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The properties of printing substrates required for thermochromic liquid-crystal printing inks

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Abstract

The color change of thermochromic liquid-crystal (TLC) printing inks occurs inside the microcapsules containing thermo-responsive material. It starts at the defined activation temperature (t_A) and occurs in several degrees wide region above the t_A where the color changes throughout the whole visible spectrum, with the effect known as "color play". Previous research showed that the "color play" effect of TLC printing ink is clearly visible if the ink is printed on a black substrate but on the white one no color can be observed. The presented research aims to answer what optical density (D) of the substrate is needed for clear observation of the "color play" effect. The results show that mentioned effect of the TLC ink is observable if it is printed on grey substrate with D of at least 0.72. The research also shows that samples printed on uncoated black paper result in stronger temperature dependent optical properties of TLC printing ink compared to the samples printed on coated black paper. This effect is related to drying mechanism of TLC printing ink and absorption properties of printing substrate.

Keywords: optical properties of substrate, activation temperature, spectral reflectance, "color play" effect

1. Introduction

Thermochromic printing inks change color in dependence on the temperature. The color change of thermochromic liquid-crystal (TLC) printing inks occurs inside the microcapsules containing thermo-responsive material (Seeboth and Lötzsch, 2008). It starts at the defined activation temperature (t_A) and occurs in several degrees wide region above the t_A where the color changes throughout the whole visible spectrum from red over orange, yellow, green and blue to violet, the effect known as "color play" (Bamfield and Hutchings, 2010). The color activation region is frequently called "the color play interval" (Christie and Bryant, 2005). The width of activation regions can vary between 1 °C and 20 °C (Hallcrest, 2014) and can be somewhere between −30 °C and 100 °C, often with very high temperature sensitivity (Sage, 2011; White and LeBlanc, 1999). The TLC inks are colorless for the temperatures below or above the activation region. The transformation from colorless state to colored one takes place gradually when temperature reaches the lower limit of the activation region, i.e. the t_A value. Above the upper limit of the activation region the purple color fades and the TLC ink becomes colorless again. The temperature needed to reach the colorless stage is called "the clearing point" (Hallcrest, 1991; Jakovljević, et al., 2017; Jakovljević, Lozo and Klanjšek Gunde, 2016). The TLC printing inks are finding many applications such as temperature indicators especially for packaging, security printing and brand protection (Sage, 2011; Hallcrest, 2014; Seeboth and Lötzsch, 2008). In electronics, liquid crystals can be used to detect electrical shorts in circuits, open circuits and inoperative devices (Sage, 2011). The ability to monitor and map the temperature of a substantial area of surface can be a great advantage in detecting a fault or localizing activity manifesting themselves by temperature changes (Kakade, et al., 2009; Abdullah, et al., 2010; Christie and Bryant, 2005; Hallcrest, 2014).

Within "the color play interval", the spectral color with given wavelength λ appears by reflection of the light on special structure of the liquid crystal when the elongated molecules inside the microcapsules develop a helical superstructure with pitch equal to λ of the light. As the temperature raises the length of helical pitches shrinks causing the shift of the peak in the reflectance spectra towards shorter wavelengths, therefore the color of the material changes towards blue shades (White and LeBlanc, 1999; Seeboth and Lötzsch, 2008; Hallcrest, 2014).

The "color play" effect of TLC printing ink is clearly visible if the ink is printed on a black substrate but on the white one no color can be observed (Jakovljević, et al., 2017). The reason for this is in the nature of the "color play" effect in TLC inks. The reflection on helical structure is rather weak effect thus most of the light transmits through the ink layer and hits the substrate. Here, it can scatter; on a white substrate majority of light scatters which practically totally obscure the light reflected on the molecular pitch. To prevent this, TLCs should be applied to black substrate which absorbs the light transmitted through the ink layer. Under such circumstances, the iridescent colors can be clearly seen (Jakovljević, et al., 2013). The effect depends on the amount of light reflected by the substrate, however, the currently available literature do not show what optical density (D) of the substrate is needed for the observation of the "color play" effect. The presented research aims to answer it.

