Colorimetric description of thermochromic printing inks

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Abstract

The dynamic colour of three commercial reversible thermochromic inks were studied. Thermochromic printing inks change their colour according to a change in temperature. The two types of thermochromic inks are based on leuco dyes and liquid crystals. The thermochromic effect achieved by liquid crystals is quite different from the effect achieved with leuco dyes. Leuco dyes change from a coloured to a colourless state, or from one colour shade to another due to structural changes inside leuco dye molecules under assistance of developer. Liquid crystal inks change colour continuously throughout the spectrum, producing iridescent colours starting from red and shifting to blue part of the spectrum with temperature. The colour change results from the way light interacts with special arrangement of liquid crystal molecules to produce coloured reflection by interference, and with the variation of this structure with temperature. In this paper we will present differences between two types of thermochromic printing inks giving careful colorimetric characterization.

Keywords: Thermochromic inks, leuco dye, liquid crystals, colorimetric properties

1. Introduction

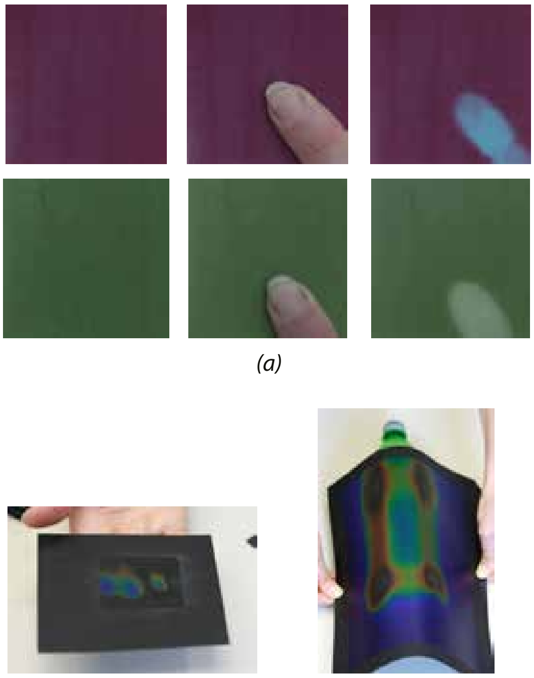
Thermochromic (TC) inks constitute one of the major groups of colour changing inks. Colour - changing inks are becoming increasingly important in various applications for smart packaging, security printing, brand protection, medical applications, marketing, toys and textile colouring (Johansson, 2006; White and LeBlanc, 1999; Phillips, 2000; Christie, 2007; Seeboth and Lötzsch, 2008; Worbin, 2010). The main purpose of such application is to carry and protect the product as well as to market it.

In most cases, the colour change occurs inside the microcapsules containing thermo - responsive materials (Seeboth and Lötzsch, 2008; White and Leblanc, 1999). There are two basic types of thermo - responsive materials, leucodye - based composites (TLDs) and thermochromic liquid crystals (TLCs) (see Figure 1). The colour change occurs at the defined activation temperature T_A (for TLDs) and in the activation region (for TLCs).

Leucodye - based inks usually change from coloured to discoloured state above the activation temperature (T_A), where the name originates from (λευκος in greek: white) (Jakovljević et al., 2016). However, in some cases the printing ink is formulated to change from one colour to another by careful selection of dye (Bamfield and Hutchings, 2010). Thermochromic composites in leucodye - based inks consist of a leuco dye (colour former), colour developer and organic solvent. The colour changes due to the structural modifications as a function of temperature (Tang et al., 2010; Zhu and Wu, 2005). To achieve the desired effect the components are mixed in specific ratios and usually encapsulated to protect the system in subsequent applications. The colour change effect of the TLDs occurs at the defined T_A and is in most cases reversible; in special situations also irreversible TLDs are possible.

Reversible TLD printing inks in most cases change from coloured to colourless state as the temperature is raised above the T_A and recolor again when cooled well below it (see Figure 1a). T_A is determined by the temperature where the solvent applied to prepare TLDs changes from solid to liquid state, causing the colour - forming components to form a colour complex below the transition temperature (coloured state) and destroyed it above this temperature (discoloured state) (Gunde et al., 2011; Kulčar et al., 2010; MacLaren and White, 2003). Microencapsulated TLDs are applied in commercial inks with various T_A, from -15°C up to 65°C. TLD inks of all basic types are available, such as water - based, solvent - based and photocuring inks for screen- and offset printing on paper, plastics, metal and textile. They are frequently mixed with conventional inks to obtain an interchange between the two single colours (Kulčar et al., 2011).

