Improving the security of conventional and UV luminescent flexographic prints by modification of the printing inks using nanoparticles

Tamara Tomašegović[1], Sanja Mahović Poljaček[1], Ivona Jurišić[1]

[1]University of Zagreb Faculty of Graphic Arts
tamara.tomasegovic@grf.unizg.hr

Abstract

The security and protection of printed products against counterfeiting have become more advanced and increasingly used in the field of graphics technology. In this research, conventional process black (PB) and UV luminescent (UVL) inks used in flexography, modified by nanoscale silicon dioxide (SiO_2), anatase and rutile titanium dioxide (TiO_2), and zinc oxide (ZnO) at different concentrations were used. The purpose of adding nanoparticles to these inks was to protect PB and observed UVL inks from counterfeiting without significantly affecting the optical appearance and colourimetric properties of the printed motives.

The results have shown that nanoparticles did not significantly affect the spectral reflectance of UVL inks observed under UV irradiation or the visual effect of UV luminescence. In addition, the nanoparticles had a negligible effect on the optical and colourimetric properties of PB inks, as evidenced by a slight increase in colour lightness after the addition of nanoparticles. Indirect detection of nanoparticles through their interaction with PB and UVL inks was possible through FTIR-ATR spectroscopy, which showed changes in the spectra of PB and UVL inks with nanoparticles compared to nanoparticle-free inks in the fingerprint region. This research opened the possibility of expanding the use of nanoparticles of different types and concentrations for process, spot, luminescent and other special and conventional inks in the field of graphic technology.

Keywords: flexography, security printing, luminescence, nanoparticles, colourimetry

1. INTRODUCTION

UV luminescent coatings can be applied using various printing techniques: in the form of a flexographic varnish, as a pigment dispersed in a screen printing base and offset printing [1, 2]. Flexographic printing, as a conventional printing technique for the rapid and mass production of a wide range of graphic products [3, 4], can use a variety of printing inks, including luminescent ones. Due to its widespread use and multiple applications, flexographic printing was the technique of choice in this research.

Fluorescent inks have the property of absorbing radiation of a certain wavelength and re-emitting photons of different wavelengths [5–7]. Pigments with such a capability are mainly based on inorganic luminescent substances and may differ in their chemical structure depending on the application. Special effect inks, especially the ones with luminescence phenomenon, are often used in the packaging industry for printing control labels, security printing, for UV sensors, etc. [8–12]. Conventional process inks (cyan, magenta, yellow and black), on the other hand, are not usually used as security features for prints. Their use and certain properties of the printed elements are standardized, and by changing their composition the impact of their colourimetric, surface and other properties of the print should be precisely evaluated.

Previously published studies have investigated the advantages and disadvantages of coatings/inks containing nanomaterials. Nanoparticles that are of great interest to the paint and ink industry and various related applications are silicon dioxide (SiO_2), titanium dioxide (TiO_2) and zinc oxide (ZnO) [13–16]. The potential benefits of coatings with nanoparticles vary. Some of them give the coating better antibacterial, fire and scratch-resistant properties, can provide better UV protection and hydrophobicity, and offer anti-corrosion properties and other functionalities. The numerous applications of these nanoparticles in graphic technology research include control of ink rheological properties, mechanical protection of the paint/ink layer, improvement of colourimetric properties after ageing, etc. [17–21].

The aim of this research was to secure the process of black and UV luminescent inks against counterfeiting. The different concentrations of nanoparticles of silicon dioxide (SiO_2), titanium dioxide (TiO_2) and zinc oxide (ZnO) were added to the base ink to determine their influence on the optical and colourimetric properties of the prints.

2. MATERIALS AND METHODS

2.1. Materials and sample preparation

Melinex printing substrate – polyester (PE) foil with a thickness of 105 µm was used in this research. The inks used were SunChemical UV-curable process black (PB) ink and UV luminescent ink "Vernis UV VFB740" (UVL), which is invisible in daylight and reflects blue colour under UV radiation. Nanoscale hydrophilic SiO_2 (Aerosil 200), anatase TiO_2, rutile TiO_2 and ZnO at different concentrations were added to the inks (Table 1). The mass concentrations of the added nanoparticles were 1% and 2% (Figure 1).

Figure 1. Samples of prepared UV luminescent inks under UV radiation source, from left to right: UVL ink without the nanoparticles, UVL + 2% TiO_2 (A), UVL + 2% TiO_2 (R), UVL + 2% ZnO, UVL + 2% SiO_2

Prior to printing, the Melinex printing substrate was cut to 5×70 cm for each sample and conditioned to 55 ± 5% relative humidity and 23 ± 1 °C. The modified inks were prepared by adding four types of nanoparticles

Table 1. Specification of the used nanoparticles

Type of nanoparticle	Name	CAS number	Average nanoparticle size (nm)	Weight (%)
SiO_2	Aerosil 200	112945-52-5	12	> 99.8
TiO_2 (A)	Titanium (IV) oxide, anatase	1317-70-0	15	99.7
TiO_2 (R)	Titanium (IV) oxide, rutile	13463-67-7	< 100	99.5
ZnO	Zinc oxide	1314-13-2	40–100	> 95

to the PB and UVL inks. Nanosized particles of silicon dioxide (SiO_2), anatase (TiO_2 (A)) titanium dioxide, rutile (TiO_2 (R)) titanium dioxide and zinc oxide (ZnO) were added into the ink at concentrations of 1% and 2%. The nanoparticles were mixed into the inks by homogenization with a UP100H Hielscher device for 2 minutes at 100% amplitude of the device.

