

CHANGES IN VISUAL APPEARANCE OF RED AND GREEN UV-VISIBLE FLUORESCENT PRINTS AS A CONSEQUENCE OF THE ACCELERATED AGEING

Abstract: *Pigments with special effects are nowadays utilized in the graphic engineering and design to achieve an added value of the final product. Daylight-invisible, UV-visible fluorescent pigments can be used as markings, sensors, as well as special design or security feature. Red and green UV-visible fluorescent pigments used in this experiment were mixed in the transparent base and screen-printed using the 60 l/cm mesh on the white uncoated paper, by applying different number of printed ink layers: one, two and three. Prints were then subjected to the accelerated ageing in a weathering chamber. Ink layer thickness and colorimetric properties of the unaged and aged prints were analyzed. Microscopic and macroscopic images of the prints were taken before and after the ageing process to assess the subjective visual difference between the unaged and aged samples. Results of this research have shown that one printed layer of the ink had inadequate visual response of fluorescence because of the effect of the optical brighteners in the paper. Higher number of the ink layers on print displayed better fluorescence effect and improved light fastness compared to the print obtained by applying only one ink layer. Results of the colorimetric measurements, as well as microscopic and macroscopic images, displayed the objective and subjective differences in the color appearance of the unaged and aged prints. Thereby, results of this research provided the guidelines for usage of the special-effect UV-visible fluorescent inks in applied graphic design.*

Key words: *screen printing, UV- visible fluorescent pigments, artificial ageing, visual appearance.*

1. INTRODUCTION

Printing inks with special effects are widely used for different applications and in various industries. The effect achieved by applying the inks with special effect on a printing substrate (paper, plastic, metal, etc.), often in the combination with conventional inks, gives the product an added value and additional functionality. UV-visible (daylight invisible) fluorescent inks belong to the group of luminescent inks. They absorb the UV radiation and re-emit it as radiation at different wavelengths [1-3]. The effect of fluorescence occurs immediately after light absorption and lasts as long as the primary radiation acts [4]. Fluorescent inks are widely used in graphic industry as a component of the design solution/idea. They are used as a feature with decorative purpose and on packaging products for different control markings, signalling, and orientation purposes. Furthermore, they can be used as functional coatings, UV sensors and for many other functions [5-8]. They can also be used as a security feature of printed products, i.e., document applications, tagging of postage stamps, etc. [9-14].

Considering the fact that UV-visible (daylight invisible) fluorescent inks can be used for different applications and on different printing substrates, their properties and lightfastness are very interesting from a viewpoint of the final product's functionality and lifespan. Production of a suitable printed product that meets the specific design and quality requirements is of high importance. Previous research on this topic investigated the lightfastness of the UV-visible fluorescent inks after the artificial ageing, as well as surface and mechanical properties of the UV-visible fluorescent inks for screen printing and flexography [15-17]. In other research, hybrid ink with UV-visible

fluorescent and thermochromic screen printing ink hybrid was prepared and analysed in terms of the compatibility of the components and colorimetric and other properties [18].

The aim of this research was to expand the previous knowledge on the lightfastness of the screen printing UV-visible fluorescent printing ink by variation of the printed ink layer thickness. Colorimetric and optical analysis of the unaged and aged prints provided the guidelines for usage of the special-effect UV-visible fluorescent inks in applied graphic design.

2. EXPERIMENTAL

2.1 Materials and preparation of the samples

Two types of UV-visible fluorescent inks were composed, by using two luminescent pigments: a luminescent red pigment (a pigment that emits red when exposed to UV radiation) and a luminescent green pigment (a pigment that emits green when exposed to UV radiation). The pigments were mixed into a transparent base by EptaInks. Their share in the base was empirically set to 3%.

The printing substrate used for printing was offset uncoated paper, approximately 200 μm thick.

Screen printing plate was produced using the screen of 60 l/cm, and two-component emulsion AZOCOL Z 133 by KIWO. Expos-it VASTEX unit, model E2331 was used for the exposure. Drying of the printing plate was conducted in Dri-Vault screen drying cabinet. Developing of the printing plate was performed using water.

