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Packaging added value solutions by Thermochromic Liquid Crystal-based printed labels

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Abstract

Thermochromic liquid crystals (TLC) printing inks show specific, temperature dependant optical properties. The color change of TLC ink appears only inside the activation region where the color changes gradually , due to specific structural changes in the microencapsulated active thermochromic material, the TLCs. Throughout the activation region the color changes as a rainbow, i.e. the spectral color along the whole visible spectrum, the effect is called "the color play". Temperature dependant optical properties of TLC materials enable the usage of these inks in various fields of application, including the functional packaging. Divers kinds of temperature indicators facilitate monitoring and control of the conditions of the packed goods. Still, the usage of TLC printing inks is not widely applied in the area of functional packaging, despite the expansion of application options. The paper presents a number of possible applications of TLC inks in the area of functional packaging and/or labels for added value packaging. The spectral reflections for each temperature within the activation region of the used TLC ink was acquired by spectrometric measurements. The CIELAB colorimetric values were calculated and presented, showing the "color play" throughout the whole spectra. The results of the presented measurements may contribute in defining the colorimetric parameters of dynamic color change of TLC printing inks as well as to the development of new applications in the field of functional packaging.

Introduction

Thermochromic printing inks change color in dependence of surrounding temperature. In most cases, the color change occurs inside the microcapsules containing thermo-responsive materials [1,2]. There are two basic types of thermo-responsive materials, leucodye-based composites and thermochromic liquid crystals (TLCs). The color change effect of the two principles differs to a great extent: leucodye-based inks usually change from colored to discolored state above the activation temperature (T_A), that's where the name originates from (λευκος in greek: white). However, in some cases the printing ink is formulated to change from one color to another. No matter the color, the color change occurs at the defined T_A. The color change effect of the leucodye-based inks can be reversible or irreversible [3,4].

TLC inks start a color change at the defined T_A but the color change occurs in several degrees wide region above the T_A. The color change temperature range is called activation region but can also be called "the color play interval". Within the activation region color changes throughout the whole visible spectrum from red, orange, yellow, green, blue to violet (Figure 1). This effect is known as "color play".

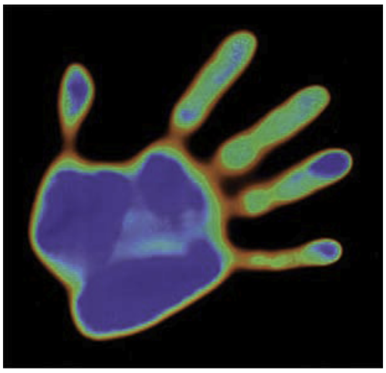


***Figure 1.** Color play effect of the TLC printing ink* [5]

For the temperatures below or above the activation region the TLC printing ink is colorless. The transformation from colorless state to colored one takes place gradually starting with the activation temperature as the lower edge of the activation region. Above the upper edge of the activation region the purple color fades until it becomes colorless again. The temperature needed to regain the colorless stage is called "the clearing point".

Within the activation region the spectral color with given wavelength λ appears when the elongated molecules of the active material inside the microcapsules develop a helical superstructure with pitch equal to λ; such material reflects only the light with the wavelength λ (Figure 2) [1,2,6]. In Figure 2 the "P" defines the length of the pitch in the helix formed by 360° rotation of directions of elongated molecules of the liquid crystal. The length of P changes in dependence on temperature. Thermochromic effect of TLC is a result of temperature dependent pitch, P. As the temperature raises the helical pitches shrink causing reflections of light with shorter wavelengths, therefore the color of the material changes towards blue shades [7].

The color change of TLC inks is reversible. Thermochromic liquid crystal materials can be formulated to show their color change over a wide range of temperatures from -30°C to 100°C and the width of activation regions can vary between 1°C and 20°C. As the TLC inks are colorless outside the activation region they should be printed on dark substrates to enable the "color play" effect be visible by naked eye. If printed on bright substrates, the effect could be registered by kinds of optical measurements [7]. Such limitations prevent the TLC being used more widely in the areas of packaging and temperature indicators, security printing and brand protection or toys. However, the fact of inability of the "color play" effect being photocopied might intensify the frequency of TLC use in the area of security printing. Another area of possible more intensive application is a newly combined TLC prints with printed electronics, as 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. In electronics, liquid crystals can be used to detect shortcuts in circuits, open circuits, inoperative devices, and map operational areas in large-scale integrated circuits [8].