The printing process was carried out with the IGT Printability Tester F1 in the laboratory, at a relative humidity of 55% and 23 °C. PB and UVL inks were printed in full-tones. An anilox roller with 90 l/cm and 18 ml/m^2 was used. The printing plate used was Flint's NEXT plate. During the printing process, the pressure was set to 300 N. Four prints were made with each printing ink modification, with the first print of each series discarded due to the different initial interaction between the cleaned and dried flexographic printing plate and the ink.

After the printing process, the samples were cured in a UV dryer (Technigraf Aktiprint L 10-1), in two passes, at a speed of 4 m/s. After stabilizing the prints for 24 hours, all measurement and analysis methods were performed.

2.2. Measurement and analysis methods

The thickness of the prints was measured with a SaluTron D4-Fe device. It works on the magnetic induction principle and can be used for measuring the thickness of layers on non-magnetic surfaces. The accuracy of the device is ± (1.5 μm + 2%). Obtained results were used to determine the influence of layer thickness on the optical and colourimetric properties of the prints.

The spectral reflectance of the UV luminescent ink layers on the melinex substrate was measured with a spectrometer (Ocean Optics USB 2000+) and a deuterium-tungsten halogen (DH-2000) UV radiation source, in the range between 350 and 650 nm.

The microscopic images of the UVL prints were obtained using Olympus BX 51 microscope. The images of the UVL and prints were captured by observing the samples under a UV source and were used to visually compare the effects of UV luminescence after adding of different nanoparticles to the ink. All images were captured under 50× magnification.

Spectro-densitometer Techkon SpectroDens B703902 was used for measuring the CIE L*a*b* colourimetric values and the optical density of the PB prints. The measurements were performed 10 times on each sample at different positions. The measurement conditions were as follows: radiation source D50, standard observer 2^o, filter M1.

FTIR-ATR spectroscopy was used to identify the presence of functional groups of interest in the printed layers with UVL and PB inks. In this research, FTIR-ATR spectroscopy was specifically used to detect changes in the UVL and PB ink layers after the addition of various nanoparticles to provide additional protection against counterfeiting. Indeed, both PB and UVL inks can be purchased without special permits, so replication of the product becomes possible for a potential counterfeiter. UVL inks themselves provide the security protection of prints as they are invisible in the daylight, but if the counterfeiter knows that the UVL ink is present on the print, counterfeiting becomes possible. PB ink, the conventional ink used in flexographic printing, is certainly easily available. The nanoparticles used in this research were not detected directly by FTIR-ATR spectroscopy, especially at low concentrations, but indirectly and by interaction with inks after the UV curing process or by changes in the bands/peaks in the area of the "fingerprint". In this way, additional protection of the inks was made possible by modification with nanoparticles, which can be detected by forensic analysis. FTIR-ATR analysis was performed using a Shimadzu IRAffinity-1 FTIR spectrophotometer (Shimadzu Corporation, Kyōto, Japan) with 15 scans per sample.

3. RESULTS AND DISCUSSION

3.1. Thickness of the printed UVL and PB layers

The results of the thickness measurements of UV luminescent and PB printed layers are shown in Table 2. The thickness of the printed layers of UV luminescent ink and PB inks was measured to define the possible changes that could affect the optical appearance and colourimetric properties of the printed samples produced with modified inks. The results presented in Table 2 indicate that most of the changes in the thickness of the printed modified inks are barely detectable compared to the unmodified ones and can be connected to the measurement error itself.

Furthermore, by the addition of SiO_2 nanoparticles to the PB ink the measured thickness of the ink is approximately the same as for the unmodified ink. Speaking generally, the nanoscale particles reduce the thickness of the printed ink layer slightly compared to the unmodified samples of UVL and PB inks. Specifically, the results show that the thickness of the printed ink modified with the addition of ZnO nanoparticles is the lowest in comparison to the other samples, which could be related to the influence of nano-ZnO on observed inks in terms of reducing their viscosity. In the continuation of this research, it will be seen that these changes in thickness did not affect the optical density of the PB prints (Table 3), and the changes in lightness were small (Figure 5). For the UVL ink, the addition of nanoparticles resulted in a slight decrease in the percentage of reflectance in the range between 425 and 475 nm, but this effect was not visible during visual inspection (Figure 4).

