INFLUENCE OF DIFFERENT APPLICATION METHODS OF SPECIAL INKS ON THERMOCHROMIC AND FLUORESCENCE EFFECT IN SCREEN PRINTING

Maja STRIŽIĆ JAKOVLJEVIĆ, Sanja MAHOVIĆ POLJAČEK, Ana MAROŠEVIĆ DOLOVSKI, Tamara TOMAŠEGOVIĆ

University of Zagreb Faculty of Graphic Arts, Zagreb, Croatia

Abstract: *Printing inks with special effects are commonly utilized in graphic technology for the purposes of added value and anti-counterfeiting methods of printed products. Thermochromic liquid crystal-based inks (TLC) and ultraviolet (UV) visible (daylight invisible) fluorescent printing inks (UVF) can be used in smart packaging - as additional security features, indicators, markings, etc. In this research, TLC ink and UVF ink with red pigment have been applied on the printing substrate as a hybrid ink system, with the aim of obtaining a functional printed product with combined added value. Two suitable paper substrates were screen-printed using two methods: overlaying the prepared UVF ink on the printed TLC ink; and by mixing the UVF red pigment directly into the TLC ink before printing. Thickness, roughness, surface free energy and adhesion parameters of printed layers were analysed. Spectral reflectance of the UVF ink, as well as thermochromic effect of TLC ink were measured. Microscopy was used to display the visual colour play effect and the effect of luminescence. Results of the research have enabled the evaluation of hybrid TLC-UVF effect obtained by screen printing technique, using different ink application methods. Analysis of the properties of obtained prints can be used for the optimization and applicability recommendation of screen-printed TLC-UVF special inks.*

Keywords: *thermochromic liquid crystal-based inks, colour play effect, luminescence, screen printing, packaging*

INTRODUCTION

Thermochromic liquid crystal-based (TLC) printing inks respond to a change in surrounding temperature. Active thermochromic liquid crystal material enables the colour change. This material must be protected from harmful environmental influence by microencapsulation [1,2]. Dynamic colour change of the TLC is defined by activation temperature T_A at which the colour change starts, and temperature activation region of the TLC ink. Inside this region, the reorientation of the molecules inside the TLC structure occurs with the change in temperature, causing the colour change, also called the colour play effect [3]. This effect implies that each colour in visible part of the spectrum occurs at a defined temperature [4]. The special colour play effect is observable only over black or grey substrate with optical density of at least 0.72 [5]. Thermochromic printing inks can be used in several different applications such as temperature indicators, intelligent packaging, security printing, textile, brand protection and marketing [6-9].

In order to produce a printed product with dual functional properties an ultraviolet (UV) visible (daylight invisible) fluorescent printing ink (UVF) with TLC printing ink was used. UVF printing inks belong to a group of a special effect inks and have the possibility of absorbing the UV radiation, and re-emitting of photons of a different radiation [10,11]. This phenomenon is called luminescence and gives UVF printing inks the possibility of their usage in a wide range of applications. They can be used in decorative and packaging industry, for different markings, signalling, and orientation purposes, in a document security application, etc. [12–14]. In printing processes, they can be used in form of a varnish in flexography, in offset printing and relief printing as well [15,16]. In screen printing process, they can be used as printing inks with special purposes or, most often, by mixing UV fluorescent pigments with the transparent base [17]. Printed UV fluorescent inks are usually invisible in a daylight or have a mild pastel tone.

The aim of the paper was to investigate the influence of printing substrate and different application methods on thermochromic and fluorescence effect of TLC and UVF printing inks, respectively. This knowledge could propose some new ideas for the application of TLC and UVF printing inks and their combination.