TLDs are easily applicable with practically no difference to conventional printing inks. Reversible TLD inks can be printed using flexography, screen gravure and offset printing methods.


(a)

(b)

Figure 1. Colour change on printed samples with thermochromic leuco dyes (a) and thermochromic liquid crystals (b)

TLC printing inks start a colour change at the defined T_A, but the colour change occurs in several degrees wide region above the T_A. This temperature range is called activation region but can also be called the colour play interval. Within the activation region colour changes throughout the whole visible spectrum from red, orange, yellow, green, blue to violet (rainbow, iridescent colour) (see Figure 1b). This effect is known as "colour play". TLC ink is colourless for the temperatures of the sample below or above the activation region. The transformation from colourless state to coloured one takes place gradually when temperature reaches the lower edge of the activation region. Above the upper edge of the activation region the purple colour fades until the TLC becomes colourless again. The temperature needed to reach the colourless stage is called "the clearing point" (Hallcrest, 2014; Jakovljević et al., 2016).

The active material in TLCs consists of elongated (rod - shaped) molecules that undergo phase changes from crystalline solid to isotropic liquid trough chiral nematic (or cholesteric) mesophase. Equally oriented molecules inside the adjacent sheets twist and the direction of the long axis of molecules traces out a helical path. Helical superstructure which is developed in chiral nematic or cholesteric mesophase (i.e. a special phase between the solid and liquid states of the material) causes special optical properties of TLC ink at temperatures inside the activation region. The degree of this effect is described by pitch length P; defined as the length of the pitch in the helix formed by 360° rotation of directions of elongated molecules of the TLC (see Figure 2). Optical effect of TLC printing inks is based on selective reflection of light from the helical structure, with P depending on temperature - if P is comparable to the wavelength of light that falls parallel to the axis of the helix, the light is reflected at a wavelength equal to the optical value of P. As the temperature rises the helical pitches shrink, causing reflections of light with shorter wavelengths (Hallcrest, 2014; Jakovljević et al., 2013; Sage, 2011). Therefore, the temperature dependent P causes the TC effect in TLCs.

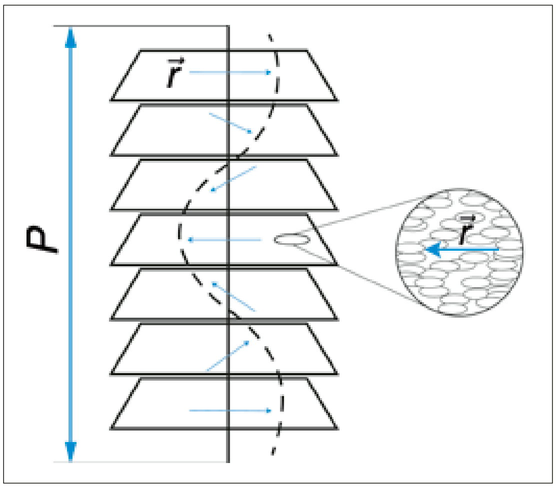


Figure 2. Helical superstructure of TLC-s (Hallcrest, 2014)

The active material in TLCs does not absorb the visible light, but reflects a narrow spectral region thus producing approximately monochromatic colour similar to colour of rainbow (i.e. iridescent colours). The colour play effect of the TLC inks is rather weak - most of the light transmits the material. This light could scatter on the substrate and largely obscure the light reflected on the molecular pitch. To prevent this, TLCs should be applied to black substrate which absorbs the transmitted light. Only under such circumstances, the iridescent colours can be seen (Jakovljević et al., 2013). The entire colour change occurs in a few degrees wide temperature range, which ensures TLCs to be much more sensitive to temperature changes then TLDs. They can have a versatile range of colour and useful colour changes between -30 and 100°C, often with very high temperature sensitivity (Sage, 2011; White and LeBlanc, 1999). The width of activation regions can vary between 1 and 20°C. The colour change of the most TLC inks is reversible (Hallcrest, 2014).