3.2. Optical and colourimetric properties of the printed UVL and PB ink layers

3.2.1. Spectral reflectance of UVL layers

Figure 2 shows the spectral reflectance of the Melinex polyester substrate and the UVL ink without the addition of nanoparticles. It can be seen that the spectral reflectance of the substrate differs from the spectral reflectance of the UVL print, especially in the range below 500 nm. UVL print is therefore the first protection against counterfeiting if the counterfeiter does not know that the print is protected by UVL ink.

Table 2. The thickness of the printed UVL and PB inks

Sample	Ink layer thickness (μm)	Sample	Ink layer thickness (μm)
UVL ink	7.60 ± 1.65	PB ink	8.75 ± 1.48
UVL + 1% SiO_2	7.10 ± 1.37	PB + 1% SiO_2	8.00 ± 1.87
UVL + 2% SiO_2	7.70 ± 1.42	PB + 2% SiO_2	8.57 ± 1.27
UVL + 1% TiO_2 (R)	7.30 ± 1.49	PB + 1% TiO_2 (R)	7.60 ± 0.51
UVL + 2% TiO_2 (R)	7.20 ± 1.81	PB + 2% TiO_2 (R)	7.22 ± 1.92
UVL + 1% TiO_2 (A)	7.00 ± 1.77	PB + 1% TiO_2 (A)	7.00 ± 1.82
UVL + 1% TiO_2 (A)	7.13 ± 1.64	PB + 1% TiO_2 (A)	7.11 ± 1.96
UVL + 1% ZnO	5.90 ± 1.28	PB + 1% ZnO	6.30 ± 1.64
UVL + 2% ZnO	6.50 ± 1.72	PB + 2% ZnO	6.13 ± 1.35

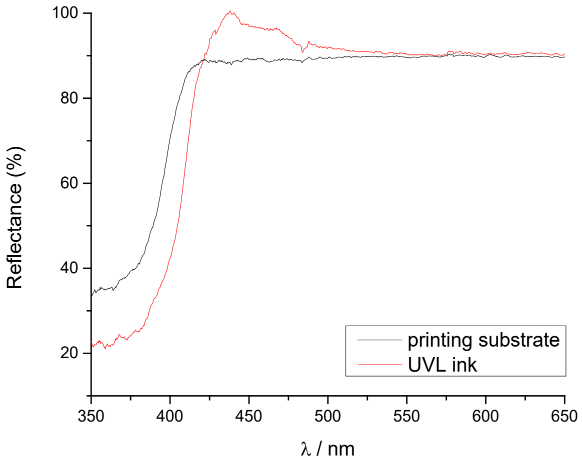
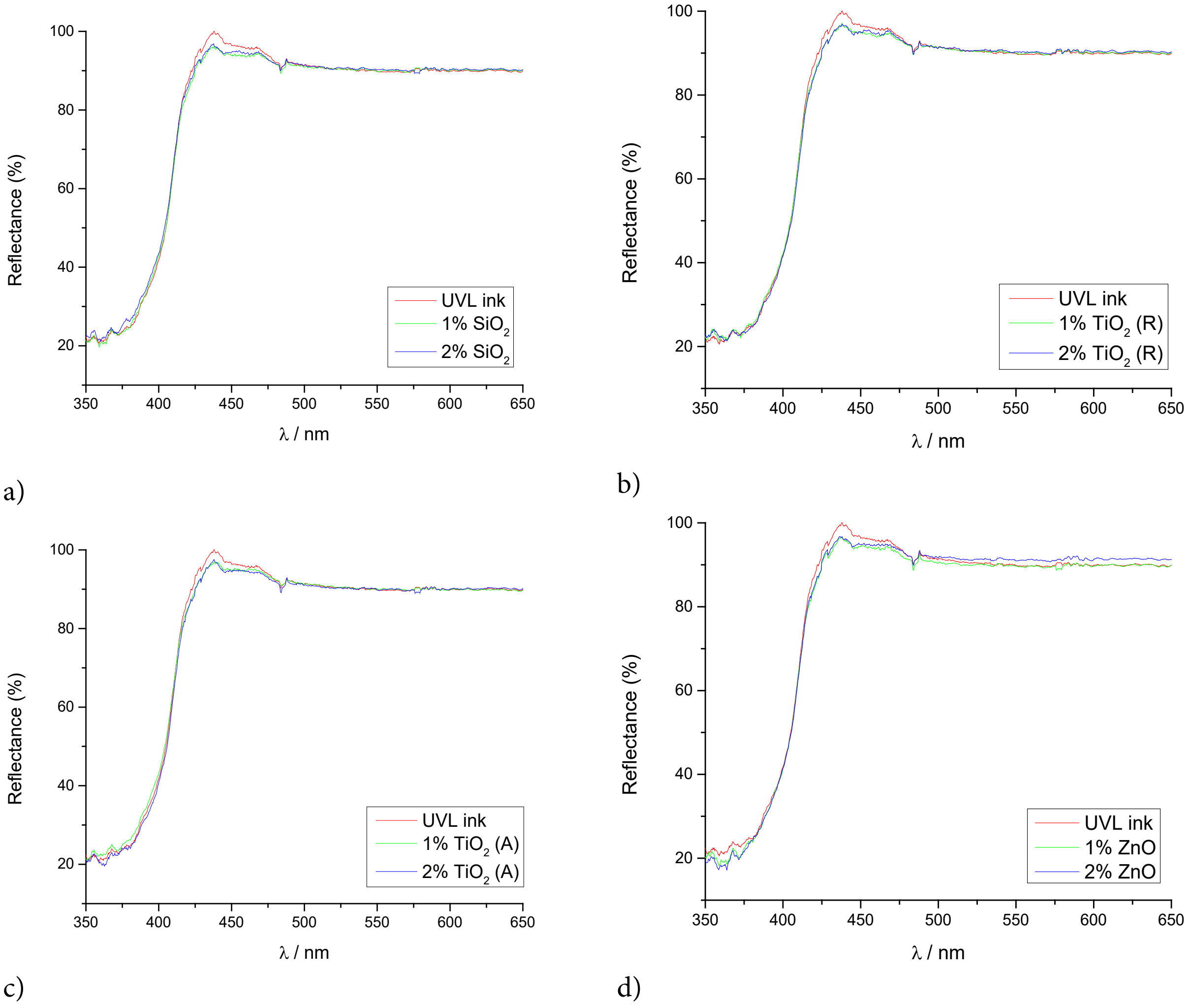


