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DYNAMICS OF THERMOCHROMIC COLOR CHANGE OF PRESSURE SENSITIVE LABELS FACESTOCK MADE FROM ENVIRONMENTALLY FRIENDLY MATERIALS

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Abstract: *To maintain a circular economy and better sustainability, it is important to minimize the use of synthetic polymers. Nowadays, agricultural and industrial wastes or by-products are increasingly being used as raw materials in industrial processes. It has been determined that agro-industrial wastes have a high potential of cellulose fibers, which makes them an excellent resource for paper production. Recently, potential resources from non-wood raw materials for paper production, as well as cheap raw materials, have become the interest of various researchers. Since our main focus is on the study of thermochromic inks (TC) and the influence of substrate characteristics on their dynamic color change, this paper will examine the possibilities of a commercially available offset TC ink printed on several environmental friendly pressure sensitive labels (PSL) facestock compared to commonly use in PSL production. For the purpose of this study, a commercially available TC ink with an activation temperature (TA) of 29°C was used. The effect of color change, from blue to colorless, was measured through one heating and cooling cycle at several selected temperatures at six different PSL materials. Three fiber-based facestock of PSL used in this research are produced with 15% agroindustrial byproducts, 40% post-consumer recycled paper and 45% virgin wood pulp to form a high-quality natural paper. In addition, one material made from biogenic polymers facestock and two materials commonly used in labels production were used as well. The results of this research show that TC ink printed on alternative materials has a similar trend of color change and may be a good choice. Also, the influence of the color of fiber-based paper substrates on the change of TC color was noticed, which indicates the importance of colorimetric analysis of paper and TC ink before their printing.*

Key words: pressure sensitive labels, facestock, thermochromic inks, eco-friendly materials, spectrophotometric measuremets

1. INTRODUCTION

Pressure sensitive labels (PSL), also known as self-adhesive labels, have gained great popularity due to their simplicity and user-friendly role (Medeiros et al., 2019). As AWA predict globally, PSL label material industry is expected to grow (Labels&Labeling, 2021). The PSL is an integrated part of the product packaging. It is very important that the label and the product packaging are made of the same materials and have the same structure. Such mono-material packaging enables recycling and reuse. Paper as a substrate for the production of labels represents more than 50%, and 20% is the siliconized part (PP and PE). When choosing an appropriate label material, it is important to choose an adhesive that will not adversely affect the recycling or reuse process of the product in any way (Huhtamaki, 2020). Each PSL from a roll consists of three basic parts: facestock (paper, foil), adhesive and liner. The paper used as facestock can be coated, uncoated, white, colored, smooth, structured and may contain some special characteristics such as security fibers. The correct selection of each part of the label is defined by various parameters. Some of the parameters are where the label will be placed and used and general information about its use such as application surface, application speed, room temperature of use and the temperature of the product itself, humidity, etc. The most common printing techniques for PSL are UV flexo printing, UV offset, UV letterpress, digital UV inkjet and electrophotography (Marošević Dolovski, 2016; Tesařová et al., 2020).

The PSL can also provide additional value by using interesting structures, designed by a hot or cold stamping process, spot varnishes etc. It is also possible to insert RFID tags or NFC and use labels for security purposes. The life cycle of a label is defined by several conditions such as printing, handling, use and deciding whether the label is to be recycled or treated as waste. All materials from which the label is made depend on various external influences such as weather and storage conditions, methods and

conditions of application, type of printing, etc. When printing, the surface of the substrate or the top layer of the label must have the appropriate quality. Print quality can be affected by surface structure, paper dust or discoloration of materials based on paper fibers. Optimum printing methods and techniques, appropriate inks and other auxiliary devices must be used to achieve the best appearance and purpose of the label (Marošević Dolovski, 2016).
This paper aims to test the functionality of one offset TC ink on the most commonly used labels and those made of biologically acceptable materials for environmental protection. Also, the influence of the shade of the facestock surface on the dynamic changes of the TC color will be examined and analyzed with spectrophotometric measurement and presentation in the CIELAB color space.

