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Advanced quality and sustainability when printing irreversible thermochromic inks

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Abstract

Worldwide, there is a growing need for use of recyclable and biodegradable materials, made from natural resources, for a variety of applications. This trend is followed by the printing industry as well, which is trying to use environmentally friendly materials and reduce the consumption of environmentally unfriendly materials. In addition, the used materials should give the satisfying quality of the end-product. Thermochromic inks can be reversible (color change is multiple) or irreversible (color change is one-time and permanent). Irreversible printing inks are initially either colorless or colored and when exposed to high temperatures they get colored or change to another color. Therefore, the aim of this paper is to examine the possibilities of two printing substrates (uncoated and coated) for the application of irreversible thermochromic inks in order to find a more environmentally friendly option that gives a satisfactory print quality. The dynamics of color change was monitored through one heating cycle every few degrees. Their colorimetric characteristics were described using spectral reflection curves and the CIELAB color system. Based on the obtained results, it can be concluded that with the change of temperature, the color tone changes slowly and continuously. The differences are evident for the selected printing substrates due to their different properties. However, these variations are imperceptible to the eye of the observer and according to the obtained results, it can be concluded that the tested inks behave similarly on the used substrates. In addition, more environmentally sustainable materials can be a good option in the use of printing with irreversible water-based thermochromic inks.

Key words

thermochromic inks, sustainable materials, colorimetric characteristics

1. INTRODUCTION

During distribution, storage and before the sale in stores, food products are exposed to various external influences that adversely affect their quality. Their premature deterioration causes large amounts of waste and thus financial losses. The validity date of the product in these cases cannot serve as a guarantee of product freshness, and due to the non-transparency of some packaging materials without opening the packaging itself, it is not possible to visually determine whether the product is still safe for consumption.

Intelligent packaging can be defined as packaging that contains an external or internal indicator that provides information about changes to which the product has been exposed over time. This type of smart packaging can detect and record internal and external changes in the production environment [1]–[3]. Chromogenic materials respond to an external stimulus by changing color. [4]. Nowadays, the use of chromogenic printing inks in the field of intelligent packaging is growing. In this area, they apply to indicator labels that make intelligent packaging "intelligent".

Thermochromic inks can be divided according to the type of color change into reversible and irreversible inks. Reversible inks return to their original state after a period of exposure to an external stimulus, while irreversible inks retain their color change without returning to the original color [5]–[7].

Some researchers are of opinion that only the reversible changes should be included in terms of thermochromism because irreversible changes in color caused by heating are, for the most part, only the results of true chemical reactions, and for that reason do not require special terminology. Closer studies reveal that the situations are in many cases not so simple and clear. The mechanism responsible for the thermochromism of organic compounds varies with the molecular structure of the compound. The color change is the result of equilibrium changes, either between two molecular species or between different crystal structures or between stereoisomers [8].

Thermochromic inks are mostly used for the production of time-temperature indicators. In this way, it is possible to visually determine whether the product has been exposed to an inadequate temperature. They are widely used in industrial applications for observing heat patterns and for detecting high and low-temperature points on surfaces of heat engines, pipelines and refrigerations fins. Thermochromic pigments have reached widespread use through different industries, including the textile industry, printing technology, military applications, plastic industry, industrial and interior design, etc. [8]–[11].

Printing inks for printing such indicators should adhere well to the label material or to the packaging material (if they are printed directly on the packaging itself). In addition, it is important that they are stable when printed and that they do not react prematurely to changes in temperature, light, etc [12], [13]. Also, it is very important that when a product is exposed to adverse conditions, the color change remains irreversible in order to obtain accurate information about the condition of the product.

Eco-friendly paper has smaller environmental impact and carbon footprint. Mostly, when taking about environmentally friendly paper, recycled paper and FSC certificated paper are considered. Paper for printing may be coated or uncoated. The main purpose of paper coating is to improve the surface quality, optical properties (brightness, gloss or opacity), smoothness, and the most important - printability and print image quality [14]. When printing coated papers, printing ink sits on top of the paper, rather than being absorbed. On the contrary, when printing uncoated porous paper, the printing ink is absorbed deeper into the paper structure resulting in duller print. In the case of coated paper, the prints color is brighter and more vibrant to the eye [14]. Uncoated papers are considered as environmental friendlier than coated papers because they yield a higher percentage of fiber for recycling. In addition, the clay coating also creates a greater amount of sludge that must be disposed of [15].