Figure 2. Spectral reflectance of Melinex substrate and UVL print without nanoparticles

The next four diagrams (Figure 3. a–d) show the reflectance spectra of UVL inks with the addition of various nanoparticles compared to the UVL ink spectra without the nanoparticles. The aim of measuring the spectral reflectance was to show whether the addition of the nanoparticles affects the change in reflectance of the basic UVL ink such that the visibility of the luminescence effect under UV radiation is reduced or shifted to certain wavelengths.



a)

b)

c)

d)

Figure 3. Comparison of the spectral reflectance of the UVL ink layer without the nanoparticles and: a) SiO_2, b) rutile TiO_2, c) anatase TiO_2, d) ZnO

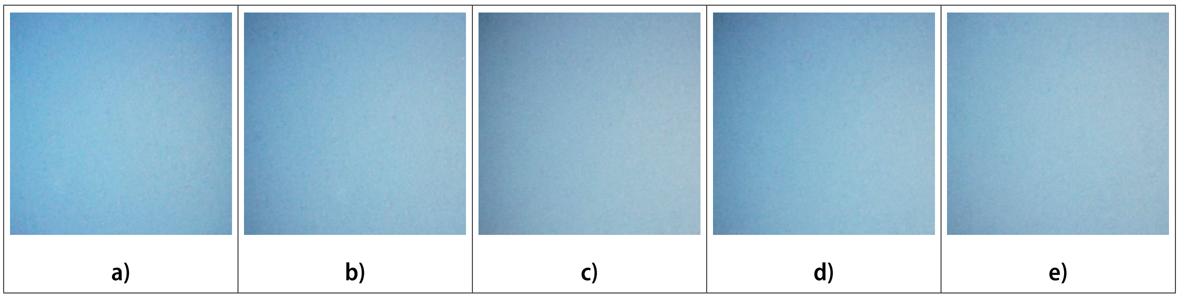

a) b) c) d) e)

Figure 4. Microscopic images of printed UVL inks on the substrate under UV radiation source and 50× magnification: a) UVL ink - without nanoparticles, b) UVL + 2% SiO_2, c) UVL + 2% TiO_2 (R), d) UVL + 2% TiO_2 (A), e) UVL + 2% ZnO

The results of spectral reflectance presented in Figure 3 show a small, insignificant decrease in UVL ink reflectance with the addition of nanoscale SiO_2, rutile TiO_2, anatase TiO_2 and ZnO in the range from 425 nm to 475 nm compared to the basic UV luminescent ink. In this range, the blue UV luminescent colour is visible under UV radiation. However, the influence of the nanoparticles on the spectral reflectance of the UVL ink is negligible, so it can be assumed that they do not affect the visual effect of the UVL ink. Furthermore, it is not possible to determine the presence of the 1% and 2% concentrations of nanoparticles in the basic UV luminescent ink from these reflection spectra.

In Figure 4 one can see microscopic images of the surfaces of the printed UV luminescent inks, viewer exposed to UV radiation source to stress the luminescence effect. These images confirm the observation that the nanoscale particles do not cause any changes in the visual effect of luminescence. There is no significant difference in the luminescence effect of the modified UVL inks with nanoparticles compared to the basic UVL ink to the naked eye.

