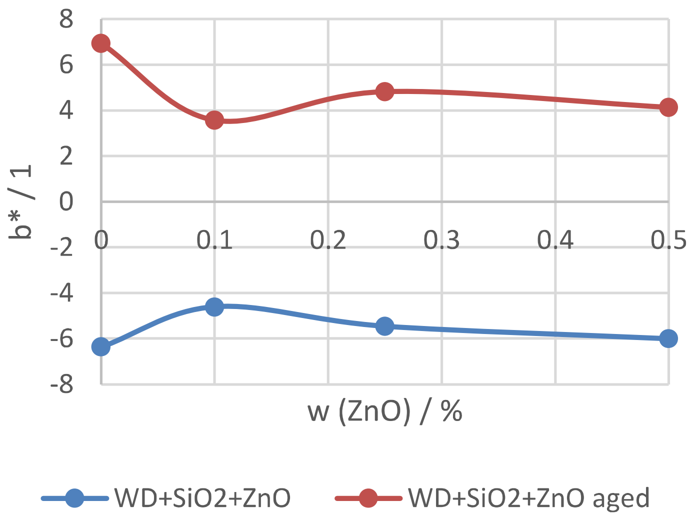
According to Bota et al. (Bota *et al.*, 2017) dissociative adsorption of water vapour is mostly occurring on the Zn– polar surface, while the molecular adsorption occurs on the O– polar surface. It was found that water molecules are mostly dissociatively onto ZnO at all temperatures in the form of OH· and H· radicals, where the adsorption of OH· radical takes place onto a Zn^+ site on a zinc oxide surface. The unpaired electron on OH· radical combines with free electron associated with Zn^+ site, which results in a strong homopolar bond.

3. 4 Results of the samples exposed to the artificial ageing process

Previous research showed that in the proposed ageing time (30h) and irradiance (550 W/m^2) black and cyan are not changed, while yellow fades most significantly (Hudika *et al.*, 2020)(Cigula *et al.*, 2020). This experiment confirmed that behaviour, so in this study, only data for the yellow are presented.



a)



b)

Figure 2: CIE b coordinate of paper coated with nanocomposites: a) WD + SiO2/ZnO b) WD + 0.5 % SiO2 + ZnO*

From the Figure 2 it is visible that adding ZnO nanoparticles is probably improving degradation of optical brighteners in paper (the used paper has high optical brighteners according to the OBA check function of spectrophotometer (Techkon GmbH, no date)). Furthermore, it can be seen that even nanocomposites with SiO_2 are improving the b* coordinate increase, i.e. degradation of optical brighteners. The same behaviour is present in the nanocomposites which include mixture of both investigated nanoparticles.

Figure 3 shows density decrease (ΔD) as a consequence of the colour fading due to UV irradiation. ΔD is calculated using equation 2:

$$\Delta D = D_b - D_a \quad (2)$$

where D_b is density of sample before artificial ageing process and D_a is density of the sample after artificial ageing.

Please note that for sample WD+SiO2+ZnO, the mass concentration of SiO_2 in all nanocomposites is set to 0.5%.