2. Experimental

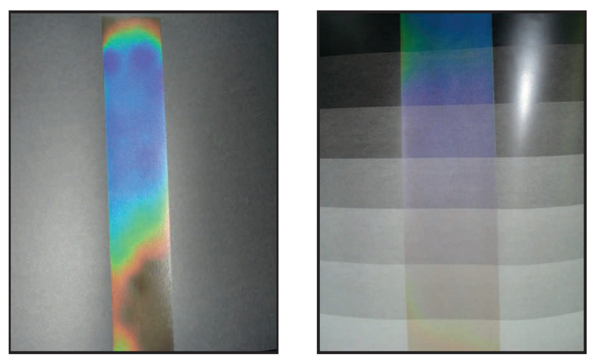
2.1 Materials

Screen-printing TLC ink (SC-140-TC/0398; Printcolor, Switzerland) in a water-based formulation was used in this research. The t_A of the TLC printing ink was 25 °C and the activation region was from 25 °C to 30 °C. Outside of the activation region the ink is colorless. The clearing point of the ink is defined at 44 °C. All color changes in the TLC printing ink are considered to be reversible.

In this research white and black papers were used as printing substrates (Table 1). The white paper was a semi gloss paper digitally printed in six different D, defined as 20, 40, 50, 70, 90 and 100 percent tonal value fields of black ink. Nominal tonal values were sent to Konica Minolta C6000 printer using original Konica Minolta black toner. Each one of these fields were measured for D (Table 2). The black substrates were uncoated and gloss-coated papers. The water-based TLC printing ink was screen-printed on all mentioned printing substrates, with two layers of ink (wet over dry), using SEFAR® PET 1500 43/110–80 W polyester mesh with 149 μm openings. The prints were dried in a hot air tunnel at ~75 °C. Different activation phases of TLC ink printed on black uncoated paper and semi gloss paper digitally printed in different tonal values of black ink are shown in Figure 1.

Table 2: Optical densities of black ink digitally printed in different tonal values

Tonal value (%)	*D*
20	0.11
40	0.30
50	0.42
70	0.72
90	1.37
100	1.65



a) *b)*

Figure 1: Different activation phases of TLC ink printed on uncoated black paper (a) and paper digitally printed in different tonal values of black ink (b)

2.2 Measurements

Temperature dependent optical properties of printed samples were determined by spectroscopic measurements. The "color play" effect of TLC ink was quanti-

Table 1: Properties of paper printing substrates used in the research

Producer	Paper color	Surface description	Thickness (μm)	Basis weight (g/m²)
Mondi	white preprocessed *(Table 2)*	semi-gloss coated	162	160
Hahnemühle	black	uncoated	232	160
BYK	black	gloss coated	350	260

fied by spectral reflectance of the printed samples, measured in dependence on temperature. The temperature-dependent iridescent colors were calculated and presented as CIELAB colorimetric values. The D50 illuminant and 2° standard observer were taken into account, as recommended for graphic arts applications (Schanda, 2007).

For reflectance measurements, the 8°:di measuring geometry was obtained using Lambda 950 (PerkinElmer, USA) spectrometer with 150 mm wide integrating sphere. This measuring geometry allows illumination at 8°, where the light reflected in all directions is detected (diffusely reflected light with specular direction included). The reflectance spectra were measured in the 350–850 nm spectral region ($\Delta\lambda$ = 1 nm).

Optical densities of the samples digitally printed in different tonal values of black ink were measured using spectrometer i1 (X-Rite), density status T.

The printed samples were heated on the surface of water heated block (EK Water Blocks; EKWB d.o.o., Slovenia). Its base plate is made of copper coated with a nickel layer and polished. The thermostatically controlled water circulates through very thin acrylic channels inside this plate, transferring the heat from the water through the plate to the sample (Jakovljević, et al., 2017). The measurements were accomplished in the temperature range from 26 °C up to 79 °C using 0.5 °C, 1 °C, or 2 °C temperature steps, as required by the dynamics of spectral changes.