This paper aims to examine the possibilities of two printing substrates (uncoated and coated) for the application of irreversible thermochromic inks to find a more environmentally friendly option that gives a satisfactory print quality. To analyze the quality of the printed ink, a colorimetric color analysis will be performed to monitor the color path through the heating process and to compare the color characteristics on both tested substrates.

2. EXPERIMENTAL PART

Two different types of papers, coated and uncoated, were used as a substrate in printing trials in order to find a more environmentally friendly option that gives a satisfactory print quality. Uncoated paper (UN) is matt wood-free printing paper grammage 100g/m^2 and the other is 70g/m^2 cellulose coated paper (CO).

Also, two commercially available screen-printing thermochromic (TC) inks were used for printing. Both inks were water-based irreversible TC inks with different activation temperatures.

MG60 was TC ink with an activation temperature of 60°C. At this temperature, the color begins an irreversible change from light pink to magenta. The second color used, IR75, has an activation temperature of 75°C and at that temperature it begins its change from colorless to pink. The third color used, MIX60/75, was a mixture of these two TC colors.

The printing trials were carried out using a semi-automatic screen-printing device (Holzschuher K.G., Wuppertal), employing 62/64 mesh for MG60 and 120 mesh for IR75. The samples were printed in full tone.

Spectral reflectance was measured by using Ocean Optics USB2000+ spectrometer using a 30 mm wide integrating sphere under (8:di) measuring geometry (diffuse geometry, a specular component included). The printed samples were heated on the full-cover water block (EK Water Blocks, EKWB d.o.o. Slovenia).

A different initial temperature was set for each sample, depending on its activation temperature. After reaching a certain temperature, a sample was placed on the circulator plate and an integration sphere was placed on it.

Reflectance spectra were measured in one heating cycle. The measurements were performed in the steps of 1 nm for the spectral region from 400 to 700 nm. Ocean Optics SpectraSuite software was used for the calculation of the CIELAB values from measured reflectance. The D50 illuminant and 2° standard observer were applied in these calculations.

3. RESULTS AND DISCUSSION

In order to show thermochromic color changes through temperature change, measurements were performed in temperature cycles depending on the activation temperatures of irreversible TC inks. Using the spectral reflection curves and the CIELAB color system, the color changes on both paper substrates were displayed. The results are presented in graphs showing the spectral reflection curves at different measured temperatures. On the MG60 sample, color change was monitored from 40°C to 80°C. Sample measurements were mostly performed every 2°C, and around the activation temperature every 1°C in order to more accurately monitor the color change on the sample. On the IR75 sample, color change was recorded from 65°C to 82°C every 1°C.

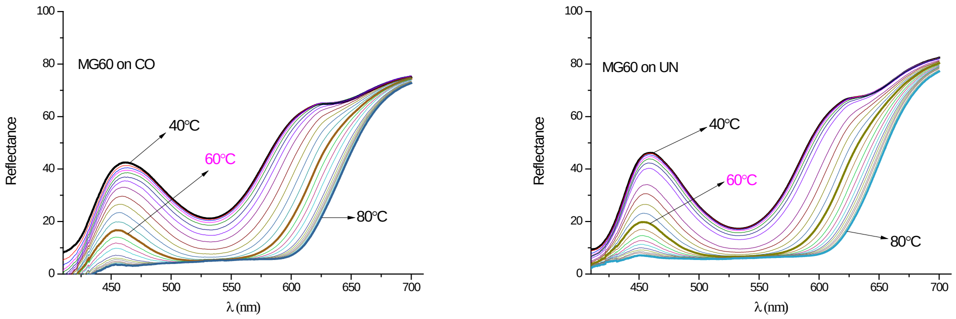

Figure 1. Spectral reflectance curves of irreversible MG60 on coated (CO) and uncoated (UN) paper substrates

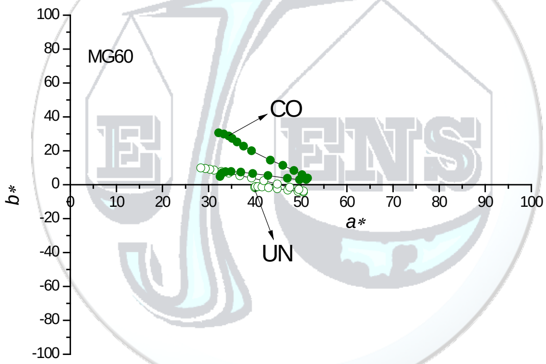

Figure 2. Changing of CIELAB values of MG60 sample in the (a,b*) plane during heating on both paper substrates*