3.2.2. Colorimetric properties and optical density of PB prints

Figure 5 shows the lightness (L*) of unmodified and modified printed PB inks. When measuring the colourimetric coordinates CIE L*a*b*, the results showed an increase in lightness for all PB prints made with the nanoparticle-modified inks compared to the nanoparticle-free prints. The highest measured lightness was observed for PB ink with the addition of SiO_2 nanoparticles and 2% ZnO. These results need to be particularly considered when adding the nanoscale particles to the ink.

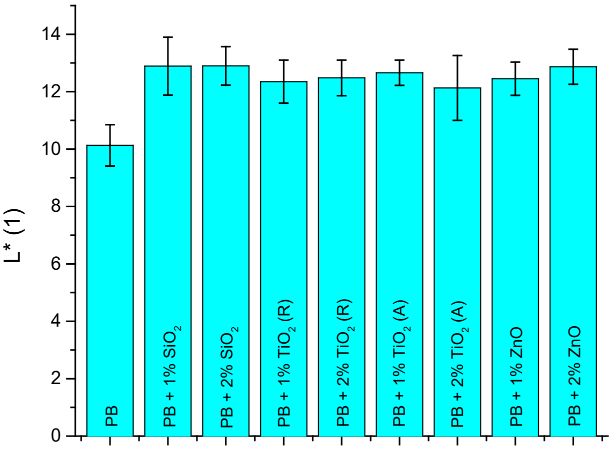


Figure 5. Lightness (L*) of printed PB inks without and with nanoparticles

Furthermore, when observing the range of measured lightness values (L*) and the standard deviation of these results for the observed PB ink, it can be said that by increasing the concentration of all nanoscale particles from 1% to 2% the lightness of the prints was not significantly changed.

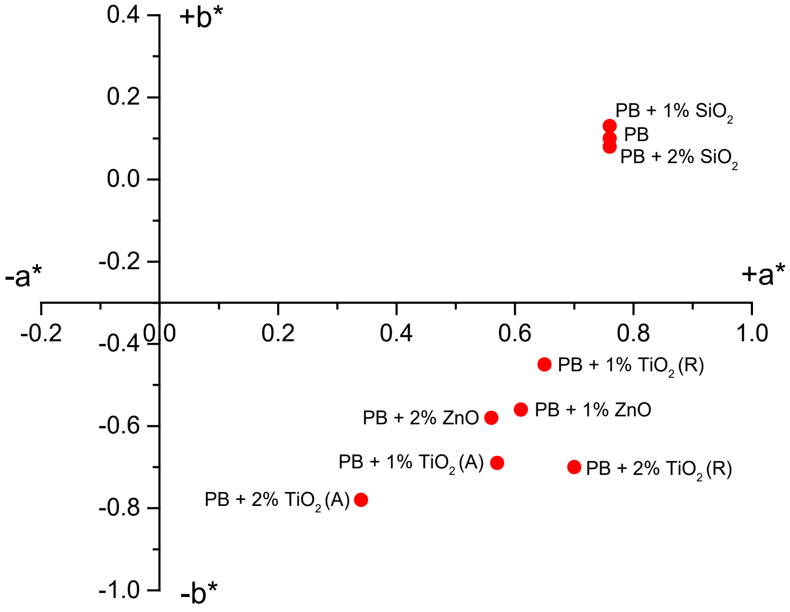


Figure 6. CIE a*/b* diagram of printed PB inks without and with nanoparticles

In the CIE a*/b* diagram, visible in Figure 6, one can see that the addition of SiO_2 nanoparticles to the PB ink had the least effect on changing the a* and b* coordinates. The largest deviations along the a* and b* axes were observed after the addition of 2% TiO_2 (A) to the PB ink. One can say that the addition of 1% and 2% of TiO_2 (A) and ZnO nanoparticles cause a color shifts of prints in blue (-b*) and green (-a*) directions. The addition of TiO_2 (R) nanoparticles causes colour shifts in the blue (-b*) direction.

The changes observed in Figure 6 are small but generally most pronounced when 2% of the TiO_2 (R) and ZnO nanoparticles and 1% TiO_2 (A) are added to the PB ink. However, when modifying some other process or spot inks, it is certainly advisable to perform colourimetric measurements and determine whether the nanoparticles do cause the changes in the L*a*b* colour values of the printed layers.

Table 3. presents the results of the optical density (D) values measured on all printed samples produced with unmodified and modified PB inks. From the presented results it can be seen that the addition of nanoparticles has no or negligible effect on the optical density of PB prints. The lowest optical density was measured for prints with an addition of 2% TiO_2 (A), but the standard deviation is the highest for this sample.