Printing process was performed by applying one, two and three layers of the red or green UV-visible fluorescent ink on the paper substrate. The printing

process was performed using a screen printing machine and the printed samples were air-dried for 48 h at a temperature of 25 ± 2 °C. In that way, 6 different prints were made. After drying, the samples were subjected to accelerated ageing in a test chamber Solarbox 1500e. An outdoor filter was used to simulate the exposure to daylight. Irradiation was set to $550 \text{ W}\cdot\text{m}^{-2}$ with the 50 °C temperature. The equipment was set in accordance with the ISO 4892-2 standard. The duration of the exposure of the samples to the accelerated ageing was 6 and 12 hours, corresponding to 6 and 12 days of the exposure to the direct sunlight.

2.2 Measurement methods

The thickness of the printing ink layer was measured ten times on the samples on each produced print. Printed ink layer thickness was measured using SaluTron D4-Fe gauge. The device SaluTron D4-Fe is based on the magnetic induction principle and can measure the thickness of nonmagnetic coatings such as synthetics, lacquers, enamels, copper, chromium, zinc, etc. on steel or iron.

Colour coordinates on prints were calculated on printed samples before and after the accelerated ageing. The samples were analysed via measuring colorimetric coordinates in compliance with CIE $L^*a^*b^*$ colour space and calculated from spectral reflectance. Measurements were performed using the Ocean Optics USB 2000+ spectrometer (Ocean Optics, Orlando, FL, USA) and Deuterium-Tungsten Halogen UV light source DH-2000.

Visual evaluation of the coating surfaces before and after the ageing process was carried out using the Olympus BX51 microscope at a magnification of 100× for obtaining the microscopic images of the printed surfaces. Macroscopic images were taken using a camera. All images were taken under UV light source to observe the effect of the artificial ageing on the visual impression of the UV-visible fluorescent inks.

3. RESULTS AND DISCUSSION

Table 1 presents the dependence of the thickness of the fluorescent green coating on the number of consecutive prints (printed ink layers).

Table 1

Number of printed ink layers	Average ink layer thickness (µm)	
	UV green	UV red
1 layer	7,50	15,50
2 layers	34,00	30,40
3 layers	41,4	53,60

It can be observed that the thicknesses of the printed layers difference between the red and green UV-visible fluorescent prints. In general, printing with UV-visible red ink results with the higher thickness of the print than printing with green UV-visible ink. This could be caused by different particle size of the red and green UV-visible fluorescent pigments, as well as by different interactions between the pigments and the transparent base. Figures 1 and 2 present the lightness coordinate (L^*) on all printed samples.

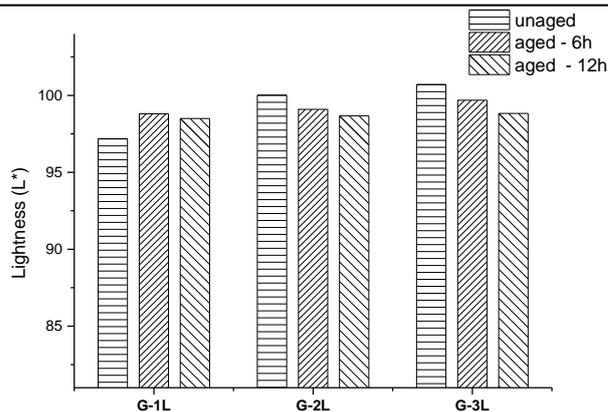


Figure 1 Lightness (L^*) of the green UV-visible fluorescent prints before and after the artificial ageing.

It is visible that the ageing process caused the decrease of the lightness on all samples, except on one layer of printed green UV-visible ink (Figure 1). This can be attributed to the lowest thickness of the one layer of the green UV-visible fluorescent ink (Table 1) resulting with the color that significantly differences from the same ink printed in two or three layers (Figure 3).