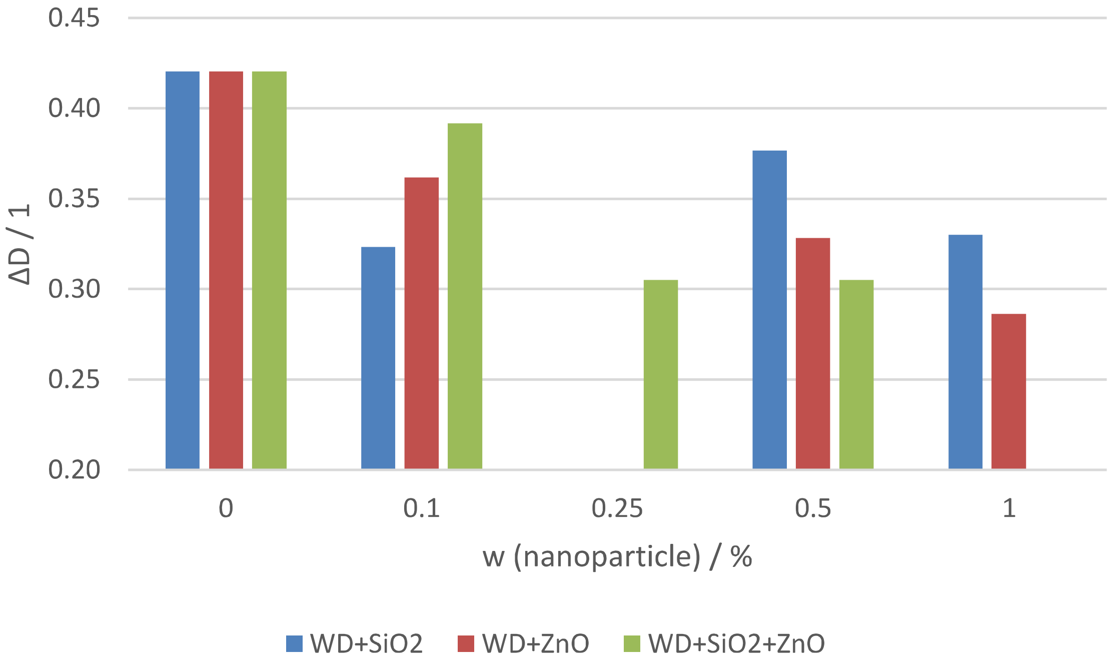


Figure 3: Density change (ΔD) of yellow after artificial ageing process

It is visible that lowest density change is achieved by application of coating with WD+ZnO where w (ZnO) was 1 %. The nanocomposites including both nanoparticles also decrease colour fading due to artificial ageing, even producing best results in the same nanoparticle concentration (w (nanoparticle) = 0.5%).

As ZnO is known to absorb UV (Wang *et al.*, 2009), it was expected that nanocomposites including ZnO nanoparticle would decrease ink fading.

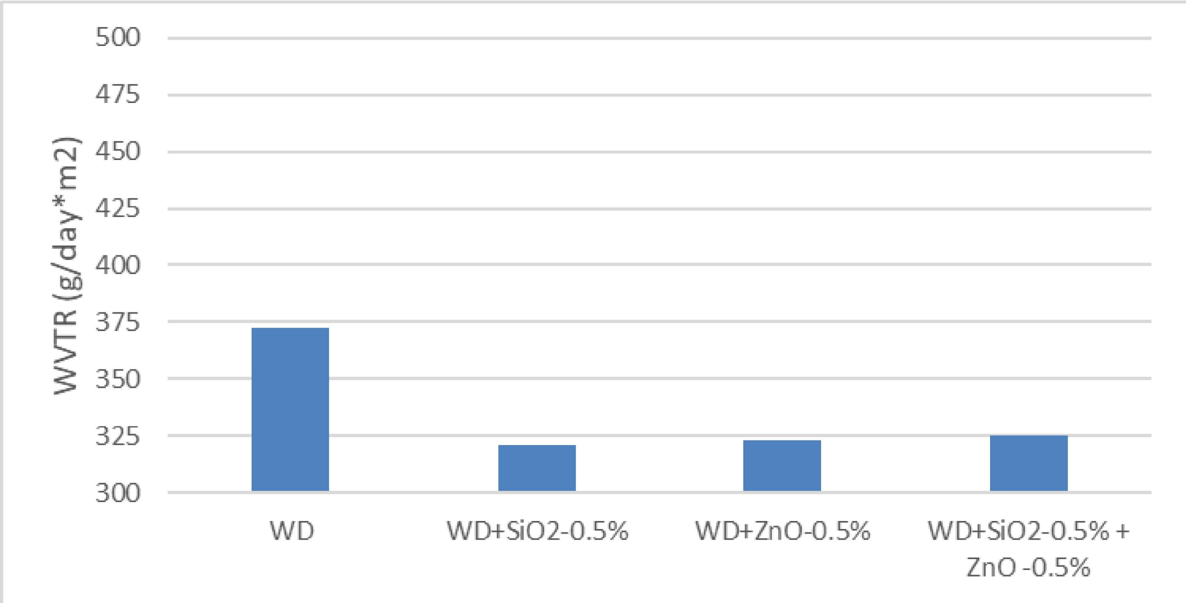


Figure 4: WVTR of aged samples

Although artificial ageing decreased WVTR of all investigated samples (Figure 1, Figure 4) it is visible that samples coated with nanocomposites have higher barrier properties to the water vapour.

4 CONCLUSIONS

The aim of this paper was to evaluate modification of commercial water-based varnish by determining its protective properties regarding colour degradation as well as barrier properties.

Results showed that applying prepared nanocomposite coatings do not cause significant colour change (max. dE_{2000} = 2.84) but do increase the tone value at 80% nominal value for almost 5%. Furthermore, barrier to the water vapour is increased by adding nanoparticles. Adding ZnO into the composite decreases yellow fading because of accelerated ageing.

