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Preparation of Reversible Thermochromic Ink for Flexography Printing on Paper and Study its Colorimetric Properties

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ABSTRACT

Thermochromic printing inks are used as security inks which respond to the color change upon exposure to different temperatures. These inks with unusual chemical and physical properties are mostly produced for flexographic, screen and rotogravure printing systems under the supervision of skilled technical experts and with precise security controls. Since flexographic thermochromic inks can be used easily for smart packaging including different substrates, in this study a thermochromic ink was prepared with an activation temperature of 31 °C for flexographic printing. The dynamic colorimetric properties were studied at 28-45 °C. TC contrast and yellowness of TC sample were calculated during heating and cooling. Prog. Color Colorants Coat. 8 (2015), 159-168 © Institute for Color Science and Technology.

1. Introduction

Color-changing inks have been very important in marketing as well as smart packaging. Today, there are also some automobiles which their color changes by altering the temperature. These inks could also be used for the printing of patience's garments to show the increase or reduce of temperature during their stay in hospitals. The first color-changing ink application was the mood ring which was introduced in 1970 [1, 2].

Thermochromic (TC) ink is one of the significant color changing inks among a few different ones whichcan be easily used in special industries [3]. Thermochromic ink changes its color with exposure to different temperatures and based on the final application, TC inks can be made to be reversible or irreversible. They are chemically categorized in two groups including liquid crystals and leuco dyes. The first one is less applicable since they are more sensitive to temperature variation comparing to leuco dye-based

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materials and are usually used in accurate applications to be able to show even the small temperature change [4, 5]. Leuco dyes-based thermochromic systems usually have three important parts including an electron-donating compound which acts as a color former, an electron acceptor as a developer and a matrix which can be a solvent [6]. So, leuco dyes could have different chemical structures to act as a thermochromic dye. The presence of lactone group as a color former or electron donator in TC material has been seen frequently. In such a chemical structure, the lactone ring is closed. When this leuco dye reacts with an electron-acceptor as a developer, opening of the lactone ring occurs. Based on this reaction, the dye loses its color since the maximum wavelength absorption peak shifts from the ultra violet to the visible range. Melting temperature of the solvent as a matrix controls the color changing temperature and enables the thermochromic reaction to be reversible. Leuco dye-based TC systems are usually colored below their activation temperature or in their solid state and become colorless above their melting temperature while transferring to liquid according to Figure 1 [7-9].

The thermochromic materials based on leuco dye are also very sensitive to environmental conditions, so they are usually used in microcapsule structure to be protected by an adjacent wall. Encapsulation of the three mentioned important parts in TC systems including leuco dye, developer and solvent could be done using emulsification followed by interface polymerization. Concentration and type of the surface active agent during the polymerization would be responsible for the final particle size of the thermochromic microcapsules. It is noticeable that the used resins for preparing the TC microcapsule should not solve in solvents and has to be stable in a range of applied temperature during their final application. Melamine and epoxy resin are usually used as a binder for producing the microcapsules during the polymerization. The melamine resin is completely insoluble in most solvents and its degree of cross-linking controls the porosity and elasticity while the epoxy resin has a higher transparency and better temperature stability [10- 12].

The present study aims to prepare thermochromic inks using a microcapsule as a slurry form with an activation temperature of 31 °C for flexography printing on paper and to evaluate its colorimetric properties.