EXPERIMENTAL

Two types of hybrid TLC-UVF ink systems were used in this research; one of them is overlaying the prepared UVF ink on the printed TLC ink (denoted as HS1 – hybrid system 1), and the other is a mixture of UVF red pigment and TLC ink (denoted as HS2 - hybrid system 2). TLC and UVF printing inks used for hybrid ink systems had a water-based formulation. Both HS1 and HS2 were screen-printed, using a screen-printing plate with a mesh density of 43 lines cm^{-1}, on two types of black paper substrates: uncoated recycled cardboard (URC), 425 gm^{-2} and pressure sensitive label material (PSL), 120 gm^{-2}. URC has thickness of 0.617 mm and was pre-printed in black, while PSL is 0.293 mm thick and coloured in mass. Pressure sensitive label material (traditionaly known as selfadhesive label material) is in recent business and science literature named pressure sensitive as these types of label materials are coated with adhesive that is sensitive to pressure and needs a pressure for its activation. Activation is crucial as pressure ensures the process of adhering the label material to the substrate, from the initial adhesion (initial tack) to final adhesion. PSL material used in this paper is an alternative fibre, environmentally friendly material traditionally and commercially used in area of speciality and decorative labels. Uncoated recycled cardboard (URC) is a one side black, one side brown cartonboard made from recycled fibres. URC is specially developed as substitution for plastic packaging of food, particularly red colour fruit and vegetables, as black side of the board gives perfect contrast and ensures maximum eye-catching effect with the end user.

Caliper was measured with micrometer DGTB001 Thickness Gauge (Enrico Toniolo S.r.l.), according to ISO 534:2011.

Thickness of the printed layers was measured by means of a device working on the magnetic induction principle (SaluTron D4-Fe, Frechen, Germany). Surface roughness of substrates and samples was defined by profiling methods following ISO 11562, DIN 4777 and DIN 4762 standards. R_a roughness parameter was measured in order to define the arithmetic mean deviation of the profile (ISO 4287).

Surface free energy (SFE) and contact angles on samples were calculated using the Data Physics OCA 30 goniometer (DataPhysics Instruments GmbH, Germany). In order to define the strength of interactions between the materials in contact, the adhesion performance was calculated as well.

Temperature-dependent optical properties of both hybrid printing ink systems were measured in a temperature range from 21°C to 47°C, using fiber-based USB 2000+ portable spectrometer (Ocean Optics, USA). CIELAB L^*, a^*, b^* values were calculated using SpectraSuite software by Ocean Optics was used, with D50/2° settings. The printed samples were temperature controlled using the surface of a water block (EK Water Blocks; EKWB d.o.o., Slovenia) [11,18].

Images of printed samples was captured by means of an Olympus BX51 microscope (Tokyo, Japan).

RESULTS AND DISCUSSION

Thickness of the printed layers

Thickness of the printed layers was measured to identify the possible influence of the thickness on the visual response of printed layers. Results are presented in Figure 1.

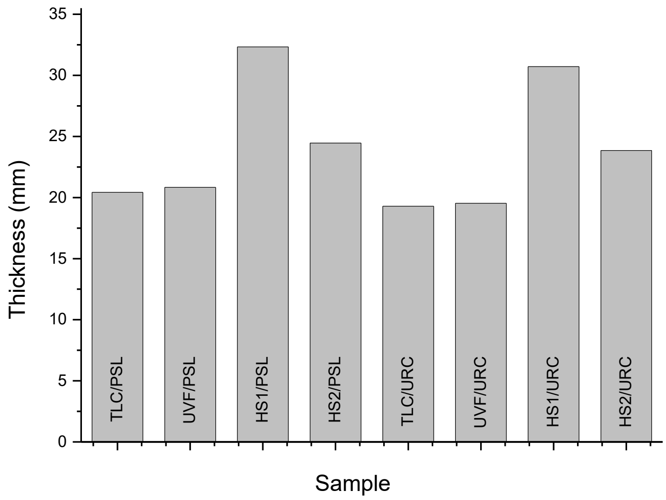


Figure 1: Thickness of the printed layers

One can see that the thickness of the TCL and UVF inks is relatively uniform, on both substrates. Substrate PSL gives slightly higher values of thickness, probably due to the better ink transfer during the printing process. One can see that HS1 layers have a significantly higher thickness on both substrates (32.333 µm on PSL and 30.714 µm on URC). This result was expected due to the application of double-layered ink system and possible interaction of the layers and drying process of the inks.