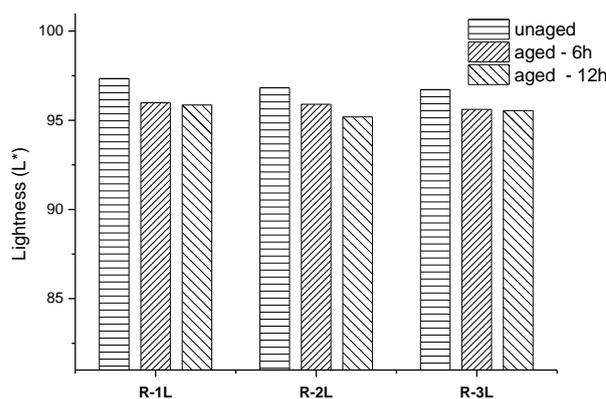


Figure 2 Lightness (L^*) of the red UV-visible fluorescent prints before and after the artificial ageing.

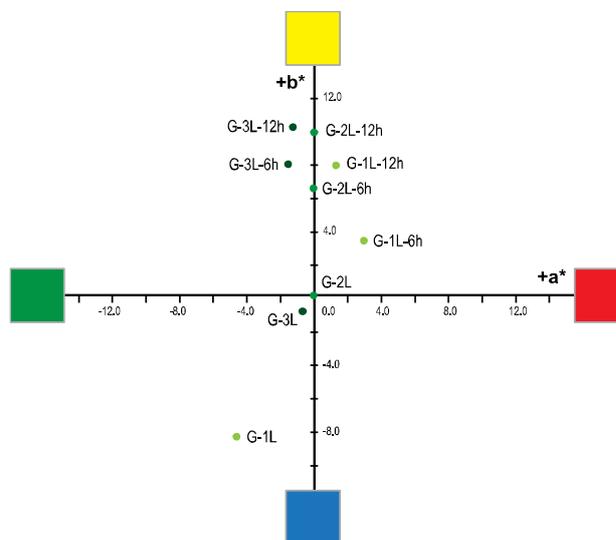


Figure 3 Comparison of a^* and b^* colorimetric values of green UV-visible fluorescent ink before and after the artificial ageing.

Figures 3 and 4 present the a^*/b^* diagrams of the unaged and aged UV-visible fluorescent prints. It is visible that the b^* coordinate of the green UV-visible ink printed in one layer significantly differs from the two and three printed unaged layers of the same ink (Figure 3). Unaged green prints and aged green prints

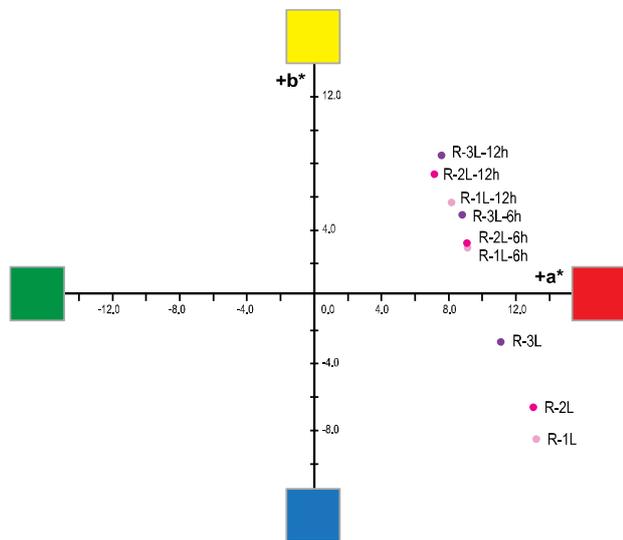


Figure 4 Comparison of a^* and b^* colorimetric values of red UV-visible fluorescent ink before and after the artificial ageing.

with three layers have a negative a^* coordinate, preserving the original colour, while the aged prints with one- and two-layers shift towards the red hue. Furthermore, it can be observed that the ageing of 12 hours results with the shift of the b^* coordinate towards the higher values for both pigments (Figures 3 and 4).

The ageing process has less dispersed effect on the red UV-visible pigment (Figure 4). Although there is a significant shift in the b^* coordinate towards the higher values after 6 and 12 hours of the ageing, a^* coordinate does not change as significantly.