2. EXPERIMENTAL

For this research, six types of different PSL were used. Figure 1 shows the spectral reflectance curves of all tested PSLs in this paper before printing while Table 1 shows their characteristics as provided by the manufacturer. Three types were made of agroindustrial by products, one is a bio-based polymer and the other two are most often used as PSL, wood-free coated on a cellulose basis. The eco-friendly labels based on agroindustrial byproducts are made from barley (B), citrus (C) and grapes (G). To produce B, C and G, the upper layer of the label, CO_2 emissions were reduced by 20%. The fibers that make up the upper layer of the labels are made from 15% agro-industrial bio products, i.e., barley, citrus, and grapes, containing 40% recycled paper and 45% virgin wood pulp to obtain high-quality natural paper. Grape fibers are obtained from the rest of the grapes used to make wine, citrus fibers are obtained from the remains of fruit and juice products, and barley fibers are collected from barley used in the production of beer and whiskey malt. The wood-free coated papers used are MC and TT and a bio-based polymer, polyethylene white (PEW-B). MC is a white, wood-free, semi-glossy paper containing an acrylic-based adhesive. PEW-B is polymer-based, made mainly from sugarcane ethanol, with a rubber-based adhesive. TT is a thermosensitive wood-free paper made from chemical pulp. The top layer is thermally coated, and below it is a black thermosensitive layer that provides good resistance to moisture, fats, oils and alcohols (AveryDennison, 2022a, 2022b; Vukoje et al., 2021) .

Table 1: Properties of used PSL given by the producer

Substrate	Abbreviation	Facestock		Liner		Total Laminate
		Basis Weight ISO 536, g/m²	Caliper ISO 534, mm	Basis Weight ISO 536, g/m²	Caliper ISO 534, mm	Caliper ISO 534, mm
Fasson®Crush Barley	B	90	110	70	61	190 ± 10%
Fasson®Crush Grape	G	90	114	70	61	192 ± 10%
Fasson®Crush Citrus	C	100	130	70	61	210 ± 10%
Fasson®MC FSC	MC	77	66	54	47	124 ± 10%
Fasson®Thermal	TT	76	82	54	47	141 ± 10%
Fasson®PE85-BIOB White	PEW-B	82	82	59	53	152 ± 10%

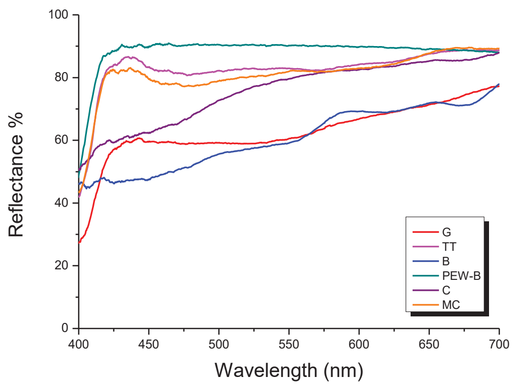

Figure 1: Spectral reflection curves of all used unprinted PSL samples

The reversible thermochromic (TC) ink used is a commercially available leuco dye-based offset printing ink with an activation temperature (T_A) of 29°C. Before reaching the T_A, the TC color is blue. By heating up and reaching the T_A, the TC ink changes to a colorless state.
Prints were printed in a printing press under standard conditions and dried using a UV drying unit of an offset printing machine.
Spectral reflectance was measured by Ocean Optics USB2000+ spectrometer using 30 mm wide integrating sphere under (8: di) measuring geometry. The printed samples were heated/cooled on the full-cover water block (EK Water Blocks, EKWB d.o.o. Slovenia). The measurements were performed in the steps of 1 nm for the spectral region from 430 to 750 nm. Ocean Optics SpectraSuite software was used for the calculation of the CIELAB values from measured reflectance. The total colour difference between *between printed PSL samples at 15°C and those at 45°C* was calculated using the formula CIEDE2000 (International Commission of Illumination, 2004).