Table 3. The optical density of printed PB ink layers

Sample	Optical density (1)
PB ink	2.77 ± 0.03
PB + 1% SiO_2	2.81 ± 0.03
PB + 2% SiO_2	2.82 ± 0.02
PB + 1% TiO_2 (R)	2.79 ± 0.06
PB + 2% TiO_2 (R)	2.78 ± 0.01
PB + 1% TiO_2 (A)	2.76 ± 0.02
PB + 2% TiO_2 (A)	2.71 ± 0.10
PB + 1% ZnO	2.80 ± 0.04
PB + 2% ZnO	2.80 ± 0.05

One can state with certainty that increasing the concentration of the individual nanoparticles from 1% to 2% does not affect the change in optical density. It can also be concluded that none of the nanoparticles were used to reduce the optical density of the PB ink on the prints, which is very important for maintaining the print quality.

In conclusion, based on all presented results that correspond to the optical changes and colourimetric properties of the UVL and PB prints and the nanoparticles used in this research, it is possible to say that no significant deviation in observed properties was detected. The most significant change was observed in the increase in the lightness of the modified PB inks compared to the unmodified ink; and in the greater distances of the a* and b* coordinates of the modified PB inks with 2% nanoparticles from the values of the unmodified PB ink. However, these differences are negligible. Accordingly, one can conclude that the nanoparticles can be added to commercial UVL and PB printing inks without fear of compromising the important optical and colourimetric properties of the printed samples.

3.3. Results of the FTIR-ATR spectroscopy of the UVL and PB layers

In the FTIR-ATR spectra of the UVL inks (Figure 7), the peaks/bands of each UVL ink spectrum with nanoparticles are indicated where the change in relative absorption or wavenumber is present compared to the FTIR-ATR spectrum of the UVL ink without nanoparticles.

Subtle changes in the spectra after the addition of the nanoparticles are visible in the labelled bands/peak regions. Therefore, indirect detection of nanoparticles in UVL ink is possible by FTIR-ATR spectroscopy.

Figures 7 and 8 show the FTIR-ATR spectra of the substrate and inks with 2% of added nanoparticles since the changes in the FTIR-ATR spectra are more pronounced compared to the changes when 1% of nanoparticles were added to the inks.

The intensity band at 1082 cm^{-1} changes noticeably compared to the adjacent band at 1059 cm^{-1} only for the ink with the addition of SiO_2. It represents the vibrations of the carbonyl group (C=O) from urethane as a component of the UV luminescent ink published previously in [22, 23]. A decrease in its relative intensity could indicate the changes in the UV luminescent print due to the addition of SiO_2 nanoparticles.

The peak at 638 cm^{-1} has reduced absorbance for all nanoparticle-modified inks compared to the same peak for nanoparticle-free ink. This peak is in the lower wavenumber area of the fingerprint region (the region between 400 cm^{-1} and 1500 cm^{-1}). By observing and comparing this part of the FTIR-ATR spectrum of different samples, it can be stated with complete

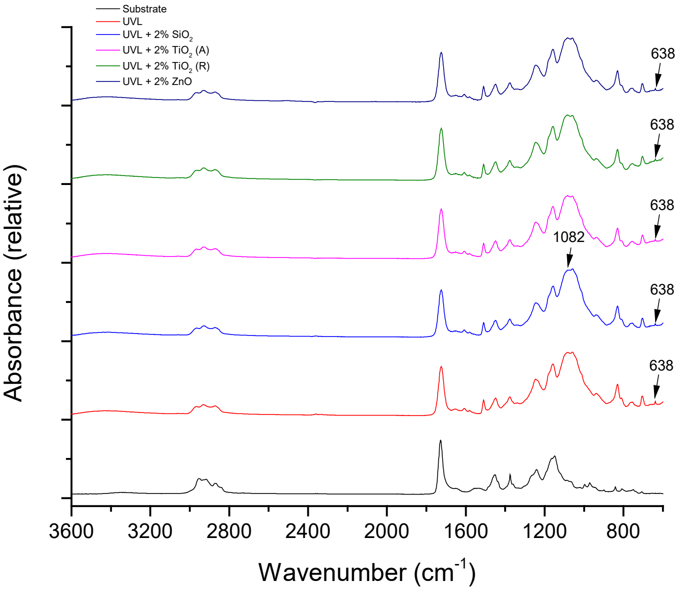


Figure 7. FTIR-ATR spectra of the printing substrate and the printed UVL inks

Table 4. Integration results and the ratio of the areas under peaks at 1724 cm^{-1} and 638 cm^{-1} for UVL inks

Ink	**The area under peak at 1724 cm^{-1} (A)**	**The area under peak at 638 cm^{-1} (B)**	**A/B**
UVL	10.12	0.42	24.09
PB + 2% SiO_2	9.63	0.06	160.05
PB + 2% TiO_2 (R)	10.52	0.07	150.29
PB + 2% TiO_2 (A)	9.96	0.06	166.00
PB + 2% ZnO	9.65	0.06	160.83

certainty whether the samples are of the same composition or not. To quantify the decrease in the absorption of the peak at 638 cm^{-1}, the baseline-corrected areas under the peak at 1724 cm^{-1} and the peak at 638 cm^{-1} were calculated and compared. The results are presented in Table 4.