Figure 5 presents the enlarged diagram with the comparison of the effect of artificial ageing on both green and red UV-visible fluorescent prints. The shift towards the higher values on b^* axis after the artificial ageing can be attributed both to pigment degradation and to the start of the degradation of paper substrate which contributes to the colorimetric values of the print, since the prepared printing inks are partially transparent. The shift of the red UV-visible print to higher b^* coordinates pointed specifically to the higher degree of the pigment degradation after the artificial ageing because of the high differences between the initial b^* color coordinates and b^* coordinates after 12 hours of ageing. This occurrence was confirmed by macroscopic images (Figure 7).

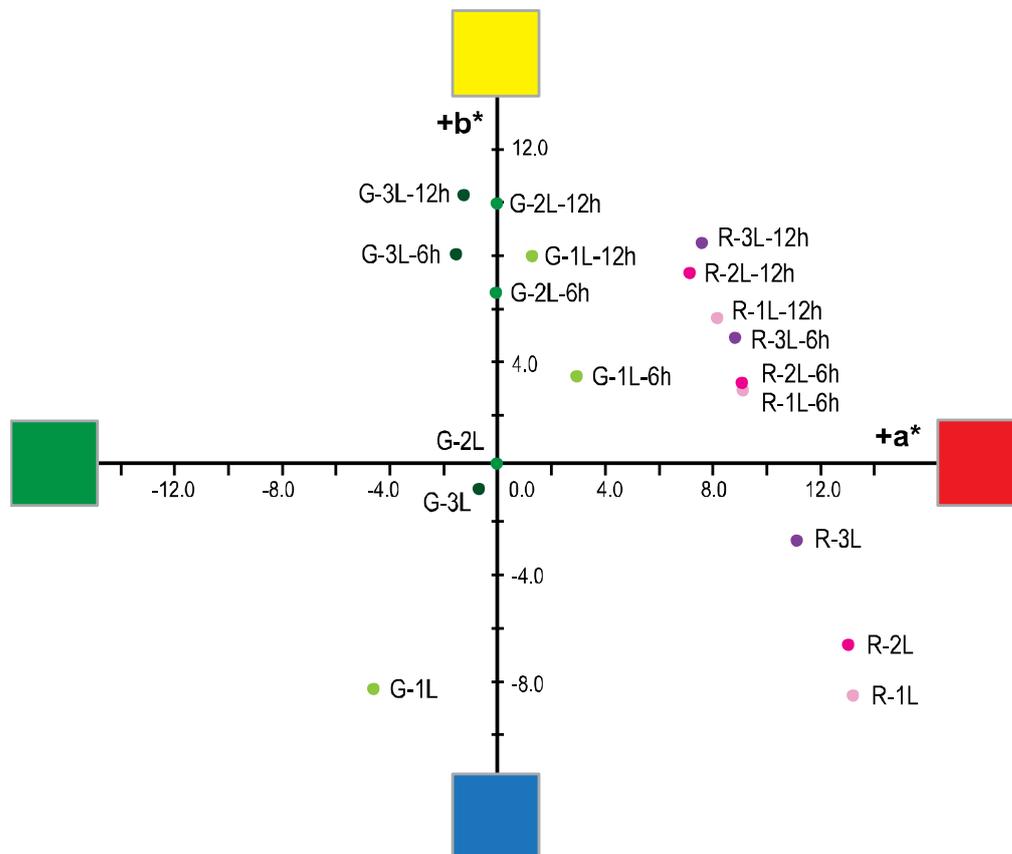


Figure 5 Comparison of a^* and b^* colorimetric values of green and red UV-visible fluorescent ink before and after the artificial ageing.