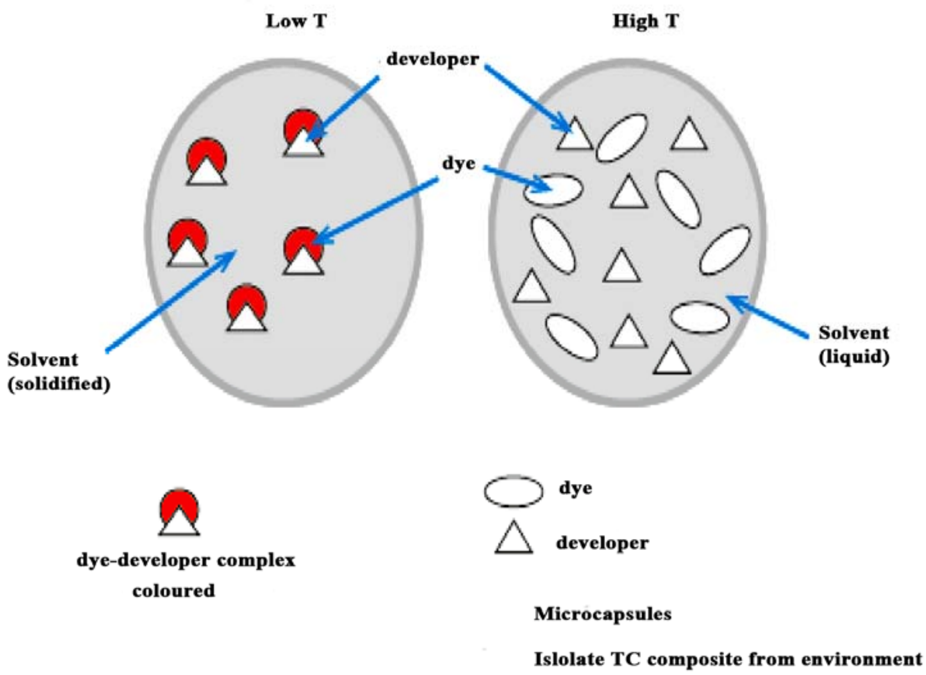

Figure 1: Schematic representation of leuco dye-developer-solvent composite system [4].

2. Experimental

This paper includes two different parts. First the specific formulation of reversible thermochromic ink was prepared based on flexography printing formulation and then the colorimetric properties of printed papers were studied.

2.1. Materials

Aqueous thermochromic pigment slurry in red shade (reversible RED186C) with activation a microencapsulated aqueous dispersion with good dispersion in water, suitable for water-based inks or paints. It contained 45 ± 5% of solid content.

Acrylic colloidal dispersion resin with Commercial name W´Cryl 8040 was provided by Worlée-Chemie GmbH, Germany which its physical properties are presented in Table 1.

2.2. Preparation of thermochromic ink

The TC pigment slurry was added to the vehicle and then mixed very slowly with magnetic stirrer. Care must be taken to ensure that the thermochromic pigment particles were not ruptured during the mixing. Hereafter, this mixture is referred to as flexo ink base. Flexo ink base was combined with TC pigment slurry to produce a flexographic ink as shown in Table 2.

Table1: The physical properties of Acryl ic colloidal dispersion resin (W´Cryl 8040).

Physical Properties	
None volatile content 1h/125 °C, DIN EN ISO 3251, part 1	40% ± 1
PH-Value DIN EN ISO 976	8-9
Density 20 °C, DIN EN ISO 2811-1	Approx. 1.02 g/cm^3
Viscosity Brookfield, 20 °C, spindel 4/30, DIN EN ISO 2555	2,500-3,000 mPa.s
Tg (calculated)	48 °C
Freeze thaw stability DIN EN ISO 1147	Min.5 cycle
Flash point DIN EN ISO 2719	23 °C
Acid value (mg KOH/g polymer) DIN EN ISO 3682	78

Table 2: Formulation used to prepare the TC ink.

Ingredient	Weight (%)
Colloidal Dispersion Resin (40 ± 5% Solids)	40
TC Pigment Slurry (Red, TA=31°C)	50
Water	10

2.3. Application of ink film on paper

To apply the ink film on paper (A4 Copimax paper), K-Control Coater machine with speed of 10 m/min and a bar coater with thickness of 100 micrometers was used (Figure 2).

2.4. Study the colorimetric properties of thermochromic ink

At first, a short overview of prepared reversible thermochromic (TC) ink in red shade with TA of 31 °C will be given. The color of this ink changes by temperature. In its cold state, the ink exhibits the color mentioned in the introduction and turns to colorless state by increasing the temperature. As it was noted above, a of was. Thus, the printed paper as the sample was prepared. Spectral reflectances of TC ink film drawn up on paper using K-Control Coater machine were measured by Konica Minolta CS2000 spectroradiometer with the following specifications:

- Wavelength range: 380-780 nm
- Wavelength accuracy: 1nm (FWHM=5nm)
- The device geometry 0/45 (according to the manufacturer's recommendations).