This research proved the positive influence of added nanoparticles into the commercial varnish by increasing its protective role in print's ageing and barrier properties while just slightly changing the primary colour apearence. Further research should be performed to determine other important aspects such as applicability in regular printing process, halftone images darkening etc.

Acknowledgments: *This research is supported by Croatian Science Foundation [grant number UIP-2017-05-4081,2017].*

5 REFERENCES

ASTM E96/GB 1037 (2013). Gravimetric Method Water Vapor Permeability Testing Standard.

Aydemir, C., and Yenidoğan, S. (2018).Light fastness of printing inks: A review, J. Graph. Eng. Des., 9 (1), pp. 37–43.

Bota, J., Krehula, L. K., Katančić, Z., Brozović, M., Hrnjak-Murgić, Z., and Kratofil Krehula, L. (2017). Surface characteristics and enhancement of water vapour properties of paperboard coated with polycaprolactone nanocomposites, J. Adhes. Sci. Technol., 31 (5), pp. 466–486.

Cigula, T., Hudika, T., Katana, M., Golik Krizmanić, M., and Tomašegović, T. (2020). The influence of PCL-ZnO coating composition on coated offset cardboard prints, in Dedijer, S. (ed.) Proc. - Tenth Int. Symp. GRID 2020, pp. 101–108.

Hudika, T., Cigula, T., Žličarić, M., and Strižić Jakovljević, M. (2020). PCL-TiO2 nanocomposite to improve ageing of offset prints, in Dedijer, S. (ed.) Proc. - Tenth Int. Symp. GRID 2020, pp. 119–129.

ISO (2013). ISO 12647-2:2013(en) Graphic technology — Process control for the production of half-tone colour separations, proof and production prints — Part 2: Offset lithographic processes.

Kipphan, H. (2001). Handbook Of Print media. 1st edn.

Leblanc, R. (2019). Smithers Pira Forecasts Global Packaging Market To $269 Billion By 2024, Identifies 7 Key Drivers And Trends For Flexible Packaging - Reusable Packaging News. [online]. Available at: https://packagingrevolution.net/smithers-pira-forecasts-global-packaging-market-to-269-billion-by-2024-identifies-7-key-drivers-and-trends-for-flexible-packaging/ (Accessed: 8 March 2021).

Lychock, G. (1995). Dot Area, Dot Gain, and n-Factors, pp. 1–9.

Mokrzycki, W., and Tatol, M. (2011). Color difference Delta E - A survey, Mach. Graph. Vis., 20 (4), pp. 383–411.

Primary, Secondary & Tertiary Packaging | Saxon Packaging (nd). [online]. Available at: https://www.saxonpackaging.co.uk/difference-between-primary-secondary-tertiary-packaging/ (Accessed: 8 March 2021).

RK Printcoat instruments (nd) K Hand Coaters, pp. 1–2.

Salla, J., Pandey, K. K., and Srinivas, K. (2012). Improvement of UV resistance of wood surfaces by using ZnO nanoparticles, Polym. Degrad. Stab. Elsevier Ltd, 97 (4), pp. 592–596.

Schoff, C. K. (2014). Nanoparticles in coatings, CoatingsTech, 11 (2), p. 52.

Sharma, G., Wu, W., and Dalal, E. N. (2005). The CIEDE2000 color-difference formula: Implementation notes, supplementary test data, and mathematical observations, Color Res. Appl., 30 (1), pp. 21–30.

Simonot, L., and Elias, M. (2004) Color change due to a varnish layer, Color Res. Appl., 29 (3), pp. 196–204.

Smyth, S. (2017). The Future of Global Printing to 2022. 1st edn, Nelson, J. (ed.). Edited by J. Nelson.

Solarbox (nd) A family of two sizes and four models tabletop xenon test chambers. [online]. Available at: http://www.n-wissen.com/files/N-Wissen-GmbH-Leaflet_Solar-Box_Xenon-Test-Chamber_w6stg641.pdf (Accessed: 23 March 2021).

Techkon GmbH (nd) SpectroDens Manual.

Wang, Z. Y., Liu, F. C., Han, E. H., Ke, W., and Luo, S. Z. (2009). Effect of ZnO nanoparticles on anti-aging properties of polyurethane coating, Chinese Sci. Bull., 54 (19), pp. 3464–3472.