3. Results and discussion

The temperature dependent colorimetric properties of the applied TLC ink were first analyzed on the layers printed over the white preprocessed paper. Spectral reflectance (R) of the TLC ink printed on printing substrate with different D are shown in Figures 2 to 7.

Figure 2 shows reflection spectra of TLC printing ink applied on printing substrate with D of 0.11. Compared to the samples with higher D, the overall reflection of light from TLC ink is the highest which is the result of reflectance on the substrate and the TLC layer causes only a negligible effect. The reflection peak appears better on printing substrate with D of 0.30 (Figure 3). At higher D the effect of the TLC ink increases (Figures 3 to 7).

At a selected temperature, the reflectance peak appears at approximately equal wavelengths, regardless of the D of the applied printing substrate. The intensity of the peaks, R_{max}, increases as the D of the printing substrate increases, reaching its maximum at D of 1.65 (100 % covered by black, Figure 7).

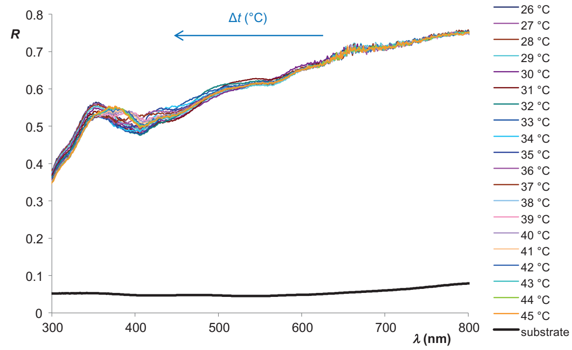


Figure 2: Spectral reflectance of TLC ink printed on substrate with D of 0.11

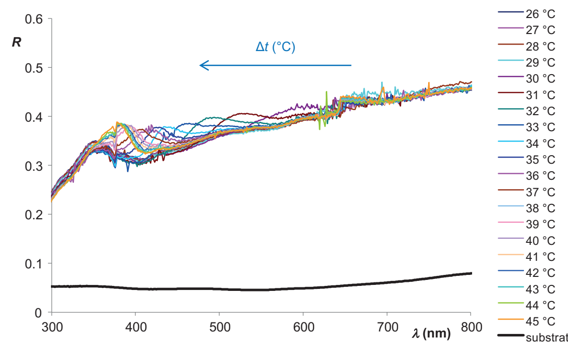


Figure 3: Spectral reflectance of TLC ink printed on substrate with D of 0.30

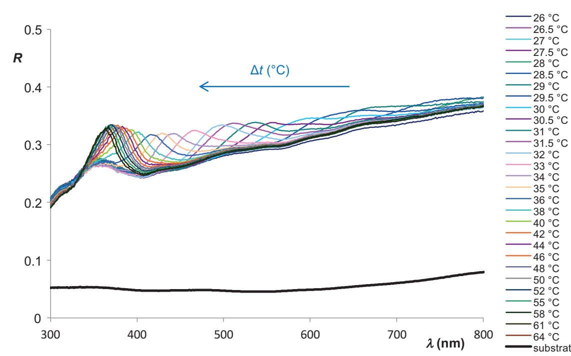


Figure 4: Spectral reflectance of TLC ink printed on substrate with D of 0.42

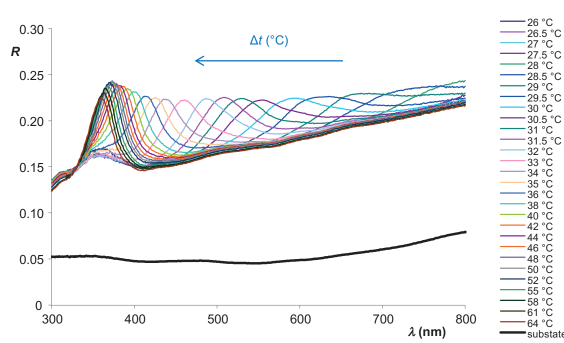


Figure 5: Spectral reflectance of TLC ink printed on substrate with D of 0.72

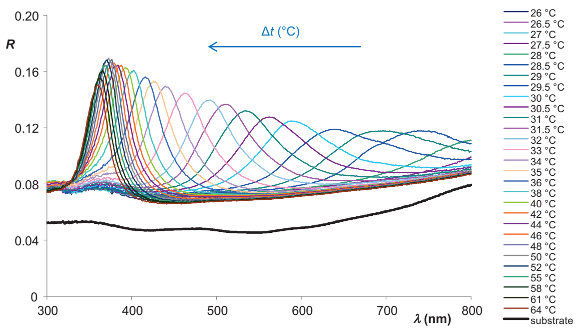


Figure 6: Spectral reflectance of TLC ink printed on substrate with D of 1.37

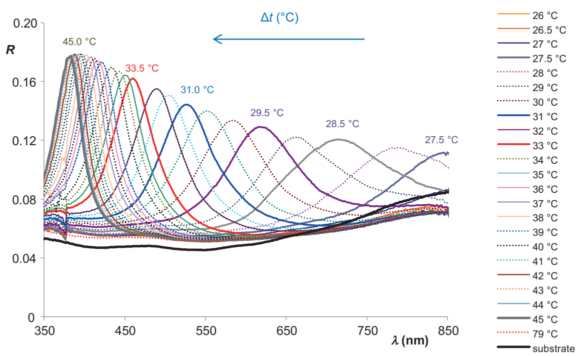


Figure 7: Spectral reflectance of TLC ink printed on substrate with D of 1.65