The light source and the Konica Minolta CS2000 spectroradiometer were placed at 45° and 0°, respectively, relative to the line perpendicular to the sample surface. The distance and the viewing angle of the device were 1 m and 1°, respectively. This angle caused providing the measured scope or the size of the area of a circle with a diameter of approximately 8 mm, on the sample. The arrangement of sample, heater and spectroradiometer is shown in Figure 3.

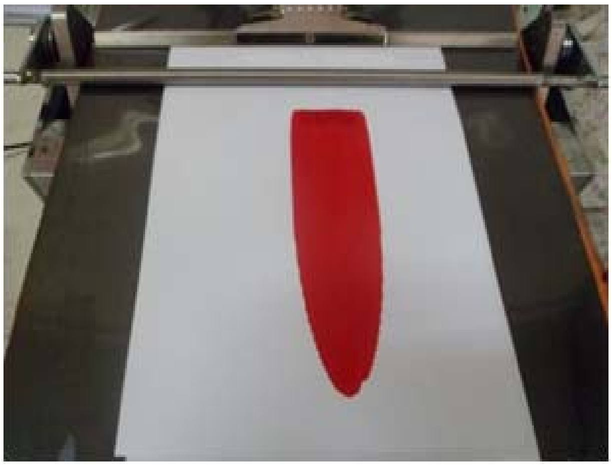

Figure 2: Application of ink film on paper with K-Control Coater machine.

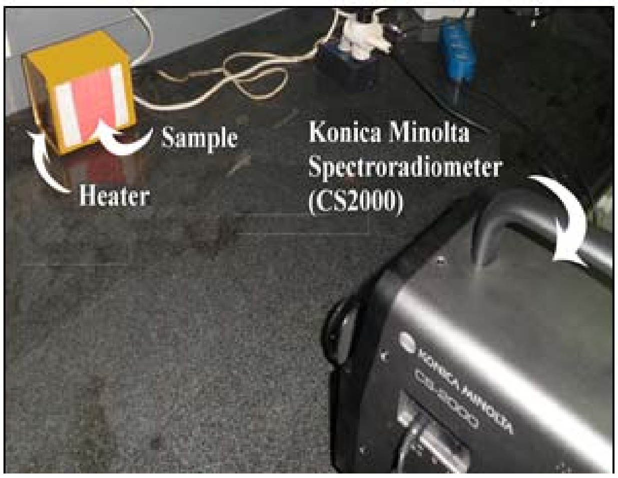

Figure 3: Arrangement of sample, heater and spectroradiometer.

Each sample was heated/cooled on a handmade heater. Sample was placed on the external wall of the heater and the temperature was transmitted by an embedded heating element. The wall of the heater had very short distance from heating element to transfer the heat through it to the sample surface. Sample temperature was measured by noncontact infrared thermometer (KIRAY). The reflectance spectra were measured from 28 °C to 45 °C for sample, where between 28 °C and 35 °C the reflectance spectra were measured in 1 °C intervals but larger temperature difference was allowed (5 °C) elsewhere [3]. A slow heating/cooling rate was applied, not larger than 0.5 °C/min. Colorimetric calculations were done in CIELAB color space applying D65 illuminant and 10° standard observer.

3. Results and discussion

Reflectance spectra during heating from 28 °C to 45 °C and cooling down to 28 °C were measured. Then the CIELAB values of the TC sample were calculated from the reflectance data by device software (CS-S10W). The obtained a*, b* and L*values are plotted in Figures 4 and 5.

It was observed that the TC sample loses its color during heating which is reversible upon cooling. There was no sudden change, and both processes happened continuously. Color changing of TC sample during cooling was slower than heating.