Surface roughness

R_a parameter was measured on the prints made by pure TLC ink, pure UVF ink and on the printed hybrid ink systems in order to define the substrates' surface structures and to observe the influence of surface roughness of the substrates on the optical properties of effects and on the adhesion performance of the materials in contact. Results are presented in Figure 2. It is visible that pressure sensitive label substrate (PSL) has significantly rougher surface in comparison to uncoated recycled cardboard (URC). R_a parameter amounts 6.940 µm on the PSL and 2.392 µm on URC substrate. By application of pure inks and proposed hybrid systems, one can see that the R_a parameter is decreased on almost all samples. One can assume that applied printing inks penetrate between the paper fibres causing the reduction of surface roughness. On the other hand, due to the usage of water-based printing inks, a certain amount of the ink is probably absorbed into the paper structure causing the reduction of roughness as well. R_a parameter measured on PSL and URC substrates has the smallest values on the prints made using UVF ink. Obviously, UVF ink layer, containing transparent base and UVF pigment, evenly overlays all depths and peaks in the surface structure, causing decreasing of surface irregularities. When observing the roughness values of hybrid ink systems one can say that printed layers cause a certain reduction of roughness. On PSL substrate higher value is detected on prints made using HS2 printing system (R_a = 4.881 µm) in comparison to HS1 (R_a = 3.984 µm). On URC substrate higher value of roughness is detected with HS1 system (R_a = 2.24 µm), in comparison to HS2 (R_a = 1.982 µm).

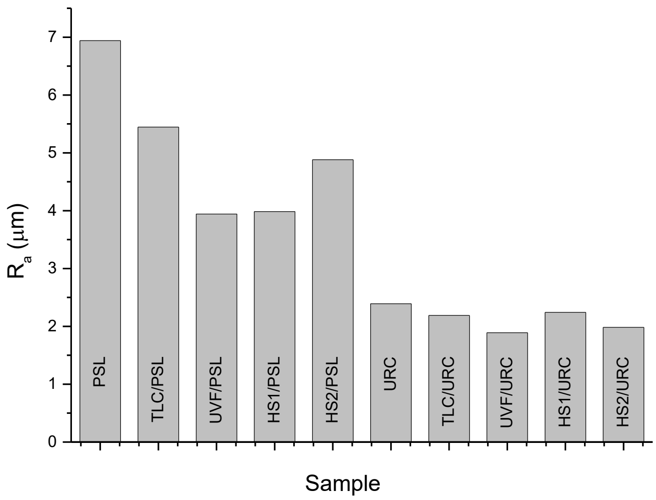


Figure 2: R_a roughness parameter measured on samples

Surface free energy and adhesion parameters

Results of the calculation of surface free energy (SFE) components of papers and printed ink layers are presented in Table 1.

Table 1. Surface free energy components of papers and printed ink layers

	Total SFE (mJ/m^2)	SD	Dispersive SFE (mJ/m^2)	SD	Polar SFE (mJ/m^2)	SD
PSL	53.86	1.28	44.16	1.00	9.71	0.79
TLC/PSL	53.20	2.88	18.58	1.58	34.62	2.41
UVF/PSL	28.00	1.39	27.46	1.36	0.54	0.28
HS2/PSL	48.65	2.29	19.57	1.29	29.08	1.89
UVF (HS1)/PSL	31.64	1.26	31.64	1.26	0.00	0.00
URC	37.71	1.47	36.94	1.43	0.77	0.35
TLC/URC	52.89	1.94	33.08	1.29	19.81	1.45
UVF/URC	29.53	0.78	29.48	0.78	0.06	0.02
HS2/URC	28.35	1.54	16.87	1.15	11.48	1.17
UVF (HS1)/URC	26.86	1.35	26.12	1.31	0.74	0.34

It is visible that paper substrates and UVF ink have a dominant dispersive component of SFE, while polar component is noticeably higher in ink systems with TLC ink. Additionally, polar SFE of the surface of pure TLC ink printed on PSL paper is higher (34.62 (mJ/m2) than the polar SFE of the pure TLC ink printed on URC paper (19.81 (mJ/m2). The same trend is visible for HS2 ink printed on two different paper substrates. This occurrence points to the different interactions between layers containing TLC ink and papers, resulting from different SFE components, roughness, and other paper parameters. Compared to the TLC printing ink, UVF ink printed on both papers as pure ink and as HS1 system, has a dominant dispersive component of SFE. The highest SFE values among the printed hybrid ink systems was measured on HS2/PSL sample (48.65 mJ/m2). This could be related to the highest roughness parameters among the hybrid printed surfaces (Figure

2). The results of SFE calculations are in the accordance with previous research, where the properties of TLC and UVF inks were analysed [17,19]. Since the SFE components significantly vary among the printed hybrid ink systems, the calculation of adhesion parameters was important for the assessment of the interactions between different papers and printed ink systems.