From the results presented in Table 4, it is clearly visible that the A/B ratio for the UVL ink without the nanoparticles is significantly lower than for the modified UVL inks.

Thus, analysis of FTIR-ATR spectra of UVL inks with the addition of the nanoparticles makes it possible to detect differences in the sample spectra, enabling a new level of UVL ink protection against counterfeiting.

The changes in the FTIR-ATR spectra after the addition of nanoparticles to PB inks are visible in the band between 954 and 1028 cm^{-1}, as shown in Figure 8. This part of the spectrum lies in the fingerprint region. The peak at 811 cm^{-1} is characteristic of acrylates [24], and changes detected in the 954 and 1020 cm^{-1} regions are visible in the spectra of the modified PB inks compared to the basic PB ink.

In particular, the addition of nano-anatase and nano-rutile TiO_2 and ZnO nanoparticles in the PB inks shifts the band in the range of 954 to 975 cm^{-1}. The addition of SiO_2 cause a decrease in the absorption compared to the same band of PB ink without the addition of nanoparticles. The band visible at 1020 cm^{-1} corresponds to the pure PB ink and the PB ink with the addition of SiO_2 that shifts to 1028 cm^{-1} after the addition of both types of TiO_2 and ZnO nanoparticles. It can be said that if all the components of the ink are known precisely, it is easy to detect differences in the FTIR-ATR

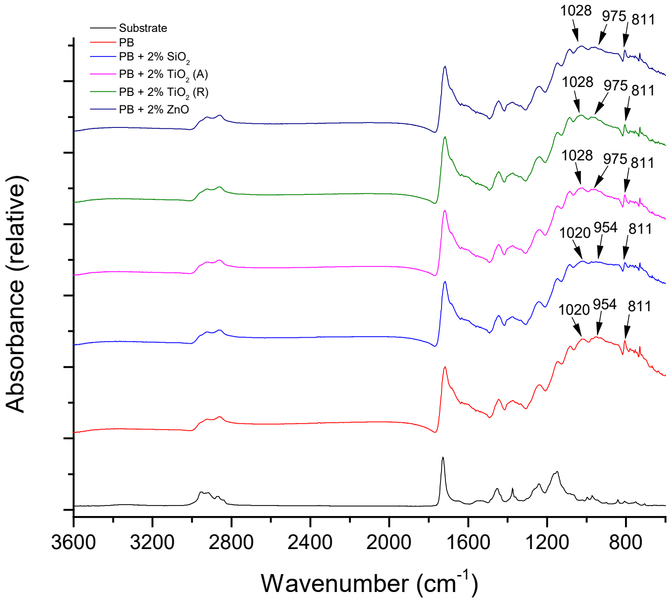


Figure 8. FTIR-ATR spectra of the printed PB inks

spectra from the fingerprint region and thus recognize that the ink has been modified by the nanoparticles.

FTIR-ATR spectroscopy can therefore be used as a method to detect intentionally altered ink to protect against counterfeiting. Although the nanoparticles could also be detected directly with other analytical methods such as EDS spectroscopy [25], the costs and the complex preparation of the samples speak in favour of using FTIR-ATR spectroscopy.

4. CONCLUSION

The development of graphic technology has enabled the application of added value and protection to various printed products. In this research, the addition of different types and concentrations of nanoparticles to commercial UV-curable process black (PB) and security UV luminescent (UVL) inks was intended to provide prints with additional protection against counterfeiting. This was achieved by indirectly detecting the nanoparticles added to the inks using FTIR-ATR spectroscopy. It was of high significance that the nanoparticles did not affect the quality of the prints.

Nanoparticles of silica SiO_2, anatase TiO_2, rutile TiO_2 and ZnO were added to the inks in concentrations of 1 and 2%. The measurement results and further analyses showed that, with the exception of ZnO, the nanoparticles did not significantly affect the thickness of the printed PB and UVL ink layers. The printed ink layer modified with the addition of ZnO nanoparticles has the lowest thickness value, which could be related to their influence of on the viscosity of the inks.

In addition to that, the presence of nanoparticles used in this research did not have any significant influence on the spectral reflectance of the UVL inks under or the visual phenomenon of UV luminescence. The influence of the nanoparticles could not be seen with the naked eye. Furthermore, the nanoparticles had a negligible effect on the optical changes and colourimetric properties of the PB ink.

Additional and, indirect detection of nanoparticles through their influence on chemical bonds and groups in printed inks was possible with FTIR-ATR spectroscopy, which proved the changes in the spectra of both, PB and UVL inks, with the addition of nanoparticles compared to samples without added nanoparticles in the fingerprint region.

The scientific contribution of this research is visible in the possibility of further protecting printed products from forgery while preserving their quality by not affecting their colourimetric and optical properties. In conclusion, this research opens up the possibility of additional application of nanoparticles, specifically in the area of spot, luminescent and other special and conventional inks used in graphic technology.