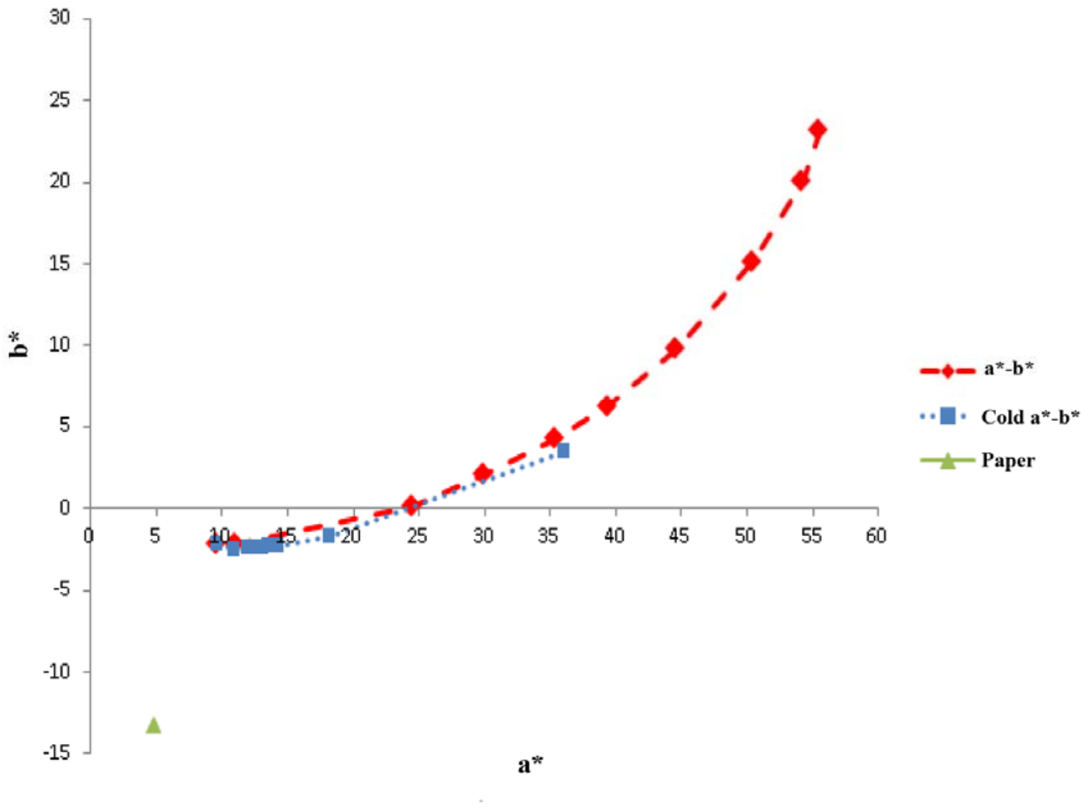

Figure 4: a*, b* values of TC sample during heating (lozenges) and cooling (squares). ▲ = the corresponding value of the non-printed substrate.