Results of the calculated adhesion parameters are presented in Figure 3a-c. All three parameters were taken into account when assessing the adhesion. Generally, for the optimal adhesion, work of adhesion.

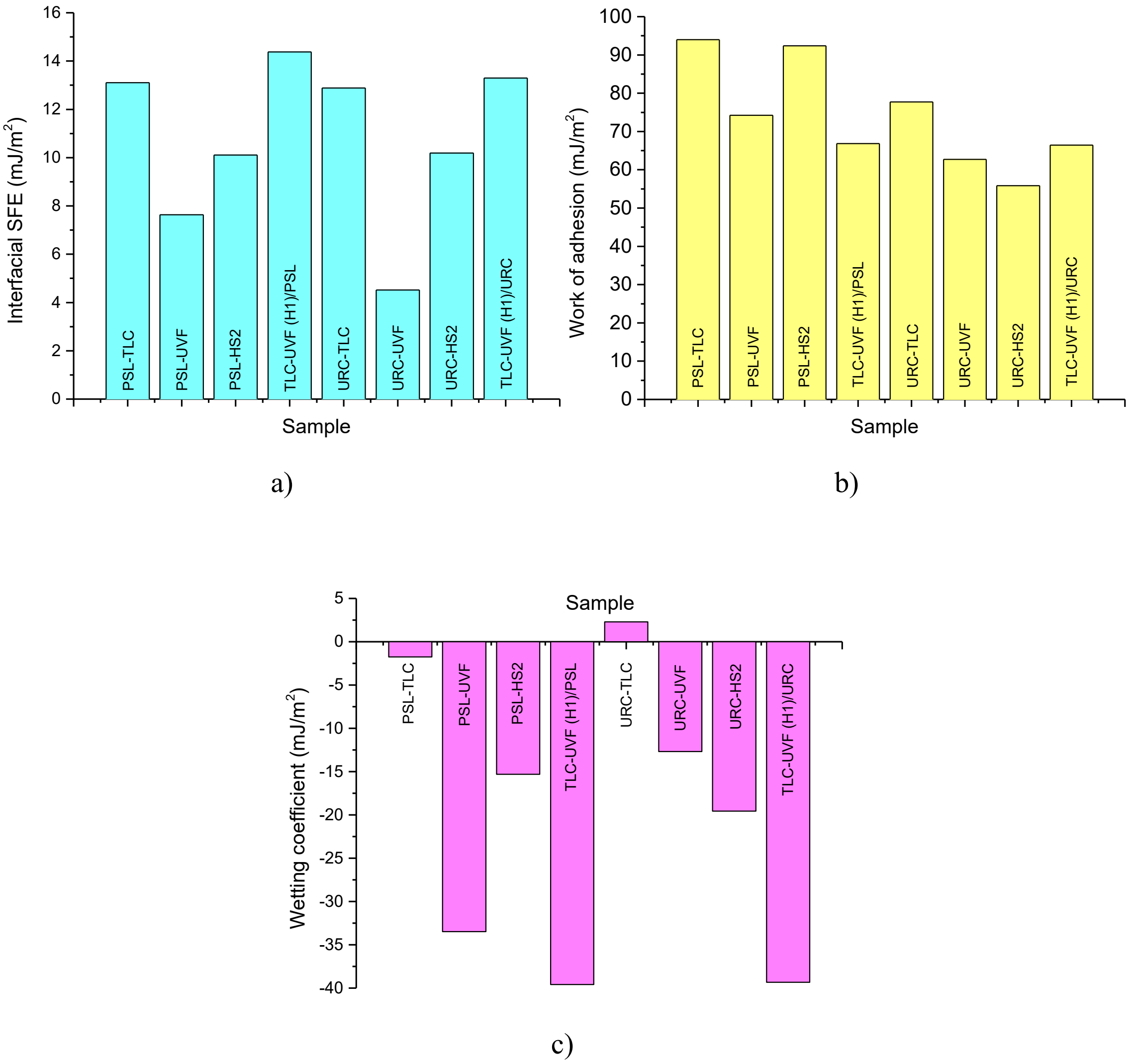


Figure 3: Adhesion parameters between the layers: a) Interfacial SFE, b) Work of adhesion, c) Wetting coefficient