3. RESULTS AND DISCUSSION

To examine the influence of the characteristics of the upper layer of the label and its color on the visual appearance, hue and the effect of changing the printed TC ink, the changes were monitored through CIE *a*b** graph, *L**T graph and spectral reflectance curves.

The dependence of the lightness *L** on the temperature T of the printed TC ink on B, C, G, MC, PEW-B and TT labels is shown in Figure 2. These are the characteristic hysteresis curves of thermochromic colors. It is evident from the graphs that during heating there is an increase in *L** because the TC changes from blue to colorless, i.e. the color of the upper layer of the label is visible on the sample. The increase in brightness occurs up to the T_A of 29°C, after which the change slowly stops and the graph becomes more continuous. During the cooling process, a sudden change occurs after crossing the activation temperature. It can be read from the graph that the curves do not have the same path of change, they do not overlap.

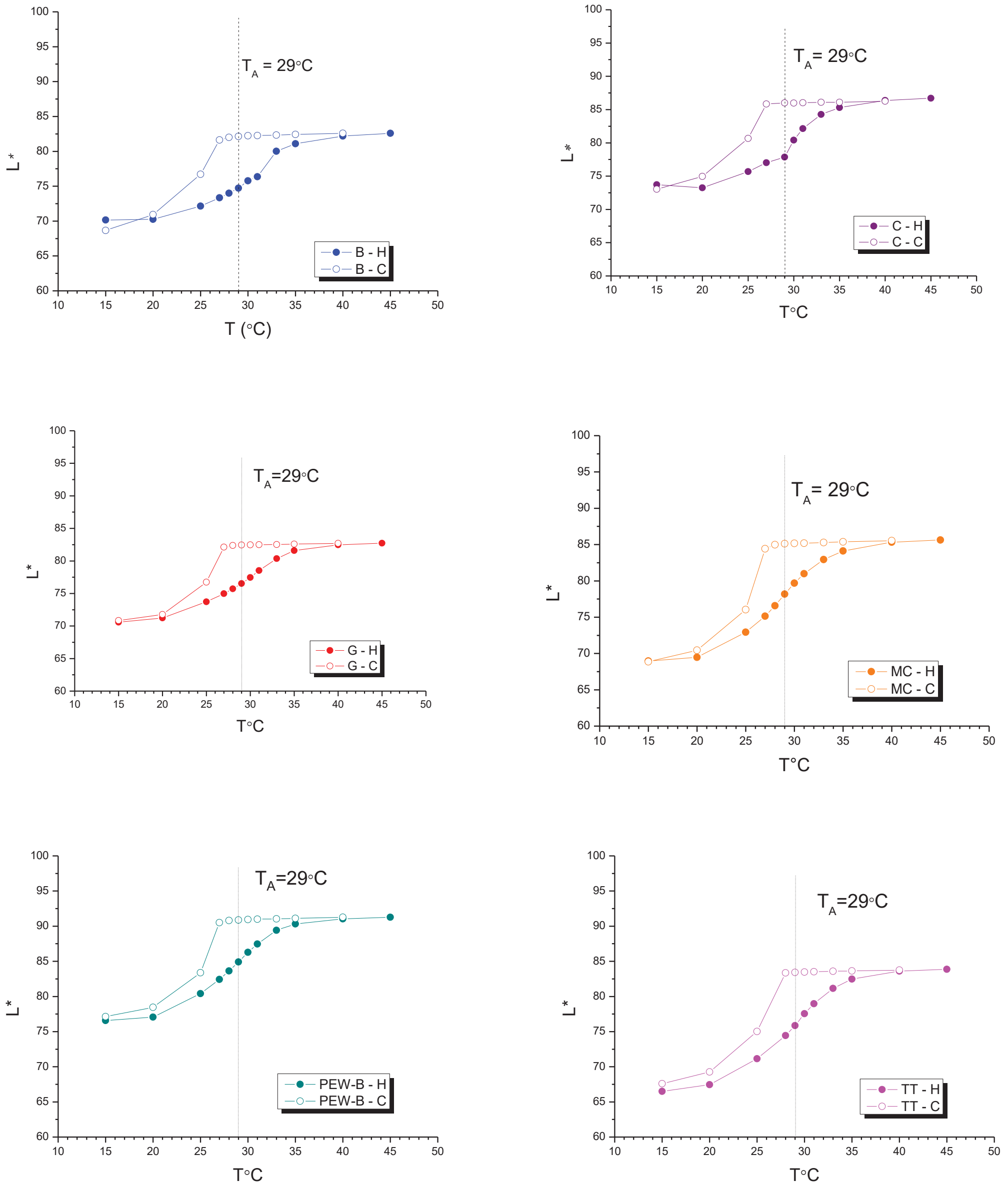

Figure 2: Hysteresis loops of all printed PSL samples during heating (closed signs) and cooling (open signs)

Based on these graphical representations, it can be concluded that during heating and then cooling, there are no equal changes in the lightness of the tested TC ink and that the reversible process is not ideal. The shape of the hysteresis for all tested samples is the same, only some small differences are observed at the hysteresis opening, i.e. at the temperature where the measurement cycle starts and ends.

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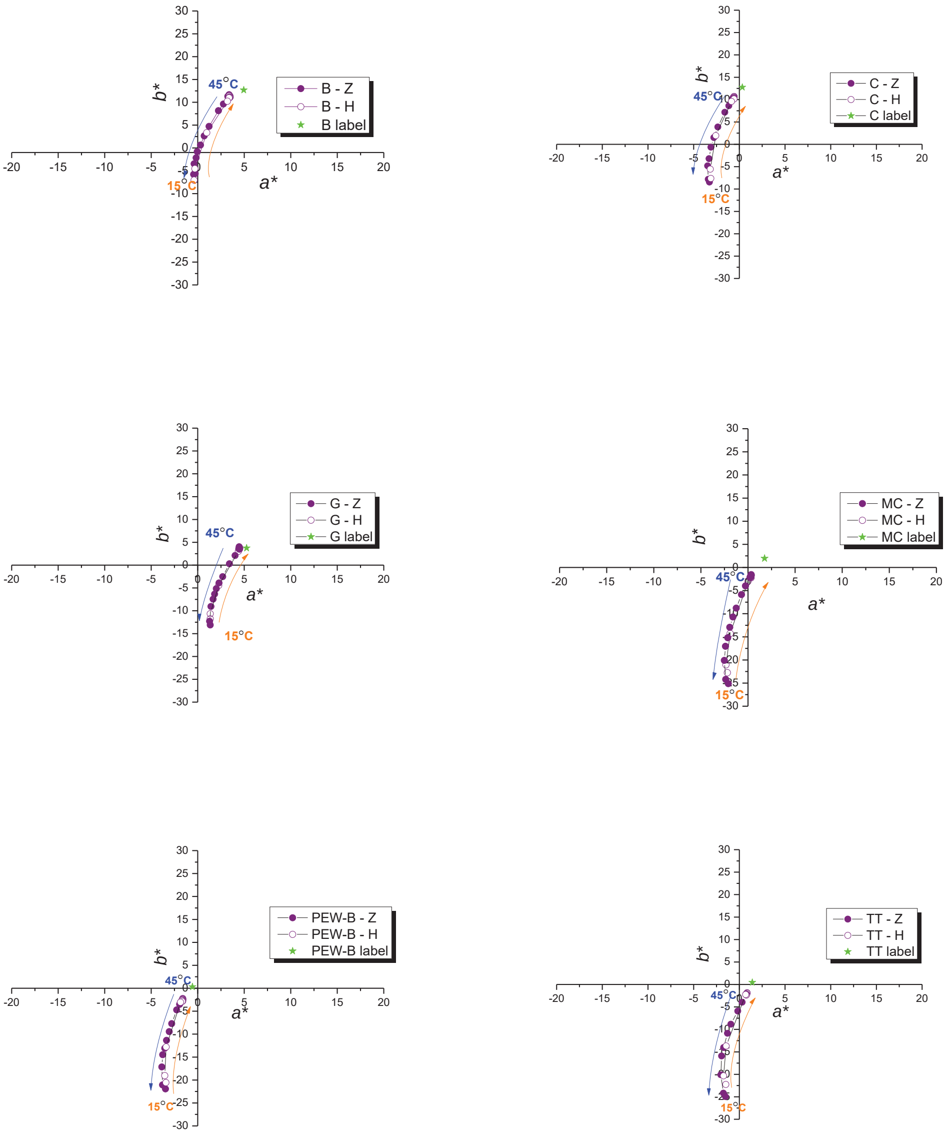