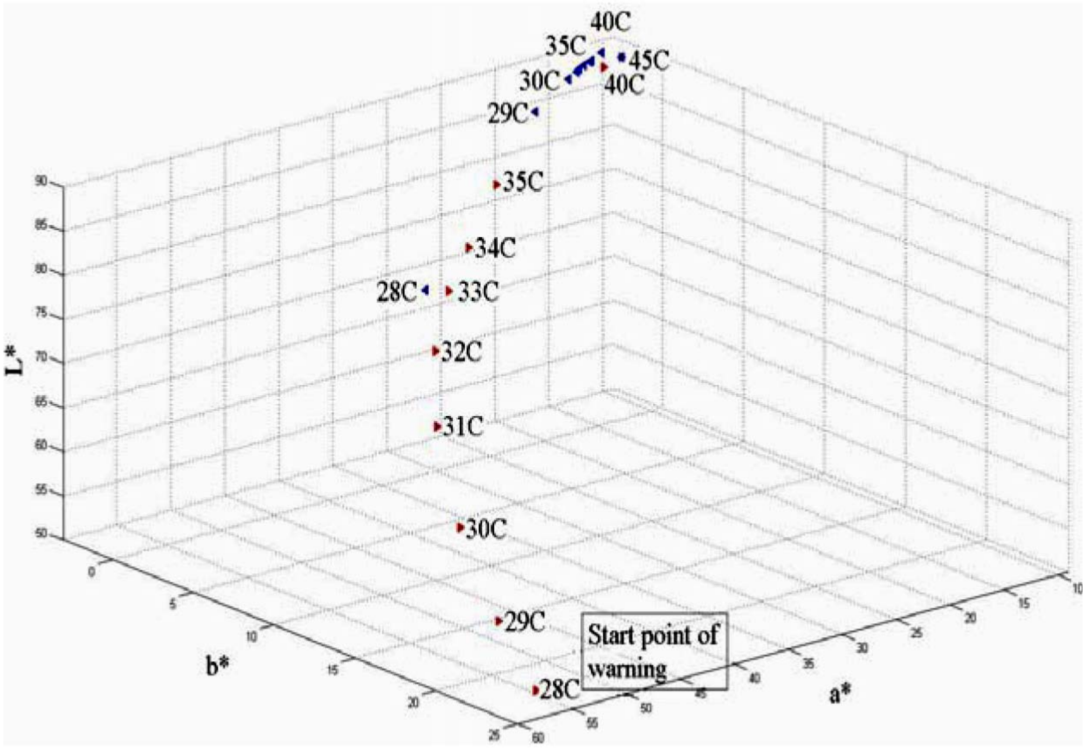

Figure 5: a*, b* and L* values of TC sample during heating and cooling.

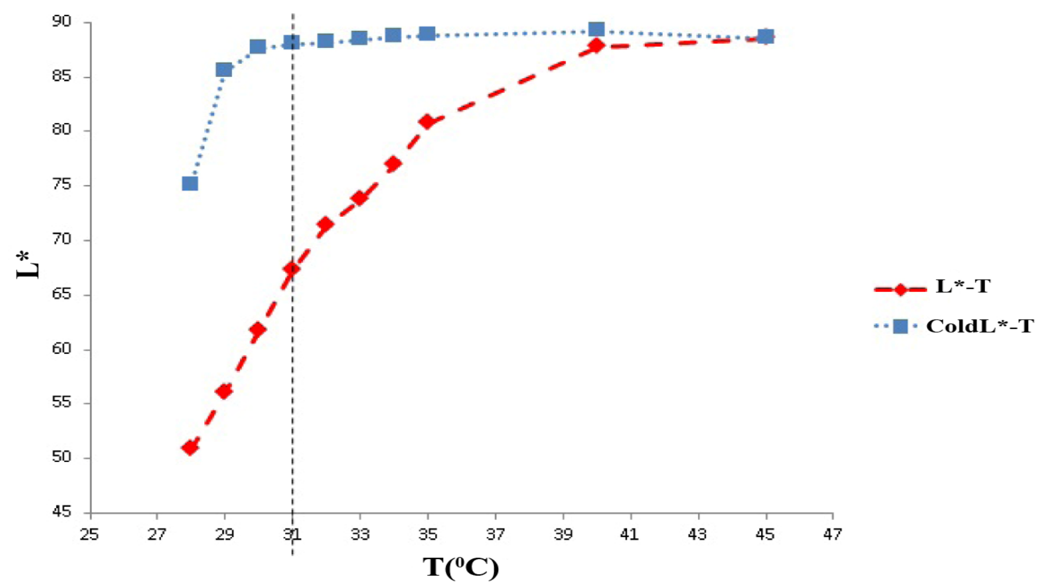

Figure 6: CIELAB lightness L* of TC sample during heating (lozenges) and cooling (squares).

Figure 5 shows that CIELAB values of the TC sample at 33 °C upon heating were nearly the same as CIELAB values for cooling the TC sample at 28 °C. As a result, it is impossible to obtain the desired properties in a restricted time only by temperature variation. Color of the TC sample can be described by a four-dimensional function. Three dimensions are color values (L*, a*, b*), and another dimension is temperature. CIELAB values of TC sample were plotted against temperature. Discoloration ⁄coloration process can be clearly described by lightness (L*) as a function of temperature (T) Figure 6.

During heating, thermochromic sample became lighter (higher L*) and vice versa. Most of the decoloration process was accomplished at temperatures above the activation temperature.

The TC system has a memory that is called hysteresis [6]. It was color hysteresis that described the color of a TC sample as a function of temperature. The temperature-dependent a^* and b^* values are represented in Figures 7 and 8. As expected, a^* values of red TC sample decreased during heating and increased during cooling trajectory. It is also observed that these trajectories were different.