5. REFERENCES

[1] Bozhkova T, Spiridonov I, Shterev K. Overview of security printing types and trends in its future development. [Internet] 2017 [cited 2022 Jun 14]. Available from: https://www.semanticscholar.org/paper/Overview-of-security-printing-types-and-trends-in-Bozhkova-Spiridonov/f2dc1c1b8bac09388a9af4845662a447b749b84c

[2] Koutsioukis A, Belessi V, Georgakilas V. Fluorescent Carbon Dots Ink for Gravure Printing. C 2019, Vol 5, Page 12 2019; 5: 12.

[3] Zhong ZW, Ee JH, Chen SH, et al. Parametric investigation of flexographic printing processes for R2R printed electronics. Mater Manuf Process 2020; 35: 564–571.

[4] Ejsmont K, Lipiak J. The model of assessment for flexographic printing technology. In: Lecture Notes in Mechanical Engineering. Pleiades Publishing, pp. 67–75.

[5] Bob T. Printing Materials Science and Technology. Pira International, 2004.

[6] Diamond AS. Handbook of Imaging Materials: Optical Science and Engineering. CRC Press, 2018.

[7] Jameson DM. Introduction to Fluorescence. 1st ed. [Internet] CRC Press, 2019 [cited 2022 Jun 14]. Available from: https://doi.org/10.1201/b16502 (2014).

[8] Europäisches Patentamt European Patent Office *EP001256609A2* [Internet] 2002 [cited 2022 Jun 14]. Available from: https://patentimages.storage.googleapis.com/c3/e4/0b/b925bd81a9e27a/EP1256609A2.pdf

[9] Bodenstein C, Sauer HM, Hirmer K, et al. Printing process and characterization of fully pad printed electroluminescent panels on curved surfaces. J Coatings Technol Res 2019; 16: 1673–1681.

[10] Yook KS, Lee JY. Fabrication and luminance switching of flexible organic bistable light-emitting diodes on flexible substrate. J Lumin 2013; 137: 105–108.

[11] Ataeefard M, Nourmohammadian F. Producing fluorescent digital printing ink: Investigating the effect of type and amount of coumarin derivative dyes on the quality of ink. J Lumin 2015; 167: 254–260.

[12] Becidyan AN. The chemistry and physics of special-effect pigments and colorants for inks and coatings. Paint and Coatings Industry 2003; 19: 65–76.

[13] Kumar S, Verma NK, Singla ML. Reflective properties of ZnS nanoparticle coatings. J Coatings Technol Res 2011; 8: 223–228.

[14] Hang TTX, Dung NT, Truc TA, et al. Effect of silane modified nano ZnO on UV degradation of polyurethane coatings. Prog Org Coatings 2015; 79: 68–74.

[15] El Saeed AM, El-Fattah MA, Azzam AM. Synthesis of ZnO nanoparticles and studying its influence on the antimicrobial, anticorrosion and mechanical behavior of polyurethane composite for surface coating. Dye Pigment 2015; 121: 282–289.

[16] Akbarian M, Olya ME, Mahdavian M, et al. Effects of nanoparticulate silver on the corrosion protection performance of polyurethane coatings on mild steel in sodium chloride solution. Prog Org Coatings 2014; 77: 1233–1240.

[17] Carneiro C, Vieira R, Mendes AM, et al. Nanocomposite acrylic paint with self-cleaning action. J Coatings Technol Res 2012; 9: 687–693.

[18] Solano R, Patiño-Ruiz D, Herrera A. Preparation of modified paints with nano-structured additives and its potential applications. Nanomater Nanotechnol; 10. Epub ahead of print 23 March 2020. DOI: 10.1177/1847980420909188.

[19] Ni S, Zhang H, Godwin PM, et al. ZnO nanoparticles enhanced hydrophobicity for starch film and paper. Mater Lett 2018; 230: 207–210.

[20] Ferch H. Amorphous synthetic silica products in powder form. Part 2. Applications [1]. Prog Org Coatings 1982; 10: 91–118.

[21] Jacobs DS, Huang SR, Cheng YL, et al. Surface degradation and nanoparticle release of a commercial nanosilica/polyurethane coating under UV exposure. J Coatings Technol Res 2016; 13: 735–751.

[22] Park J, Kim SY, An S, et al. UV-Curable Fluorinated Crosslinkable Polyurethane-Acrylates for Marine Antifouling Coatings. 2017; 23: 148–157.

[23] US20150225597A1 – UV cured varnish and process for preparing the same - Google Patents [Internet] 2015 [cited 2022 Jun 14]. Available from: https://patents.google.com/patent/US20150225597A1/en.

[24] Nguyen TV, Nguyen-Tri P, Azizi S, et al. The role of organic and inorganic UV-absorbents on photopolymerization and mechanical properties of acrylate-urethane coating. Mater Today Commun 2020; 22: 100780.

[25] Cigula T, Hudika T, Tomašegović T. Lightfastness, surface and interfacial properties of colour-printed paper substrates coated with PCL/ZnO and PCL/TiO_2