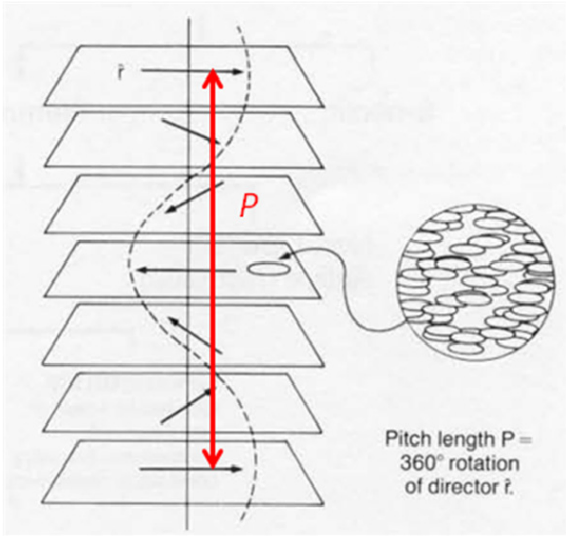


Figure 2. Helical superstructure of TLC-s [6]

Materials and methods

The SC-140-TC/0398 (Printcolor Screen Ltd., Switzerland) water-based ink was used and screen-printed, 149 µm mesh openings, on the black coated paper, 260 g/m^2, printed in three subsequent layers and hot air dried at 75°C. The ink was colorless outside the activation temperature, T_A was at 25°C and the activation region from 25°C to 30°C. Within the activation region the TLC ink showed the full "color play" effect changing throughout the whole visible spectrum, with the effect being reversible. For the temperatures above the activation region the ink still showed some color change, but the effect faded gradually till the complete loss of color above 44°C (clearing point), becoming colorless again (Table 1).

Table 1. Technical specification of the TLC ink

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

Spectrometer Perkin Elmer Lambda 950 was used with 150mm wide integrating sphere, the measurement geometry applied was (8°:di). Figure 3 shows the measurement geometry: the sample is illuminated under 8° angle from perpendicular axis and gathers the diffusely reflected light. The measurements were performed in the steps of 1 nm for the spectral region from 250 to 850 nm.

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*)* and as $L^*(T)$ graphs.

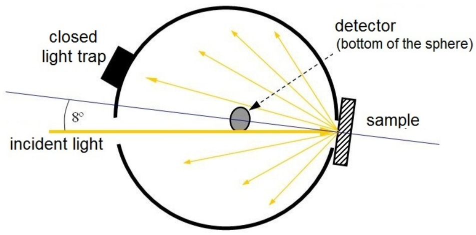


Figure 3. (8°:di) applied measurement geometry [9]

Results and discussion

Spectral reflections R were measured on the TLC samples gradually heated between 25 and 45°C in the steps of 1°C, results are presented in Figure 4. The thermochromic effect becomes visible at 27°C; At this temperature the reflection spectrum shows a peak with the maximum beyond visible spectral region. At lower temperatures the reflection spectrum is almost flat indicating that no helical structure is formed, thus the thermochromic effect is not in power yet. The temperature shift in activation of the color play effect respect to producer's data is most probably due to the thickness of the ink carrier, i.e. printing substrate.

At higher temperatures, only one reflection peak appears in each spectrum. The peak in spectral reflection, measured at 28°C, peaks at 745 nm, thus the color play effect begins in red color, followed by orange, yellow, green, blue and purple as the temperature raise. (Figure 4).

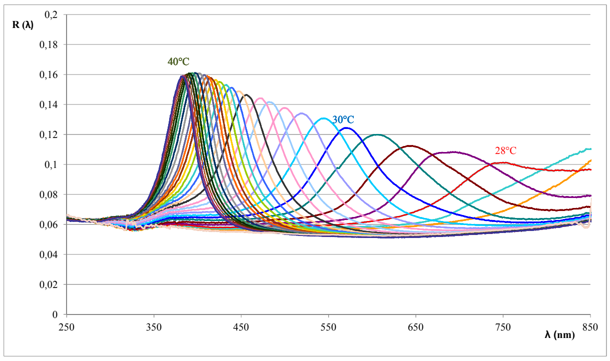


Figure 4. Reflectance spectra of the TLC printing ink measured as a function of temperature

In Figure 5 the chromatic CIELAB values are shown as (*a*,b**) diagram showing the corresponding values of the TLC sample for temperature range of 25 to 45°C. It shows that gradual color change describes the entire color circle, from red to green, a*, and from yellow to blue, b*. The color starts at point closest to the origin showing the chromatic values of the TLC ink below the activation temperature, thus in colorless stage. By heating, the color changes into red and then yellow in relatively short temperature steps. In the following, it changes into green, blue and finally purple take several degrees more, the change can be described as slower in comparison to red-yellow change, i.e. requires larger temperature gradient to occur. These results correspond to the visual observation with red and yellow color being of short and less intensive appearance followed by longer lasting green color, but dominated by blue in length and intensity of color appearance. Above 40°C the color play effect declines, the color fades and chromatic values regain starting values at the diagram origin. The presented curve describes the dynamics of the TLC color change with almost closed loop caused by colorless status outside the activation region.