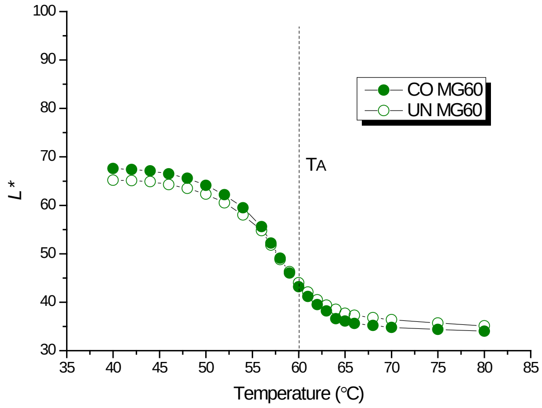

Figure 3. CIELAB lightness L of MG60 in dependence on temperature during heating on both papers*

Figure 1 shows the spectral reflection curves of the printed irreversible color MG60 on both papers. There is a similar trend of change on both paper samples. At the initial measurement temperature, 40°C, on both substrates, the curves are almost identical. The reflection decreases with increasing temperature and the curves narrow, i.e. at higher temperatures the differences are less noticeable and the color retains the same color characteristics. Although the activation temperature is at 60°C, the color at higher temperatures becomes more intense and the color saturation increases, which can be seen at the *a*/b** graph. The MG60 on both substrates has a similar color change path during heating (Figure 2). Figure 3 shows a decrease in the brightness *L** even before the activation temperature.

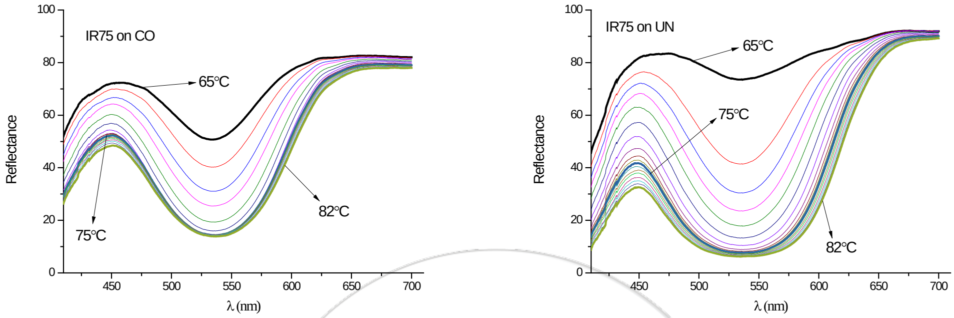

Figure 4. Spectral reflectance curves of irreversible IR75 on coated (CO) and uncoated (UN) paper substrates

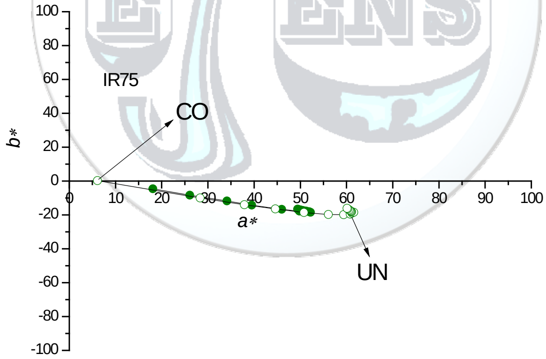

Figure 5. Changing of CIELAB values of IR75 in the (a,b*) plane during heating on both paper substrates*

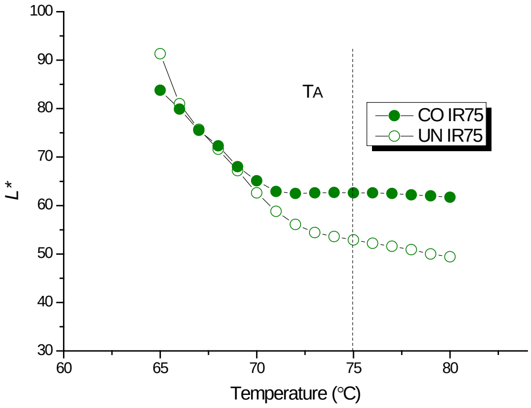

Figure 6. CIELAB lightness L of IR75 in dependence on temperature during heating on both papers*

The IR75 inks has a slightly different trend of change on the examined papers. At the initial measurement temperature, 65°C, the difference between the spectral reflection curves on these two substrates is most noticeable (Figure 4). The reason for this is probably that uncoated paper has higher whiteness. Since the IR75 ink is colorless before an irreversible change occurs, the initial spectral reflection curve is higher on that paper. Based on the *a*/b** graph (Figure 5), the IR75 on both papers has an almost identical color change path during heating. On the *L**/T graph (Figure 6), the difference between the two prints is more noticeable and the color is more saturated on the uncoated paper. Also, as with the MG60, it can be observed that the irreversible change started even before the activation temperature, and this is the same on both paper substrates.