*Figure 3: TC color change path on CIE a*b* graphs during the heating and cooling process on all PSL labels*

The CIE *a*b** graph (Figure 3) shows the color change path of a TC ink through the entire heating and cooling cycle. The color of the top layer B of the label is within the yellow part of the CIELAB color space. One of the reasons for this is that the top layer of that sample has a yellow shade. When heating (minimum temperature is 15°C), the curve takes the direction from the blue part to the yellow part of the CIELAB color space. The curve of print on the B label is mostly on the right side of the graph, where red-yellow, warmer hues predominate. With cooling (the maximum temperature is 45°C), the curve takes a direction from the yellow area towards the white, achromatic center of the graph and slightly enters the light blue area. Unlike the B label, the print on the C label is mostly within the blue area although the top layer of the label also has a yellowish shade. From this, it can be concluded that the hiding power of the TC ink on the C label is better than the B label. The curves of prints on the C label are located on the left side of the graph, green–blue part. During heating, the curve takes the direction from the blue part to the yellow part of the CIELAB color space. With cooling, the curve takes a direction from the yellow area to the blue. The color of the top layer of the G label is within the red part of the CIELAB color space.

The curves of the printed G label are located on the right part of the graph where red-blue, warmer tones predominate. Unlike the B and C labels, the G label is mostly inside the blue part, and the reason for this is probably the color of the top layer of the G label itself. During heating, the curve takes the direction from the blue part to the red part of the CIELAB color space. With cooling, the curve takes a direction

from the red area to the blue. The color of the top layer of the MC label is within the central, white, achromatic part of the CIELAB color space, which is also visible on the MC label, which is white. The curve of the MC label is located on the left side of the graph where blue predominates. Unlike the previous graphs, here the hiding power of the TC ink is the best because the curve is entirely within the blue part of the CIELAB space. The top layer of the label itself, which is coated and smooth contributes to such good hiding power. During heating, the curve takes the direction from the blue part towards the central part of the graph. With cooling, the curve takes the direction from the central part towards the blue.
The color of the top layer of the PEW-B label lies within the very central, white, achromatic part of the CIELAB color space. Compared to the MC label, the color of the top layer of the PEW-B label is closer to the center, which means it is whiter. The curves of prints on the PEW-B label are on the left side of the graph, where blue predominates. As with the curves of the MC label, the hiding power of the TC color of the PEW-B label is very good, because the entire part of the curve is inside the blue part of the CIELAB space. The top layer of the label itself, which is smooth, uniform and white, contributes to such good hiding power.
The color of the top layer of the TT label is within the central, white, achromatic part of the CIELAB color space, which is also visible on the MC and PEW-B labels, which are white. The curves of the printed TT label are located on the left side of the graph where blue, cold hues predominate. As with the previous graph, the covering power is very good, and the reason for this is the top layer of the label itself, which is smooth, uniform and white. During heating, the curve takes the direction from the blue part towards the central part of the graph. With cooling, the curve takes the direction from the central part towards the blue. These graphs show that the shade of the top layer of the labels has an effect of TC color. Also, it shows that the reversible process is not ideal because the heating and cooling curves do not exactly match.