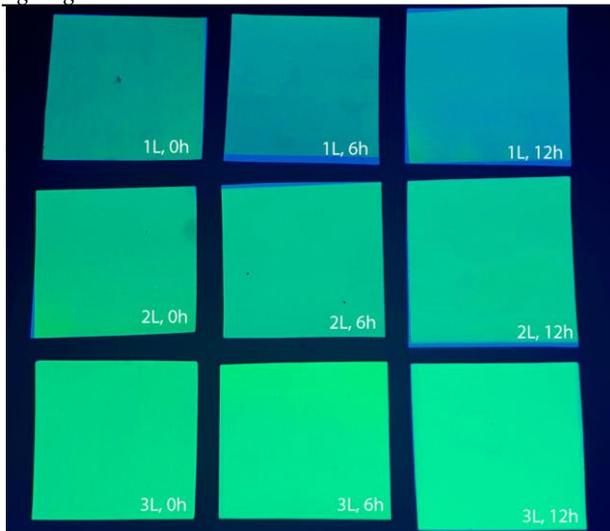


Figure 6 Macroscopic images of unaged and aged green UV-visible fluorescent prints obtained by applying one, two and three ink layers on the printing substrate, taken under UV light source.

Figure 6 presents the appearance of unaged and aged green fluorescent prints under UV light source. Numbers of printed layers are denoted on each sample (1L, 2L and 3L), as well as the duration of the artificial ageing (0h, 6h, 12h). As the number of printed layers increases, the print is more stable after the ageing process, and UV-visible luminescent colours remain more vivid. As expected, the highest optical stability of the colour was achieved on the prints with three ink layers – no expressed visual changes of the luminescence effect after the ageing were observed.

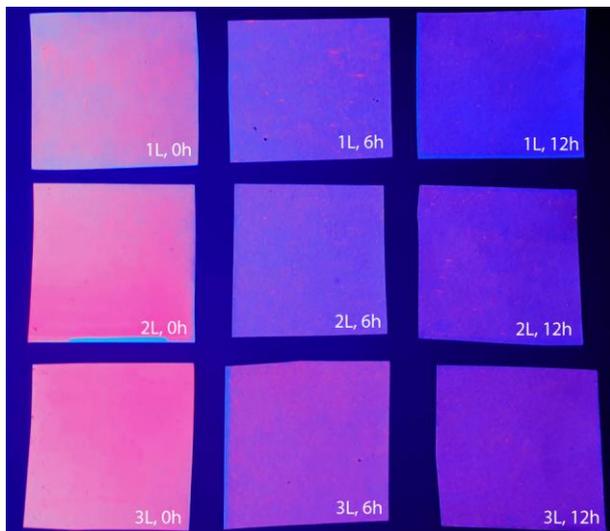


Figure 7 Macroscopic images of unaged and aged red UV-visible fluorescent prints obtained by applying one, two and three ink layers on the printing substrate, taken under UV light source.

Figure 7 presents the appearance of unaged and aged red fluorescent prints under UV light source. Numbers of printed layers are denoted on each sample in a similar way as for the green prints (Figure 6). It is visible that the

increased number of printed layers has an effect on the visual impression of the UV-visible fluorescent inks, but the ageing process has significantly decreased the luminescence effect. It can be concluded that UV-visible red pigment is more sensitive and more prone to the degradation as a consequence of the ageing process compared to the UV-visible green pigment.

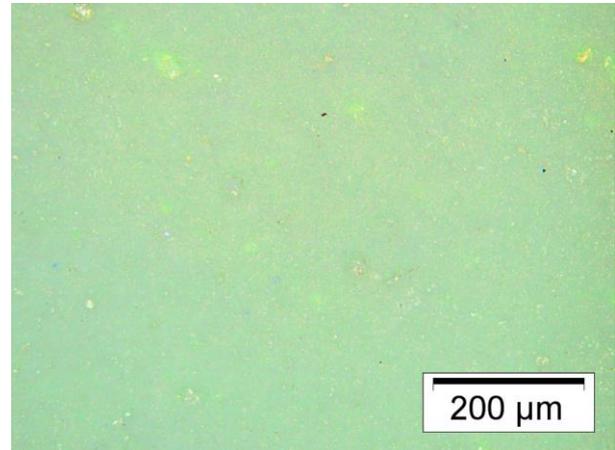


Figure 8 Microscopic image of 3-layered green UV-visible fluorescent print, unaged (magnification of 100x).