(W12) should be as high as possible, interfacial tension (γ_{12}) should be close to zero, and wetting coefficient (S12) should be positive or equal to zero. In Figure 3a one can see that the interfacial tension was positive for all samples. However, it was lower between the URC paper and UVF ink (4.52 mJ/m2), than between PSL paper and UVF ink (7.63 mJ/m2). When comparing the interfacial tension between different substrates and TLC or HS2 ink, as well as between UVF and TLC in HS1 system on different substrates, the difference of γ12 was not significant. Observing Figure 3b, it is visible that higher work of adhesion was obtained between PSL paper and TLC ink, compared to TLC ink printed on URC paper (93.96 mJ/m2 vs. 77.72 mJ/m2). In hybrid ink systems (HS1 and HS2), the highest work of adhesion was achieved between PSL paper and HS2 ink (92.4 mJ/m2), while the lowest work of adhesion was achieved between the URC paper and HS2 ink (55.87 mJ/m2). Wetting coefficient was not optimal between most analysed surfaces (Figure 3c). Since all wetting coefficients in the hybrid systems, as well as between UVF ink and paper substrates presented the negative values, it can be concluded that the wetting between the layers was not complete. This occurrence is not favourable in most systems. However, in the printing process, negative wetting coefficient can decrease the mottling, resulting with the improved quality of the print [20].

To establish a possible relation between surface roughness and the adhesion, Pearson product-moment correlation coefficient (r) was calculated between Ra parameter of the prints, and the work of adhesion. Significant correlation (r = 0.81) was found. This points to the conclusion that the increased arithmetic mean deviation of the profile is directly related to the higher work of adhesion, i.e., higher work necessary to separate two layers. It can be concluded that the best adhesion in hybrid ink systems was achieved between the papers and HS2 ink. Compared to the HS2 ink, higher interfacial tension, lower work of adhesion and highly negative values of the wetting coefficient between TLC and UVF ink in HS1 system pointed to the weaker adhesion.

Colorimetric analysis was used to describe thermochromic colour play effect of the TLC component in both hybrid ink systems. The CIE L*, a*, b* colour values of all samples printed on URC and PSL paper substrates were calculated from measured reflectance spectra. Both hybrid ink systems printed on URC and PSL show full colour play effect caused by the active material inside microcapsules of the TLC ink (Figure 4). The loop starts to form at TA of the TLC ink, passes through red, yellow, green, blue and violet, ending at almost the same point at (a*,b*) graph, describing the thermochromic effect of the TLC component inside hybrid ink systems. HS2 on PSL results in the most intense colour play effect, forming the widest loop in (a*,b*) graph. Less diminished colour play effect within the same curve limits can be observed for HS1 on PSL. HS2 results in less intense colour play effect printed on URC paper substrate, than the ones on PSL.

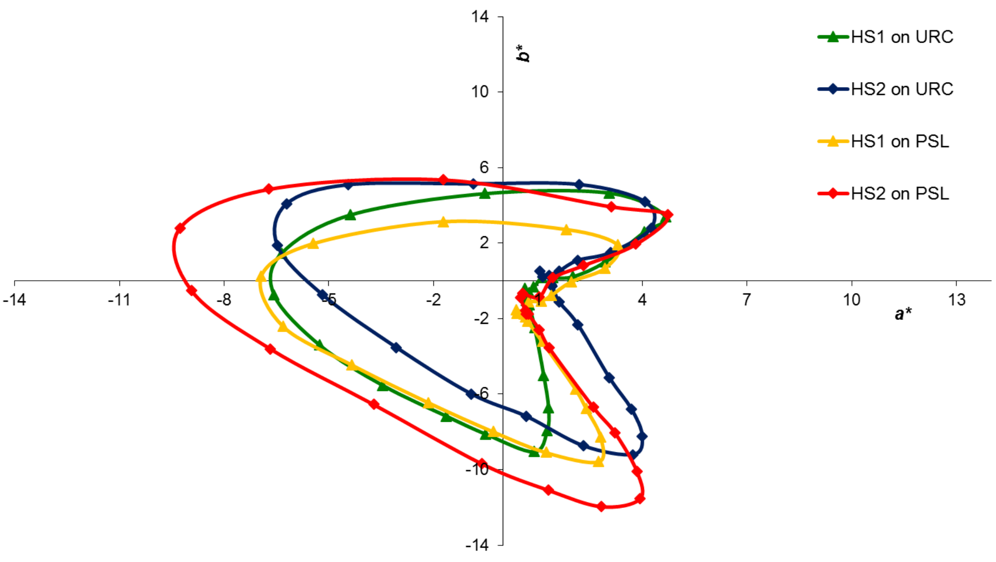


Figure 4: CIELAB colour values of the HS1 and HS2 printed on URC and PSL printing substrates, presented in (a, b*) diagram*