The CIELAB color values were calculated from the corresponding reflectance spectra and are shown in Figure 8. Printing substrate with *D* of 0.11 results in tightly closed curve in (*a**, *b**) graph. The curve extends only within the first quadrant of (*a**, *b**) graph, where colorimetric values are $a^* > 0$ and $b^* > 0$. This indicates very weak thermochromic effect of TLC printing ink. With higher *D* of the substrate, the color loop becomes larger and crosses the boundary of the first quadrant at *D* of 0.42 where *a** values extend also slightly towards green ($a^* < 0$). The first occurrence of a closed curve that extends across all quadrants of (*a**, *b**) graph appears at *D* of 0.72. This is the lower limit for *D* of printing substrate where the TLC layer could expose the entire "color play" effect. Printing substrates with higher *D* enable even stronger thermochromic effect of TLC printing inks, especially in the blue-green region ($a^* < 0$ and $b^* < 0$).

The results on Figure 8 show that the red-yellow shades of the TLC layer appear also on substrates with lower *D*, but much higher values are needed for resolving the blue-green colors. The results presented in $L^*(t)$ graph (Figure 9) show direct temperature dependent properties of TLC printing ink. Temperature activation region of the ink is seen very clearly. $L^*(t)$ graph shows a single peak at the same temperature (30.5 °C) for all measured samples, i.e. at all *D* of the substrate. Temperature dependent effect is barely noticeable for the sample with *D* = 0.11. First sign of temperature dependent effect is visible in $L^*(t)$ graph for sample with 0.30, while *D* of 1.65 results in the strongest effect of all samples. The effect of different *D* of the printing substrate printed digitally with black ink on the differences in lightness (ΔL^*) of the TLC ink is shown in Table 3.