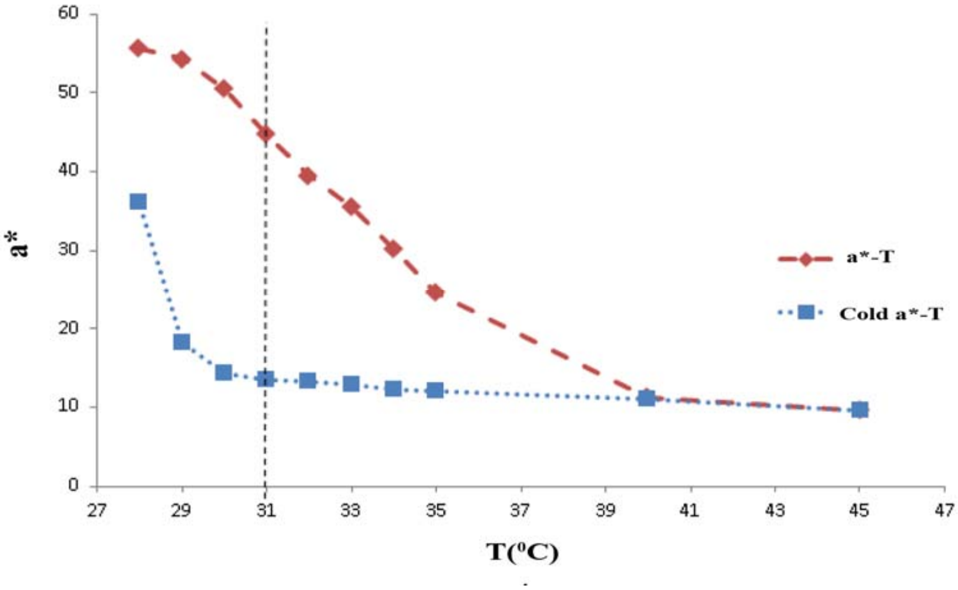

Figure 7: a* values of TC sample during heating (lozenges) and cooling (squares).

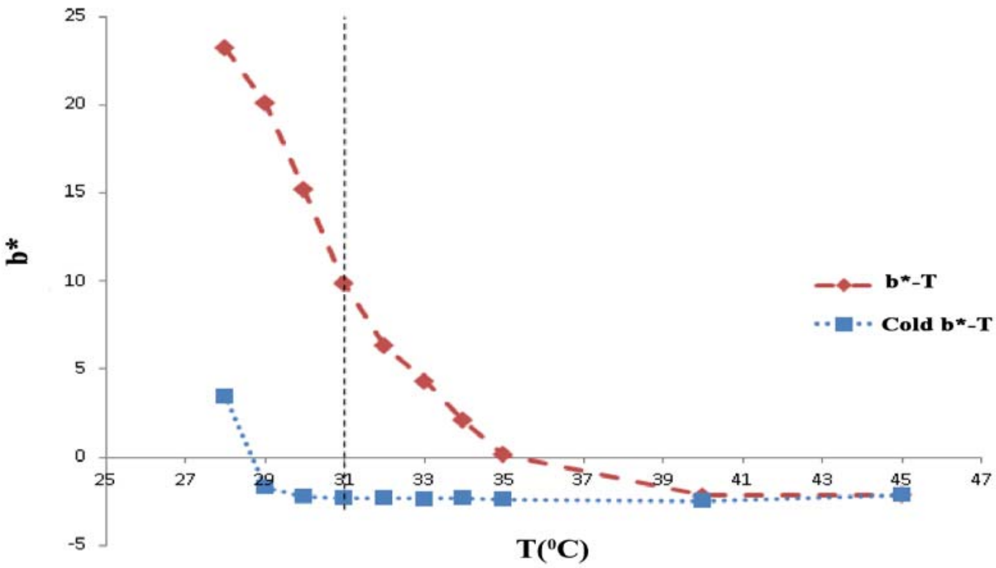

Figure 8: b* of TC sample during heating (lozenges) and cooling (squares).

During heating, b* values of TC sample showed a decreasing trend. On the contrary, they increased during cooling.