The values of lightness L* measured at each individual temperature of the printed samples are shown in Figure 4, describing temperature-dependant properties of printed hybrid ink systems. The curve for each sample in L*(T) graph extends from 21 to 47 °C, showing a single maximum inside temperature activation region of TLC ink. L*max occurs at almost the same temperature for all samples (Table 2), but the intensity of lightness ΔL*max is different for each sample. HS2 on PSL shows the highest intensity in lightness, confirming the results from (a*, b*) diagram (Figure 4). The same printing substrate results in second highest result of ΔL*max for HS1, then follows HS1 on URC and HS2 on URC.

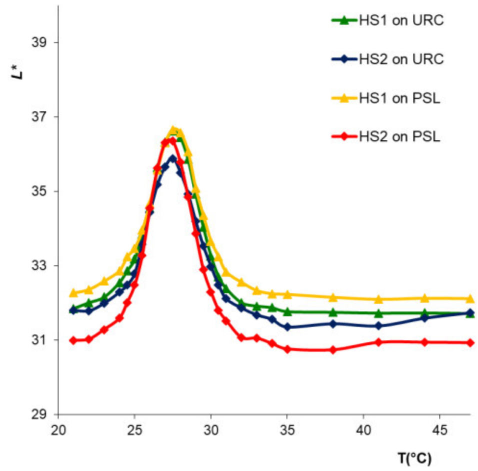


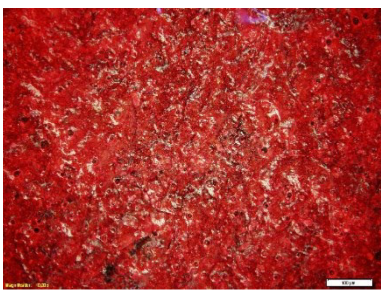
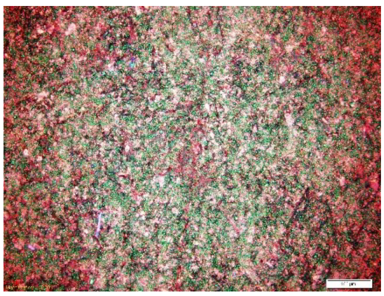
Figure 5: CIELAB colour values of the HS1 and HS2 printed on URC and PSL printing substrates, presented in L/T diagram*

Table 2. Properties of HS1 and HS2 printed on URC and PSL paper substrates: temperature at which the L(T) curve has its maximum is denoted by T(L*max), and its intensity by ΔL*max. See also Figure 5.*

Sample	$T(L^*_{max})$ (°C)	ΔL^*_{max}
HS1 on URC	27.5	4.82
HS2 on URC	27.5	4.09
HS1 on PSL	27.5	4.42
HS2 on PSL	27	5.49

Microscopy of printed layers

Microscopic images of the printed layers are presented in Figure 6. The images were taken at a room temperature of 25 ± 1 °C and 50–55 % relative humidity. Images present the surfaces of printed layers produced in hybrid printing ink systems captured when exposed to UV radiation to ensure the visibility of the fluorescence effect. Thermochromic effect of printed layers was proven by colorimetric analysis of prints. Observing the Figures 6a and 6c one can see that the fluorescence effect is clearly visible on both substrates. TLC layer with microcapsules is not visible since it is completely covered with UVF printing ink. On the other hand, when observing the HS2 system, containing UVF pigment mixed in the TCL ink, a complex structure with properly distributed thermochromic microcapsules and fluorescent pigments is visible (Figures 6b and 6d). One can say that fluorescence effect is visible, but it is more expressed in HS1 systems, in comparison to HS2 systems.

a)  b) 