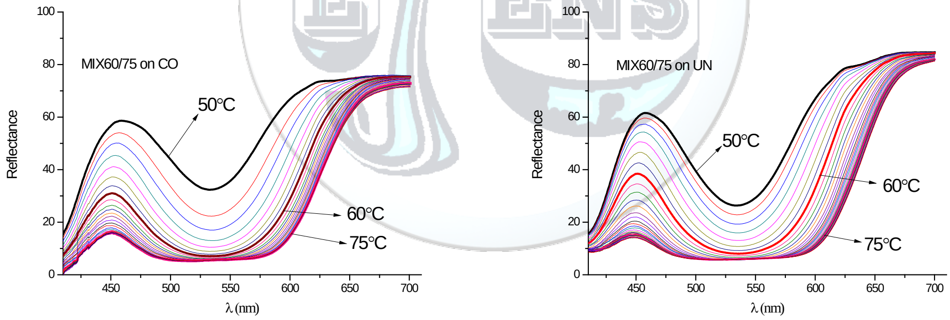

Figure 7. Spectral reflectance curves of MIX60/75 on coated (CO) and uncoated (UN) paper substrates

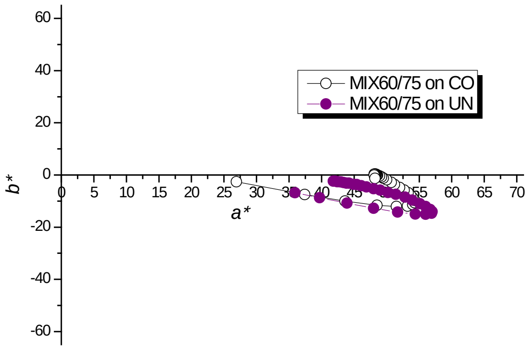

Figure 8. Changing of CIELAB values of MIX60/75 in the (a,b*) plane during heating on both paper substrates*

The MIX60/75 sample is a combination of two tested colors in a 50:50 ratio. Because of their different characteristics, the goal was to determine the differences in prints with respect to the different characteristics of the paper. It can be concluded that the color path is not completely identical, however, the changes are relatively small and quite imperceptible to the eye of the observer as shown in Figures 7 and 8.

4. CONCLUSION

In this paper, the print quality of two irreversible thermochromic inks on two different types of paper was examined in order to establish the assumption that environmentally sustainable materials can be a good option for their printing, in this case uncoated paper due to higher fiber yield. Coated papers, compared to uncoated, have lower ink demand, i.e. the ink penetration into the paper sheet is smaller. Therefore, the ink does not spread as much, and the print image is clear and sharp resulting in the enhanced print density and the print gloss. Comparing the obtained measurement results for selected thermochromic inks, it can be concluded that by changing the temperature the hue of both TC inks changes slowly and continuously on both paper substrates.

Although the values are not completely identical, these variations are imperceptible to the eye of the observer. Larger differences were observed on the IR75, which is also affected by the color of the paper substrate due to the initial colorless condition. These differences disappear after the TC color changes irreversibly.

From the L^*/T graph it can be noticed that the thermochromic reaction (color change) occurred even before the activation temperature itself and that at higher temperatures both TC inks become more saturated. The mix of the two tested TC inks on the same substrates also shows very small differences and the changes are similar to each of these two colors.

Even though paper coating increases printability and print image quality, based on this work, it can be concluded that the tested TC inks behave similarly on coated and uncoated paper. In addition, more environmentally sustainable materials (uncoated papers) can be a good option for printing with irreversible thermochromic inks.

In the following research, it is planned to include a larger number of environmentally friendly materials in order to monitor their stability to some external conditions and to determine the impact of the substrate on the stability of TC inks.

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CONFLICT OF INTEREST STATEMENT

The author(s) declare(s) that there is no conflict of interest.

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