Figures 8 and 9 present the microscopic images of the 3-layered green UV-visible fluorescent print before the ageing process (Figure 8) and after the 12 hours of the artificial ageing (Figure 9). The images were captured under the UV light source. The effect of the ageing of the paper substrate (colorimetric change in +b* direction, towards the yellow colour – Figure 3) can be visually observed.

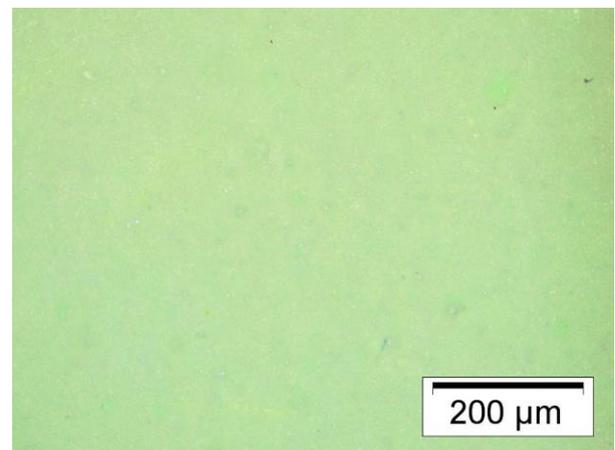


Figure 9 Microscopic image of 3-layered green UV-visible fluorescent print, after 12 hours of ageing (magnification of 100x).

Figures 10 and 11 present the microscopic images of the 3-layered red UV-visible fluorescent print before the ageing process (Figure 10) and after the 12 hours of the artificial ageing (Figure 11). The images were captured under the UV light source. It can be seen that the prints are not as homogenous as the prints produced using the UV-visible green pigment.

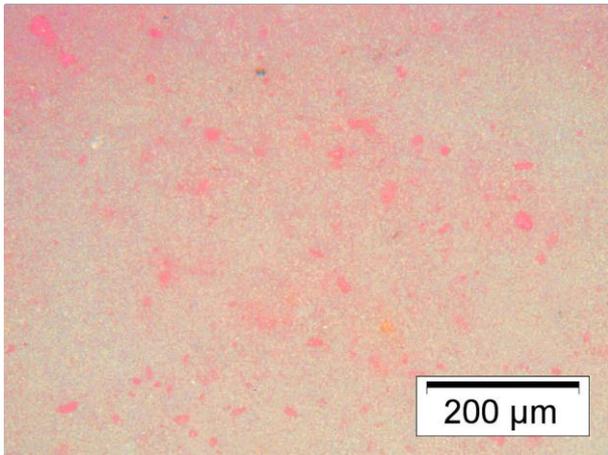


Figure 10 Microscopic image of 3-layered red UV-visible fluorescent print, unaged (magnification of 100x)

The cause could be surface properties of the red UV-visible pigment, which result with the pigment agglomeration and weaker dispersion in the transparent base. Furthermore, the effect of the ageing is highly pronounced on the UV-visible red prints, pointing to the high UV sensibility of the pigment. Therefore, the recommendation for the usage of this type of red UV-visible pigment should be limited to the indoor surroundings, without the direct exposure to light.

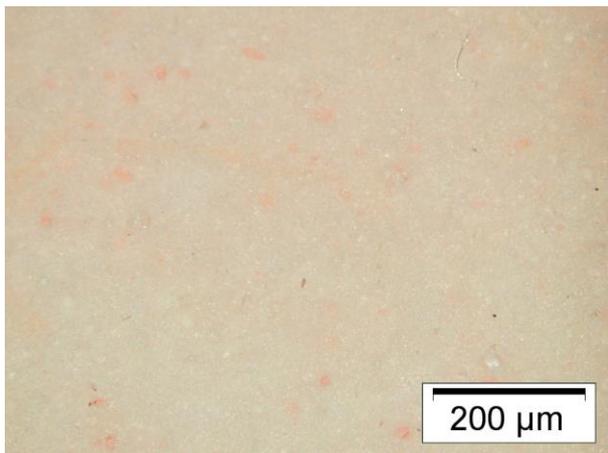


Figure 11 Microscopic image of 3-layered red UV-visible fluorescent print, after 12 hours of ageing (magnification of 100x)