TLC printing inks are finding increasing use in applications such as temperature and packaging indicators, security printing and brand protection. An application area which has seen consistent focus is the use of thermochromic liquid crystals in engineering applications. The ability to monitor and map the temperature of a substantial area of surface can be a great advantage in detecting a fault or localising activity. In electronics, liquid crystals can be used to detect short circuits, open circuits, inoperative devices, and map operational areas in large - scale integrated circuits (Sage, 2011).

The active material of TC inks, whether it is leuco dye or liquid crystal, is in most cases microencapsulated, in order to protect the active material from negative impacts of the environment. Microcapsulation enables printing of thin layers of TC inks on almost any type of printing substrate. Printing thicker layers of TC inks is recommended for stronger TC effect and better resistance to UV light. Microcapsules of TC printing inks are dispersed in a suitable binder. The colour, mechanism of its change and temperature where the change occurs are determined by the material inside microcapsules whereas the binder defines the printing and curing technology (Seeboth and Lötzsch, 2008; White and LeBlanc, 1999).

The differences between TLD and TLC printing inks are presented here, giving careful characterization of temperature dependent colorimetric properties.

2. Experimental

The results obtained for commercially available TC inks are shown here. Three TC inks were used, from three different manufacturers and with different activation temperatures. The data given from the suppliers of these inks are given in Table 1.

Table 1: Basic data of the TC inks applied here: manufacturer, type of ink, printing technique, drying method and activation temperature/region.

Ink	**TLC25**	**TLD63**	**TLD27**
Manufacturer	Printcolor	CTI	LCRHallcrest
Type of ink	liquid crystals	leuco dye	leuco dye
Printing technique	screen	offset	offset
Drying	air	air	air
Activation (°C)	25	63	27

TLD inks were printed on Prüfbau MZ II Multipurpose Printability Testing Instrument over white uncoated paper (140 g/m^2). TLD27 ink change colour from blue to colourless and TLD63 ink change from burgundy to blue colour.

The reflectance spectra were measured in three cycles. In each cycle the sample was heated from the lowest to the highest temperature and then cooled back to the lowest one. Around the T_A the reflectance spectra were measured every 0.5°C or 1°C intervals. TLD27 was measured from 12°C to 40°C, TLD63 from 38°C to 74°C and TLC25 from 24°C to 45°C.

TLC25 (Printcolour Screen Ltd., Switzerland) water-based ink was screen - printed, using 149 μm mesh openings, on the black coated paper (260 g/m^2). This ink was printed in two subsequent layers (wet over dry) and hot air dried at 75°C. T_A of the TLC ink was at 25°C and the activation region from 25°C to 30°C. Within the activation region the TLC ink showed the full "colour play" effect changing throughout the whole visible spectrum, with the effect being reversible. The ink was colourless outside the activation temperature. For the temperatures above the activation region the ink still showed some colour change, but the effect faded gradually till the complete loss of colour above 44°C (clearing point), becoming colourless again (Table 2).

Table 2. Technical specification of the TLC ink

TLC T_A	Red	Green	Blue	Clearing point
25°C	25°C	26°C	30°C	44°C

The measurements were obtained from the samples heated on the thermostatically controlled water inside water block (EK Water Blocks, EKWB, Slovenia). From the obtained reflectance spectra the corresponding CIELAB values were calculated and presented as *(a*,b*)*, *L**(*T*) and *(L*,C*)* graphs.

Spectrometer Ocean Optics USB2000+ with 50mm wide integrating sphere was used for measuring temperature - dependent colorimetric properties of the TC inks. Ocean Optics SpectraSuite software was used for the calculation of the CIELAB values *L**, *a**, *b** and *C** from measured reflectance. The D50 illuminant and 2° standard observer were applied in these calculation. The measurements were performed in the steps of 1 nm for the spectral region from 370 to 730 nm.

3. Results and discussion

The measured reflectance spectra of the samples printed with TLDs and TLCs are shown in Figs. 3–8. TLD27 sample become discoloured during heating and coloured again during cooling (Fig. 3, 4). TLD63 sample change from burgundy to blue during heating and then back to burgundy during cooling (Fig. 5, 6). No abrupt change was observed and both processes are continuous. Decolourization of TLD27 is not complete even at the highest temperature applied in our experiment. This could be the result of incomplete transparency of the TC composite inside microcapsules at high temperature.