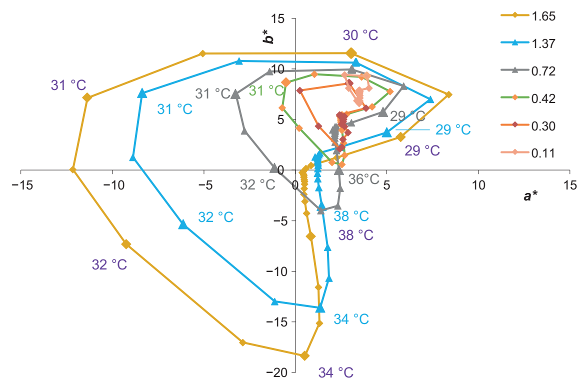


Figure 8: CIELAB (a, b*) color values of TLC printing ink printed on substrates with different D*

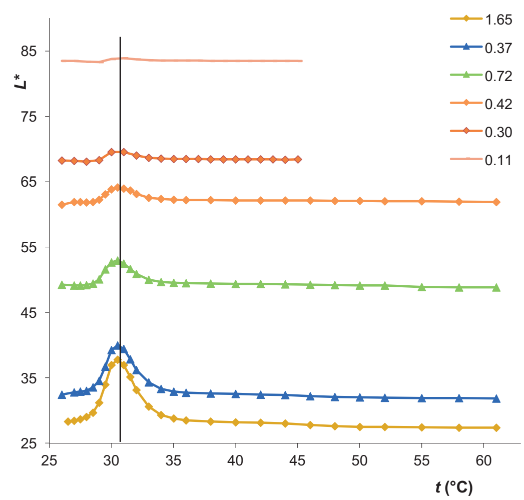


Figure 9: CIELAB L(t) temperature dependent color values of TLC printing ink printed on substrates with different D given in the legend*

Table 3: Temperature dependent characteristics of TLC printing ink measured from the peak in the L(t) graph; ΔL* is the relative height of the peak*

Tonal value (%) / *D*	ΔL^*	FWHH (°C)
20 / 0.11	0.04	–
40 / 0.30	1.03	3.0
50 / 0.42	1.90	2.5
70 / 0.72	3.50	3.0
90 / 1.37	8.11	3.0
100 / 1.65	10.44	3.0

Full width at half height of the $L^*(t)$ peak (FWHH) is almost the same for all samples. Presented results show that different D do not affect the activation region of the ink, but ΔL^* changes as shown in Table 3.

The TLC layers printed on the uncoated black paper show stronger "color play" effect than the samples printed on the coated black paper (Figures 10 and 11). The (a^*, b^*) values obtained from the layer on the uncoated paper are larger and the effect gives larger color gamut (Figure 10) and stronger peak in the $L^*(t)$ graph (Figure 11).

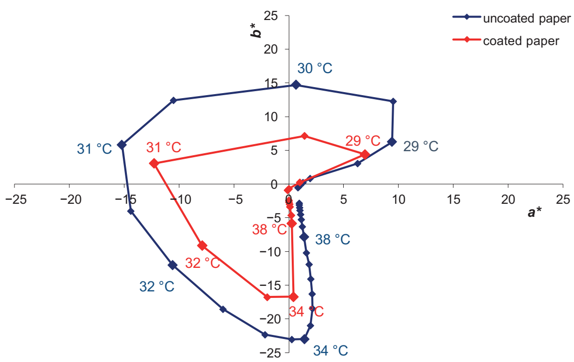


Figure 10: CIELAB (a, b*) color values of TLC ink printed on black uncoated and coated paper*

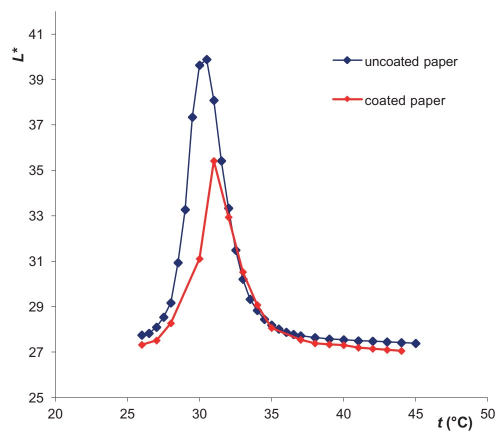
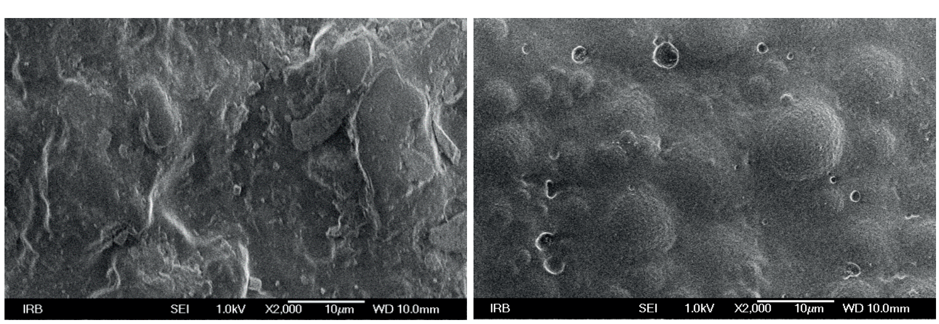