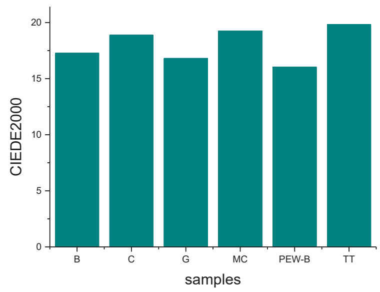

Figure 4: CIEDE2000 color difference between printed PSL samples at 15°C and those at 45°C

The bar graph (Figure 4) shows the CIEDE2000 color differences between all TC ink samples during the heating process at 15°C and 45°C, which is the so-called total color contrast. It is evident from the graph that there is a large noticeable difference in the thermochromic color for each sample when it is at 15°C and when it reaches a temperature of 45°C. Large color changes are the result of discoloration of the TC ink by the heating process, which results in a stronger and more noticeable TC effect. The smallest color difference is achieved by the printed pattern on the PEW-B label and the largest color difference is achieved by the pattern on the TT label.

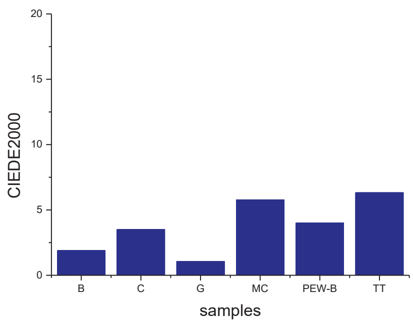

Figure 5: CIEDE2000 color difference between unprinted PSL and printed PSL with TC color and measured at 45°C

Figure 5 shows that there are larger and smaller visual differences in color. Eco-friendly samples have small color differences, unlike bio-based polymers and wood-free samples, which have visible color differences. Of the ecological samples, the print on the C label has the biggest difference in color, and the G sample has the smallest color difference. The TT wood-free sample has the largest change in color difference, and the PEW-B label has the smallest. From the results in Figure 6, it can be concluded that B and C samples with rough surfaces have the smallest color difference. They have the smallest hiding power with TC ink, which is probably why the visual difference isn't that obvious. MC and TT labels with smooth surfaces have the greatest visual difference in color and have the best hiding power with TC ink. The reason for the lower hiding power of rough samples is that they are structured and more absorbent and the dye penetrates more into the structure of the paper in contrast to smooth samples.

4. CONCLUSIONS

Based on this research, it was confirmed that the characteristics of the upper layer of the label and its color have a significant impact on the visual appearance, color shade and the effect of TC color change. Eco-friendly labels have a weaker TC effect compared to bio-based polymer and wood-free labels. Due to their rough surface structure, TC color have low hiding power on eco-friendly labels, which is also reflected in lower CIEDE2000 color difference values compared to smoothly structured papers with large color difference values. However, the TC effect is still clearly visible on these substrates. It has been proven that the reversible process of TC ink is not ideal for any of the tested materials. Analyzing the results of the spectrophotometric curves, it was determined that the discoloration of the TC color is not complete in any of the tested samples and that all the tested samples have a yellowish undertone. The reason for this could be different scattering or absorption that occurs due to different optical properties of the capsule in its discolored state and the binder, i.e. as a result of incomplete transparency of the TC composite inside the capsule itself at high temperatures. This test, among other things, showed the possibilities of offset TC ink, which, despite its poor hiding power still has a significant TC effect that is visible. This is the most important factor for the thermochromic indicators on the packaging to fulfill their functional role that gives the product itself additional value.

5. ACKNOWLEDGMENTS

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