The reflectance spectra of TLC samples (Fig. 7) are completely different from that of TLDs. The effect of iridescent colour starts with rather broad reflectance peak with typical Lorentzian shape. Each individual spectrum show single reflectance peak. The peak in spectral reflection measured at 29°C peaks at 700 nm, so the colour play effect starts accordingly with the red colour. When temperature rises, the peak narrows and moves towards shorter wavelengths, i.e. from red colour further to orange, yellow, green, blue and purple. Above 40°C the colour play effect gradually declines and the colour fades approaching to the clearing point temperature. Due to black substrate and reflectance from cholesteric liquid crystal structure inside microcapsules of the TLC inks, spectral reflectance of TLC sample is much lower than spectral reflectance curves of TLD samples. The comparison of the three sets of reflectance curves is shown in Figure 8.

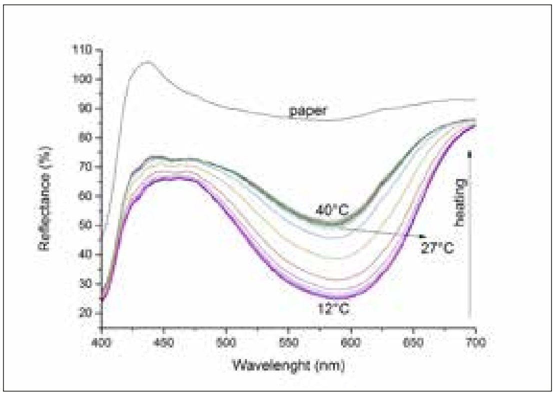


Figure 3. Spectral reflectance curves of TLD27, heating

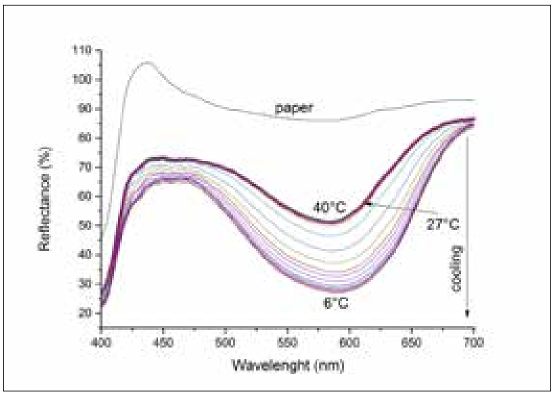


Figure 4. Spectral reflectance curves of TLD27, cooling

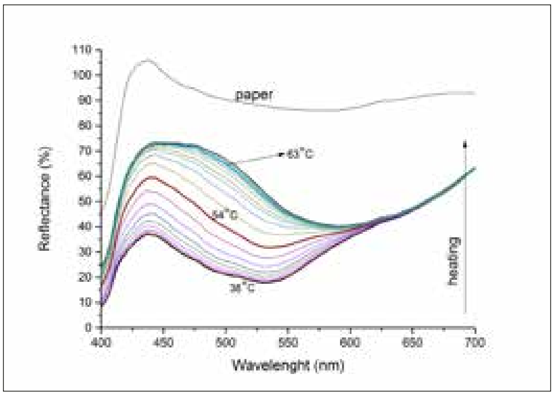


Figure 5. Spectral reflectance curves of TLD63, heating

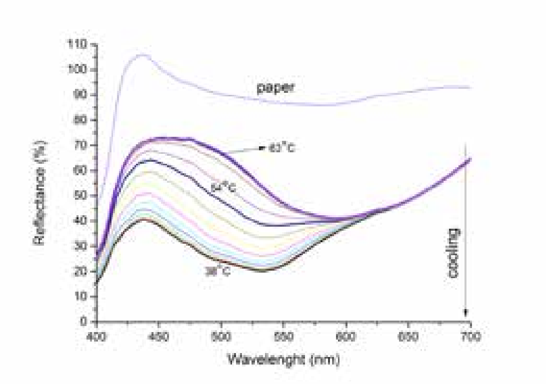


Figure 6. Spectral reflectance curves of TLD63, cooling

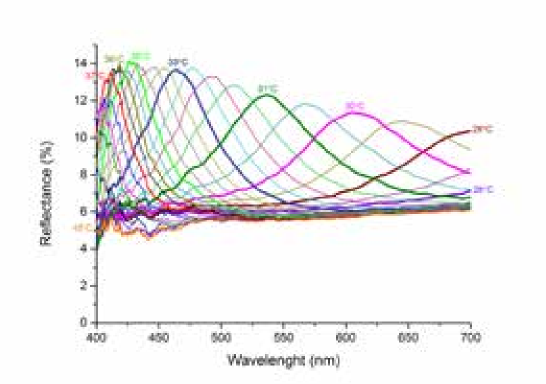


Figure 7. Spectral reflectance curves of TLC25, heating

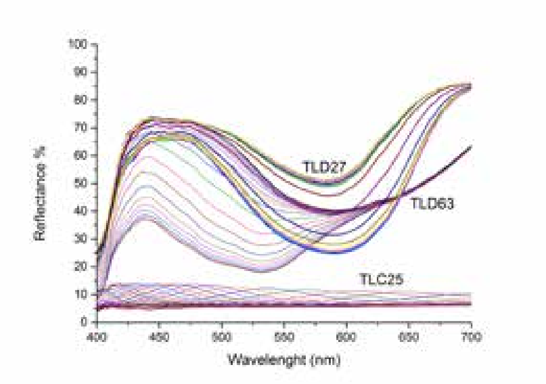