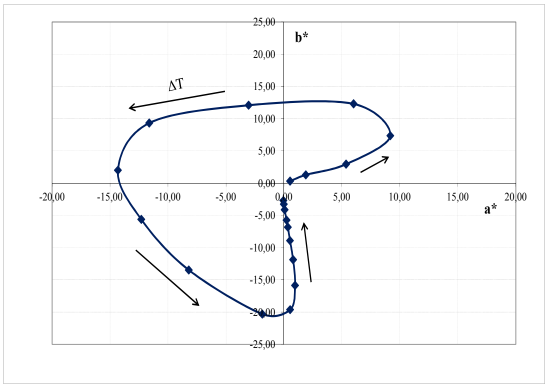


Figure 5. *CIELAB values of TLC ink presented as (a*,b*) graph. The temperature was changed from 25°C to 45°C in 1°C interval. The arrows indicate the direction of temperature change.*

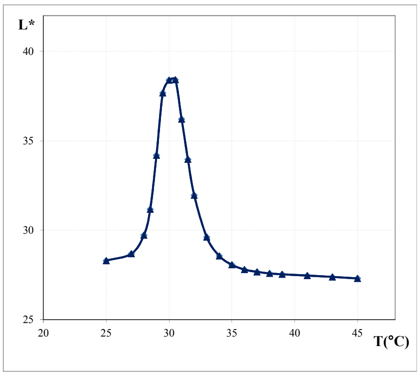


Figure 6. *CIELAB values of TLC ink as a function of temperature, presented as (L*, T) graphs*

The lightness L^* as a function of temperature is shown in Figure 6. The peak in the $L^*(T)$ graph corresponds to the TLC activation region as outside it the sample is black when the ink is colorless [7].

At 25°C the value of L^* is 28,29. By further increase of temperature the lightness values raise reaching the maximum value at 30°C. Above 30°C the lightness decreases, the color play effect declines to complete fading above clearing point at 44°C.

TLC printed labels

The printed labels by this kind of TLC might be used whenever an information about the temperature elevation above 25°C is needed, for safety reasons of the sensitive packed contents, in packages of baby food, cosmetics or similar.

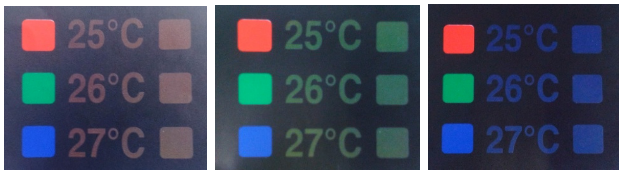
An example of the designed indicator is shown in Figure 7. Below the activation temperature the label is black, by temperature elevation the activation temperature is reached at 25°C, changing the appearance of the so far black label into colorful one. This kind of elevated temperature detection might be used in storage departments, in transport or during the shelf life of packed products.

(a) **(b)** **(c)**

Figure 7. *TLC printed labels; T=25°C* ***(a)****, T=26°C* ***(b)****, T=27°C* ***(c)***

Other types of labels might be used for detection of graduate increase of temperature. The help of legend printed in conventional inks is needed, as the conventional printed areas in red, green or blue would be used to compare the achieved color by TLC and thus enable detection of the precise temperature within the activation region of the TLC (25°C to 30°C) (Figure 8). Such indicators might be helpful in detection of temperature changes within a range for pharmaceuticals or other sensitive goods.

This kind of indicator can also be used in product production monitoring if applied on metal bins or tubes. Should the activation region of the applied TLC ink be too narrow the combination of multiple TLC inks is applicable each one covering different activation region.



(a) **(b)** **(c)**

Figure 8. *TLC printed labels; T=25°C* ***(a)****, T=26°C* ***(b)****, T=27°C* ***(c)***

Conclusions

The temperature indicators based on TLC printing inks are not in wide commercial use, partly because of the specific application requests for such inks, like printing on dark substrate or similar. The presented spectrometric research helps in determination of colorimetric parameters of the color changes of TLC inks. The presented application examples, in conjunction to performed measurement, might contribute to faster development of new kinds of indicators based on TLC printing inks, in the areas of functional packaging, security printing and others.

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