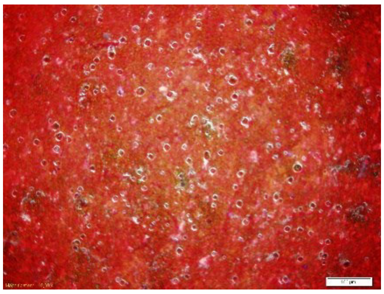
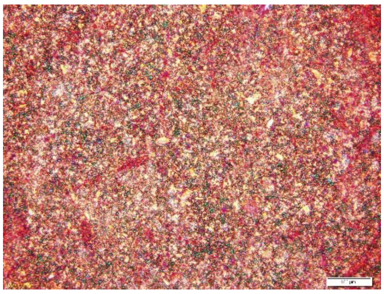
c)  d) 

Figure 6: Microscopic images exposed to UV radiation: (a) HS1/PSL; (b) HS2/PSL; (c) HS1/URC; (d) HS2/URC (mag 100×)

CONCLUSIONS

The compatibility of the proposed hybrid ink systems and printing substrates is confirmed in this research. TLC and UVF printing inks are also mutually compatible and create a hybrid ink system, which was screen-printed on the substrates in individual layers (HS1), and as a mixture of UVF pigment and TLC ink (HS2). The highest SFE value among the printed hybrid ink systems was measured on HS2/PSL sample. This could be related to the highest roughness parameters among the printed hybrid surfaces. Lowest total SFE and lowest polar component of SFE were measured on the surfaces of UVF ink. Furthermore, higher work of adhesion was achieved between PSL paper and printed ink layers than between URC paper and printed layers. Specifically, in hybrid ink systems, the highest work of adhesion was achieved between PSL paper and HS2 ink. Correlation between Ra parameters of the printed layers and work of adhesion between the layers in contact presented correlation coefficient of 0.81. Both HS1 and HS2 resulted in full colour play effect of the TLCs and fluorescent effect of UVF pigment, on both substrates. However, there are some differences between the samples. Temperature-dependant colorimetric measurements showed PSL enables stronger thermocromic effect of the TLC component in hybrid ink systems, than URC. These results could be linked to the selective reflection of liquid crystals over printing substrate coloured in mass, where the colour of the backing has significant role in colour play effect. Resulting differences also may occur because of the moisture barrier inside URC paper substrate, since the hybrid ink systems are water-based and drying mechanism is absorption/penetration into the paper substrate. The proposed hybrid ink systems could be used in the development of applications considering functional packaging, monitoring systems, security printing and sustainable applications. Further research should include investigation of lightfastness properties and parameters of hybrid prints related to the product protection.

REFERENCES

[1] Seeboth, A. et al: THERMOCHROMIC POLYMER MATERIALS, *CHINESE JOURNAL OF POLYMER SCIENCE (ENGLISH EDITION)*, **VOL.** 25, PP. 123–135, ISSN 1439-6203

[2] Liquid Crystal Formulations (LCs), *AVAILABLE FROM* https://www.hallcrest.com/technology/liquid-crystal. *ACCESSED:* 2021-11-01

[3] Bamfield, P.: *CHROMIC PHENOMENA*, RSC PUBLISHING, ISBN 978-1-84755-868-8, LONDON, (2010)

[4] Christie, R.M., Bryant, I.D.: AN EVALUATION OF THERMOCHROMIC PRINTS BASED ON MICROENCAPSULATED LIQUID CRYSTALS USING VARIABLE TEMPERATURE COLOUR MEASUREMENT, *COLORATION TECHNOLOGY*, **VOL.** 121, PP. 187–192, ISSN 1478-4408

[5] Strižić Jakovljević M., Lozo, B. & Klanjšek Gunde M.: THE PROPERTIES OF PRINTING SUBSTRATES REQUIRED FOR THERMOCHROMIC LIQUIDCRYSTAL PRINTING INKS, *J. PRINT MEDIA TECHNOL. RES*, **VOL.** 4, PP. 165–170, ISSN 2414-6250

[6] Seeboth, A., Lötzsch, D.: *THERMOCHROMIC PHENOMENA IN POLYMERS*, SMITHERS RAPRA, ISBN 978-1-84735-112-8, SHRAWSBURY, (2008)

[7] Aitken, D. et al: TEXTILE APPLICATIONS OF THENNOCHROMIC SYSTEMS, *REVIEW OF PROGRESS IN COLORATION AND RELATED TOPICS*, **VOL.** 26, PP. 1–8, ISSN 0557-9325