Figure 8. Spectral reflectance curves for three different TC inks (TLD27, TLD63 and TLC25), heating

The temperature dependent reflectance spectra were used for colorimetric analysis, to calculate the dependence of CIELAB values on temperature.

During heating/cooling cycle the *a**, *b**, *L**, and *C** values of a TC sample describe a path on the (*a**,*b**) and (*L**,*C**) planes (Fig. 9, 10). These paths of TLDs are in general not the same at heating and cooling, but differences are small.

TLC show completely different dynamical colour properties. When temperature rises from 25°C to 45°C the TLC ink continuously changes from transparent below T_A, followed by red, orange, yellow, green, blue and purple. As the rising temperature reaches the clearing point temperature (44°C), purple colour gradually fades until it completely disappears. Specific colour play effect of TLC printing inks describes the entire colour circle in (*a**,*b**) graph (Fig. 9). The shape of the curve demonstrates that the system was producing richer colours in green and blue regions than in the red region, which agrees with visual observation.

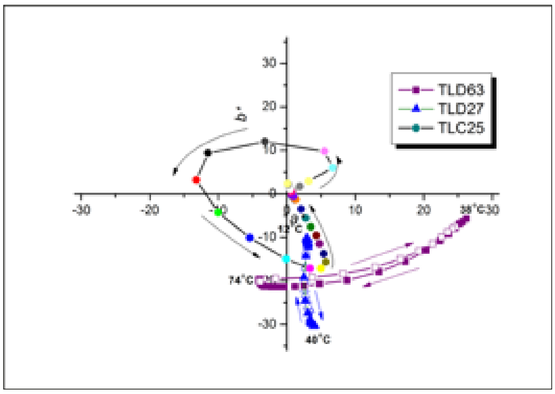


Figure 9. Changing of CIELAB values of TLD27, TLD63 and TLC25 samples in the (a*,b*) plane at heating (solid signs) and cooling (open signs).

The TLC describe practically closed loop which in all states remains at much lower L^* values than that of TLDs. Therefore, the two types of TC inks are clearly distinguishable in CIELAB colour space.