Studying the colorimetric properties of Leuco dye-based thermochromic ink can explain more clearly the formation and disappearance of colored complex in heating and cooling process. A few parameters such as TC color difference and yellowness of the thermochromic ink were calculated. To calculate the total color difference, the CIELAB color difference formula was used. This formula is as follows [7]:

$$\Delta E^{*} = \sqrt{(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})}$$

Color hysteresis is indicated by the color difference between heated and cooled states of the sample (Table 3 and Figure 9).

Table 3: Total color difference between heating and cooling cycle

Temperature	Delta E (CIELAB)
28	36.751
29	51.440
30	47.684
31	39.344
32	32.344
33	27.832
34	21.900
35	15.098
40	1.501
45	0.000

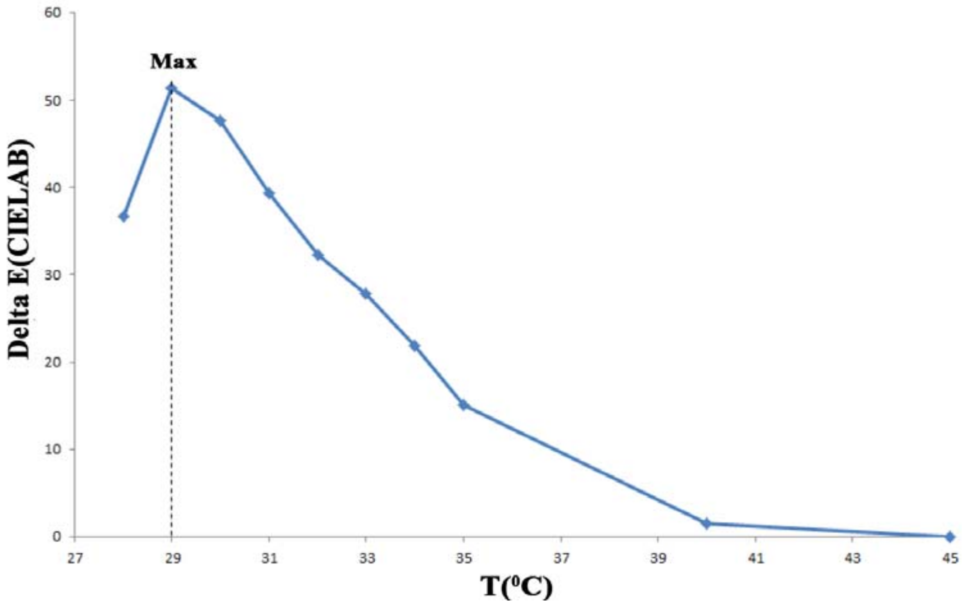

Figure 9: Total color difference between heated and cooled sample as a function of temperature.

Table 4: Selected parameters of colorimetric properties for the TC sample.

Yellowness	T_{max}	ΔE_{max} (CIELAB)
12.41	29	51.440

Figure 9 shows that the largest color difference (CIELABmax) between heated and cooled sample was in T_{max} =29 °C and this value was $CIELAB_{max}$ = 51.440. $CIEDLAB_{max}$ showed larger color change at TC reaction.

Yellowness of TC sample (total color difference between the applied paper substrate and TC sample) in decolorized form (T = 45 °C) was calculated. Table 4 shows the colorimetric parameters for mentioned thermochromic ink sample which better represents the color hysteresis during heating and cooling cycles.

4. Conclusions

In this study, a thermochromic ink (leuco dye-based TC ink) with an activation temperature of 31 °C for flexographic printing was prepared. Leuco dye-based TC ink was colored at low temperatures and transformed into non-colored state by heating. It was also observed that heating and cooling trajectories were different. It was shown that the TC ink color depends on the temperature as well as the thermal history or the so called hysteresis. Activation temperature is the only known parameter which describes the color of a TC ink. The color difference between colored and discolored sample was more significant at temperatures lower than activation temperature. The ability of a TC sample to become discolored was calculated by yellowness which is defined as the color difference between the discolored state and the uncoated paper substrate. Colorimetric properties of TC ink provide some information about its behavior and operation at different temperatures.

Acknowledgements

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