After the analysis of the impact of the artificial ageing on the visual appearance and colorimetric changes in green and red UV-visible fluorescent prints, one can conclude that the thickness of the printed layers plays a significant role in the lightfastness of the prints. The thickness of approximately 35 μm and 50 μm of green and red UV-visible pigment resulted with the preserved lightfastness of the printed layers after 6 hours of the artificial ageing, respectively. Thick ink layers can be obtained by multiple printed layers, or by using a screen of lower mesh count. The choice of the screen should be made in the dependence on the design features of the printed motive, i.e., the fineness of the lines and existence of other fine design elements. Performed

research has pointed to the limitations of the used UV-visible fluorescent inks in terms of the exposure to the sunlight and a need for the consideration of the storage and exposure of the product during its lifespan.

4. CONCLUSIONS

In this research, the reproduction and characterization of UV-visible fluorescent prints obtained by screen printing technique was performed. UV-visible fluorescent inks are characterized by the ability to emit visible radiation after being illuminated by high-energy UV radiation. In daylight, such colors are transparent or have a mild, pastel response. They are often used in industry, and most recently for promotional purposes and in the production of marketing materials, due to their special properties and added value they give the product. UV-visible fluorescent inks are also used for protective purposes in the printing of protected documents, but also for the purpose of various markings, as well as a design feature.

Fluorescent UV-visible red and green pigments were used in the research, and were mixed into a transparent base, which was specifically designed for the application in screen printing technique.

Colorimetric and optical analyses were performed on the obtained prints to evaluate the UV luminescence of the pigments and the stability of the printed colours due to accelerated ageing.

Based on the performed research, it is possible to conclude:

- printing plates with a screen count of 60 l/cm are not recommended for printing of the UV-visible fluorescent print in one application layer on uncoated paper because of the low thickness of the obtained printed layer;
- after the accelerated ageing, the fluorescence effect of green and red inks was diminished due to the degradation of the pigments;
- exposure of the samples to accelerated ageing lead to degradation of the UV-visible fluorescent pigments, but also to degradation of the printing substrate (paper). Degradation was already pronounced when the samples were exposed for only 6 hours and was visible through the shift of the b^* coordinate to higher positive values;
- prints with higher ink layer thickness (obtained by applying two and three ink layers on the substrate) showed greater colorimetric stability after the ageing process.

Performed research has shown that by printing of two or more consecutive layers on the paper substrate, it is possible to get a stable print of optimal visual effect of UV luminescence, which was preserved to extent even after the artificial ageing. This finding can be used as a guideline for the application of UV-visible fluorescent pigments in screen printing. In other words, it is not necessary to use the screen with very low mesh count when printing UV-visible fluorescent inks. It is also possible to use the screen with finer mesh count (most often used to reproduce motives with higher level of

complexity), and to apply the higher number of printed layers. Thereby, the optimal colorimetric properties and optical stability of the print after the ageing process which occurs naturally when the print is exposed to light can be obtained.