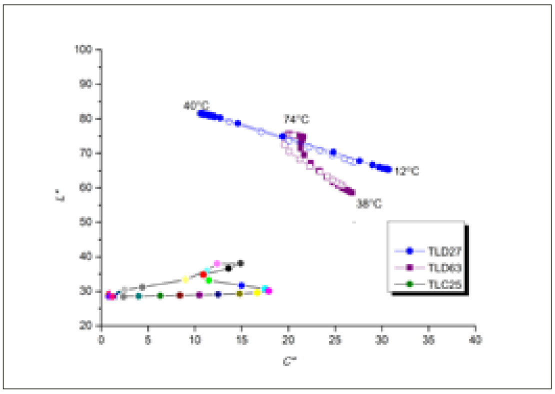


Figure 10. CIELAB (L*,C*) graphs of two TLDs and TLC ink

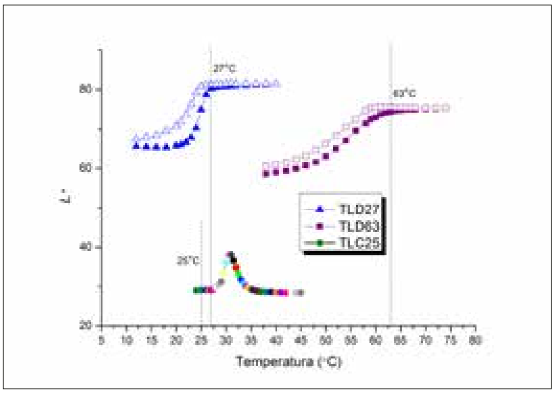


Figure 11. CIELAB lightness L* of TLD27, TLD63 and TLC25 samples in dependence on temperature at heating (solid signs) and cooling (open signs)

The process is also illustrated by change of lightness L^* as a function of temperature (Figure 11). The TLDs entire L^*(T) curves have a form of a loop, known as hysteresis loop (Kulčar 2010). The TC system has a sort of memory-it is not possible to predict its output without knowing the path that it followed before the current state was reached. Such a phenomenon is called hysteresis. TC materials belong to several physical systems with hysteresis. It is colour hysteresis that describes the colour of a TC sample as a function of temperature.

The TLD samples do not show equal colour hysteresis: they differ in the temperatures where the loop starts and finishes. If a completely reversible process is assumed, a thermochromic sample should return to the same colour after the whole heating/cooling cycle. Hysteresis loop of such a sample is closed.

The analysed TLC sample shows a single L^* peak with maximum at 30°C spreading over the entire activation region. At 25°C the L^* value is 29.1 and rises by further increase in temperature, reaching the maximum value at 30°C. Further temperature increase results in decreasing values of lightness, followed by a decline of the colour play effect. Above the clearing point temperature at 45°C the colour of the TLC completely fades. While the corresponding colour is essentially monochromatic (almost pure spectral colour are obtained) and changes with temperature over the visible spectral region, the L^*(T) curve cannot describe the colouration properties well enough and should be compared with other graphs, such as presented in Figures 9 and 10.

4. Conclusions

Thermo - responsive optical properties of two types of thermochromic printing inks presented in this research are very different. As the temperature is raised above the T_A, TLD printing inks change from coloured to colourless state and regain colour when cooled. TLD inks exibit colour as a result of selective absorption of light. Below activation temperature, i.e. in the coloured state, all effects are similar to that known for conventional inks. A light shade background is recommended when printing with TLD inks, since the TC composite is not opaque. If they are printed on a background colour other than white, the background colour will influence the colour of the ink. On the other hand, TLCs should be applied to black substrate - its high absorption prevents scattering of light which could obscure the weak reflection on TLCs.

Two analysed TLD samples show colour hysteresis: their colour does not depend only on temperature but also on the way this temperature was reached. A system with hysteresis has memory, i.e. it exhibits a path-dependence. The colour of samples prepared with a thermochromic ink is different when the same temperature is reached by heating or by cooling. Different colour hystereses were obtained. Printing inks based on TC leuco dyes are characterised by their relatively low accuracy (wide hysteresis of temperature change). Therefore, functional applications of these inks tend to be for visual or indicative purpose only.

TLC printing inks provide special type of thermochromic effect inside the temperature activation region of the ink. The so-called colour play effect is based on selective reflectance of light from the helical structure of the TLCs. As the temperature rises, the colour play effect takes place inside temperature activation region of the ink, with the light being reflected in a narrow band within visible spectral region.

The presented research of temperature dependent colorimetric properties of thermochromic inks will contribute in understanding differences between leuco dye - based and liquid crystal - based printing inks. Although thermo - responsive properties are a common feature for both types of thermochromic printing inks, mechanism of the colour change differs in a great extent. As a result, each type of TC inks has specific temperature dependent colorimetric properties, which can determine the field of application for this functional materials. For this purpose the CIELAB values could be presented in (a^*,b^*) or (L^*,C^*) planes of the colour space. To provide an efficient application, the L^*(T) graphs are also required.

5. References

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