[8] Sage I., THERMOCHROMIC LIQUID CRYSTALS, *AVAILABLE FROM* Https://Doi.Org/10.1080/02678292.2011.631302. *ACCESSED:* 2021-11-01

[9] Kerry J., Butler, P.: *SMART PACKAGING TECHNOLOGIES FOR FAST MOVING CONSUMER GOODS*, JOHN WILEY & SONS, ISBN:9780470028025, HOBOKEN, (2008)

[10] Jameson, D.M.: *INTRODUCTION TO FLUORESCENCE*, CRC PRESS, ISBN 9780429192890, BOCA RATON, (2014)

[11] Becidyan, A.N.: LUMINESCENT PIGMENTS IN SECURITY APPLICATIONS, *COLOR RESEARCH & APPLICATION*, **VOL.** 20, PP. 124–130, ISSN 1520-6378

[12] Bodenstein, C. et al: PRINTING PROCESS AND CHARACTERIZATION OF FULLY PAD PRINTED ELECTROLUMINESCENT PANELS ON CURVED SURFACES, *JOURNAL OF COATINGS TECHNOLOGY AND RESEARCH*, **VOL.** 16, PP. 1673–1681, ISSN 1547-0091

[13] Elenbaas, W.: FLUORESCENT LAMPS, *AVAILABLE FROM* https://books.google.hr/books?id=vVJdDwAAQBAJ. *ACCESSED:* 2021-11-01

[14] Yook, K.S., Lee, J.Y.: FABRICATION AND LUMINANCE SWITCHING OF FLEXIBLE ORGANIC BISTABLE LIGHT-EMITTING DIODES ON FLEXIBLE SUBSTRATE, *JOURNAL OF LUMINESCENCE*, **VOL.** 137, PP. 105–108, ISSN 0022-2313

[15] Bozhkova, T., Spiridonov, I. & Shterev, K.: OVERVIEW OF SECURITY PRINTING TYPES AND TRENDS IN ITS FUTURE DEVELOPMENT, *BULGARIAN CHEMICAL COMMUNICATIONS*, **VOL.** 49, PP. 195 -201, ISSN 0324-1130

[16] Talebnia, F., Nourmohammadian, F. & Bastani, S.: DEVELOPMENT OF NOVEL FLUORESCENT OFFSET INK BASED ON COUMARIN DYES: SYNTHESIS AND PROPERTIES, *PROGRESS IN ORGANIC COATINGS*, **VOL.** 77, PP. 1351–1359, ISSN 0033-0655

[17] Poljaček, S.M. et al: EFFECT OF SIO_2 AND TIO_2 NANOPARTICLES ON THE PERFORMANCE OF UV VISIBLE FLUORESCENT COATINGS, *COATINGS*, **VOL.** 11, PP. 928, ISSN 2079-6412

[18] Becidyan, A.N.: THE CHEMISTRY AND PHYSICS OF SPECIAL-EFFECT PIGMENTS AND COLORANTS FOR INKS AND COATINGS, *PAINT AND COATINGS INDUSTRY*, **VOL.** 19, PP. 65–76, ISSN 0884-3848

[19] Marošević Dolovski, A. et al: THERMOCHROMIC EFFECT AND ADHESION PARAMETERS OF LIQUID CRYSTAL-BASED PRINTING INK ON RECYCLED PRINTING SUBSTRATES, *PROCEEDINGS OF THE 2ND INTERNATIONAL CONFERENCE ON CIRCULAR PACKAGING*, Karlovits, I. (ED.), PP. 305–310, ISBN 978-961-90424-6-5, LJUBLJANA, OCTOBER 2021., PULP AND PAPER INSTITUTE, LJUBLJANA, (2021)

[20] Joshi, A. V., Bandyopadhyay, S.: EFFECT OF INK TRANSFER ON PRINT MOTTLE IN SHRINK FILMS, *JOURNAL OF COATINGS TECHNOLOGY AND RESEARCH*, **VOL.** 12, PP. 205–213, ISSN 1547-0091

Corresponding author:

Maja STRIŽIĆ JAKOVLJEVIĆ
Department of graphic materials and printing plates
University of Zagreb, Faculty of Graphic Arts
Getaldićeva 2
10000 Zagreb, CROATIA
Phone: +385-1-2371 080 (254)
maja.strizic.jakovljevic@grf.unizg.hr