Figure 11: CIELAB L(t) color values of TLC ink printed on black uncoated and coated paper*

For coated paper, the maximum value of L^* is 9.01 at 31 °C and for uncoated paper it is 12.41 and appears at 30.5 °C. These results confirm that the entire "color play" effect is obtained for the layer on both black substrates, but it is stronger on the uncoated one. The reasons for the above shown effect were analyzed by the help of SEM analysis (Figure 12). The micrographs of the TLC layer on the uncoated black paper shows microcapsules containing thermochromic material (Figure 12b), but such a structure is not visible for the layer on the coated black paper (Figure 12a). Appearance of microencapsulated pigments on the surface of the TLC layer can be explained taking into account the drying mechanism of the ink and absorption of ink into the printing substrate. Uncoated black paper is more absorbent than the coated one, therefore less binder remains in the dry ink layer. The large microcapsules (at least 10 μm in size) cannot protrude the substrate and remain in the ink layer and are, in general, larger than the thickness of the remaining binder. This is why the microcapsules shapes are seen on the SEM micrographs. The coating on the paper prevents penetration of the binder into the substrate, thus it practically entirely covers the microcapsules (Figure 12a). It is reasonable to conclude that the "color play" effect in TLC pigments is weaker when they (i.e. the microcapsules) are well covered by the binder and stronger when they are on the top of the layer, practically with no covering of the binder. The TLC ink printed on uncoated black paper caused more revealed microcapsules after drying compared to coated paper. Microcapsules with a smaller amount of binder around them result in stronger reflection of light from helical superstructure of TLCs. In the case of coated paper, part of the incident light is most likely scattered due to the surface layer of the binder, leaving smaller portion of light which causes reflection from TLCs.

4. Conclusions

The results confirm that "color play" effect of the TLC inks is observable if it is printed on grey substrate with D of at least 0.72. The larger D gives stronger effect. The "color play" effect of TLC printing ink is best shown on



a) *b)*

Figure 12: SEM analysis of TLC ink printed on coated (a) and uncoated (b) black paper

(a^*, b^*) graph. The entire effect is visible if this curve extends across all four quadrants. Samples printed on substrate with D between 0.30 and 0.42 have resulted in closed (a^*, b^*) curves, but extending only within the first quadrant of (a^*, b^*) plane.

Appearing of blue and green shades needs higher D of the printing substrate, at least 0.72; larger D gives more deep green and blue colors. This effect was confirmed by spectroscopic measurements on preprinted white paper, showing the strongest reflection peak in each curve for the sample with D of 1.65 (100 % black). When comparing the black papers, the samples printed on uncoated black paper result in stronger colors than the samples printed on coated black paper. This effect is related to the amount of binder covering the TLC pigments (microcapsules). This amount is smaller for uncoated substrate and larger for coated one and depends on drying of the ink on the substrates with different absorption properties. Microcapsules are more revealed if there is less binder around them. The effect of light reflection from helical superstructure of TLCs is stronger if the ink is printed on uncoated paper. The binder present around microcapsules after drying on coated paper represents a kind of light barrier, so the smaller amount of incident light causes reflection from the TLCs. The result is weaker reflection, i.e. "color play" effect of TLC ink printed on coated paper.

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