REFERENCES

- [1] Thompson, B. (2004). *Printing Materials Science and Technology*, Pira International, ISBN 1858029813, Leatherhead.
- [2] Diamond, A.S. (2018). *Handbook of Imaging Materials: Optical Science and Engineering*. CRC Press, ISBN 0367396572, Routledge.
- [3] Jameson, D.M. (2014). *Introduction to Fluorescence, 1st ed.*, CRC Press, ISBN 9780367865702, Routledge.
- [4] Becidyan, N. (2003). *The chemistry and physics of special-effect pigments and colorants for inks and coatings*, Paint and Coatings Industry, vol. 19, no. 6, pp. 65–76, Jun-2003, ISSN 0884-3848.
- [5] Hirschmann, H., Schweizer, G., Pohé, J. (2002). *Europäisches Patentamt European Patent Office *EP001256609A2**, available at: <https://patentimages.storage.googleapis.com/c3/e4/0b/b925bd81a9e27a/EP1256609A2.pdf>, Accessed: 2022-03-30.
- [6] Bodenstein, C., Martin, H., Katrin, S., Hirmer Dörsam, E. (2019). *Printing process and characterization of fully pad printed electroluminescent panels on curved surfaces*, J. Coatings Technol. Res., vol. 16, no. 6, pp. 1673–1681, Nov. 2019, ISSN 1547-0091.
- [7] Kyoung Soo, Yook, Jun Yeob, Lee. (2013). *Fabrication and luminance switching of flexible organic bistable light-emitting diodes on flexible substrate*, J. Lumin., vol. 137, pp. 105–108, May 2013, ISSN 0022-2313.
- [8] Ataefard, M., Nourmohammadian, F. (2015). *Producing fluorescent digital printing ink: Investigating the effect of type and amount of coumarin derivative dyes on the quality of ink*, J. Lumin., vol. 167, pp. 254–260, Jul. 2015, ISSN 0022-2313.
- [9] Becidyan, N. (1995). *Luminescent pigments in security applications*, Color Res. Appl., vol. 20, no. 2, pp. 124–130, Apr. 1995, ISSN 1520-6378.
- [10] William M., Yen, Shiego, Shionoya, Hajime, Yamamoto, (Eds.). (2018). *Fundamentals of Phosphors*, CRC Press, ISBN 9780367389642, Routledge.
- [11] Elenbaas, W. (1971). *Fluorescent Lamps*, Macmillan Education, ISBN 0333054172, New York.
- [12] Stewart, R., Lin, L. (2003). *Enclosed laser processing of laminated metallised polymer films for security marking*, Proceedings of ICALEO 2003 - 22nd International Congress on Applications of Laser and Electro-Optics, pp. 809, ISBN 978-0-912035-75-8, Jacksonville, Florida, October 2003, Jacksonville.
- [13] Tae Ha, Kwon, Sung Hyun, Park, Jee Youl, Ryu, Hyek Hwan, Choi. (1998). *Zinc oxide thin film doped with Al₂O₃, TiO₂ and V₂O₅ as sensitive sensor for trimethylamine gas*, Sensors Actuators, B Chem., vol. 46, no. 2–3, pp. 75–79, Feb. 1998, ISSN: 0925-4005.
- [14] Izdebska, J. (2016). *Printing on Polymers: Fundamentals and Applications*, in Printing on Polymers: Fundamentals and Applications, J. Izdebska and S. Thomas, (Eds.), pp. 371–388, William Andrew Publishing, ISBN 9780323375009, New York.
- [15] Mahović Poljaček, S., Tomašegović, T., Leskovšek, M., Stanković Elesini, U. (2021). *Effect of SiO₂ and TiO₂ Nanoparticles on the Performance of UV Visible Fluorescent Coatings*, Coatings, vol.11, no.8, p. 928, Aug. 2021, ISSN 2079-6412.
- [16] Tomašegović, T., Mahović Poljaček, S., Jurišić, I., Galaš, M. (2021). *Flexographic reproduction of UV luminescent coating modified with SiO₂ nanoparticles*. Proceedings of the MATRIB 2021, Danko Ćorić, Sanja Šolić, Franjo Ivušić (Eds.), pp. 467–476, ISSN 2459-5608, Vela Luka, Croatia, 30 June–2 July 2021, University North, Varaždin.
- [17] Mahović Poljaček, S., Tomašegović, T., Slišković, A. (2021). *Characterization of UV fluorescent coating modified with TiO₂ nanoparticles printed on polymer substrate in flexography*, Proceedings of the MATRIB 2021, Danko Ćorić, Sanja Šolić, Franjo Ivušić (Eds.), pp. 406–416, ISSN 2459-5608, Vela Luka, Croatia, 30 June–2 July 2021, University North, Varaždin.
- [18] Tomašegović, T., Mahović Poljaček, S., Stržič Jakovljević, M., Marošević Dolovski, A. (2021). *Properties and Colorimetric Performance of Screen-Printed Thermo-chromic/UV-Visible Fluorescent Hybrid Ink Systems*, Applied Sciences, Vol. 11, no. 23, p. 11414, December 2021, ISSN 2076-3417.

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