https://doi.org/10.24867/GRID-2024-p10 Original scientific paper

INVESTIGATION OF THE IMPACT OF CHEMICAL AGENTS AND SUBSTRATES ON THE STABILITY OF THERMOCHROMIC PRINTING INKS

Rahela Kulčar , Ivona Kračun, Marina Vukoje ,
Katarina Itrić Ivanda , Tomislav Cigula
University of Zagreb, Faculty of Graphic Arts, Zagreb, Croatia

Abstract: *This research aims to analyse the chemical stability of thermochromic (TC) prints to determine which substances affect the TC effect and which parameters contribute to their better stability. Two different types of paper were chosen: synthetic and bulky, each distinguished by its unique chemical composition and absorbency characteristics. This study employed two TC inks based on leuco dyes-a 45°C activation temperature offset TC ink and a 31°C activation temperature TC screen printing ink. The offset TC printing ink dries through oxidative polymerisation, whereas the screen printing TC ink dries using UV radiation. Following printing, the samples underwent a chemical stability test in accordance with the ISO 2836 standard by employing water, ethanol, oil, and alkali. From the obtained results, we can conclude that the printing substrate significantly affects the stability of the TC ink. Samples printed on bulky paper were found to be less stable compared to those printed on synthetic paper. The paper's structure enables bulky paper to absorb more ink and chemicals, thereby accelerating the degradation of the TC ink. The greatest impact on the TC ink was shown by samples exposed to alkali printed with offset TC ink, while a slightly lesser impact was observed on samples printed with screen printing TC ink and exposed to oil and ethanol. UV TC inks require special drying conditions and drying units, while TC inks that dry by oxidative polymerization require an adequate air source and fewer conditions, making them cheaper. All these parameters ultimately define the cost of the product itself and the profitability of the entire printing process. The results of this study show that it is necessary to consider the type and purpose of the product itself and accordingly choose the appropriate TC ink and substrate for printing.*

Key words: thermochromic printing inks, chemical stability, bulky paper, synthetic paper

1. INTRODUCTION

Thermochromic inks have two primary applications: functional and promotional. In the functional application, thermochromic inks display the current temperature, while in the promotional application, a specific hidden message becomes visible or shelf presence is enhanced at the activation temperature (Bamfield, 2010; Homola, 2008; Thamrin et al., 2022).

As with all other inks, the application of thermochromic inks depends on the type of substrate used. Additionally, the method and type of printing used to apply the ink to the product must be considered (Kulčar et al., 2022; Rožić et al., 2016).

For a wide range of substrates such as cardboard, flexible or rigid plastics, other plastic products, and coated papers, flexographic and screen printing are used to apply UV thermochromic inks or solvent-based thermochromic inks, which exhibit good resistance to abrasion (WRAP, 2020).

Water-based thermochromic inks are used on absorbent printing surfaces and can be applied by flexographic, gravure, or screen printing methods. Thermochromic inks based on leuco dyes are very easy to apply, and the printing process is almost indistinguishable from other packaging inks.

Printed thermochromic inks can last for years while undergoing colour changes; however, excessive exposure to UV radiation will negatively impact the longevity of the printed ink. UV sensitivity is one of the main reasons why thermochromic inks are not used in advertising posters or the automotive industry. Additionally, as with other inks, aggressive solvents and extremely high temperatures of 120°C or more negatively affect the durability of thermochromic inks. Thermochromic inks are as durable as other inks if they are not exposed to high temperatures and prolonged UV radiation (Vukoje, Huzjak & Kulčar, 2022; Friškovec, Kulčar & Gunde, 2013).

As previously mentioned, the printing substrate can significantly impact the thermochromic print's stability. This can be particularly noticeable due to certain external factors that may negatively affect the print and thus impair the thermochromic colour-changing effect. Therefore, for this study, the stability of the thermochromic ink was tested on two different printing substrates, synthetic and bulky paper.

Synthetic papers consist of fibers similar to paper fibers but made from synthetic resin, serving as a substitute for conventional papers made from interwoven cellulose fibers. In many cases, the synthetic resin used to make synthetic paper is treated to impart paper-like characteristics. The porous structure gives synthetic paper properties very similar to those of paper made from cellulose pulp but significantly reduces its mechanical properties. Bulky papers are more environmentally friendly, provide satisfactory quality, are cheaper, contain no fluorescent whitening agents, and have a high proportion of mechanical pulp. Due to their low grammage, they reduce the overall weight of the finished product and lower transportation costs.

A chemically stable print is one in which no significant change in the print occurs when exposed to certain chemical substances. Chemical changes can manifest as changes in colour, fading, reduction in the mechanical properties of the ink and substrate, and other factors.

The international standard ISO 2836:2021 in graphic technology specifies methods for evaluating the resistance of printed materials to liquids, solids, solvents, varnishes, and acids (ISO, 2021).

This research aims to analyze the chemical stability of prints with thermochromic inks to determine which substances affect the thermochromic effect, which is a crucial factor when such inks are used as indicators on packaging. The goal is to identify which type of paper is preferable and, considering the different chemical compositions of dyes, to determine which are more chemically stable. It is expected that some substances used for chemical stability will have a lesser impact, while others will have a greater effect on the thermochromic effect. Additionally, it is hypothesized that UV inks might be more chemically stable.

2. METHODS

2.1 Materials

This study selected two printing surfaces: synthetic and bulky paper. Synthetic Yupo paper, weighing 73 g/m², is extruded from polypropylene pellets, while bulky Munken Print White paper, weighing 80 g/m², contains more than 10% mechanical pulp. The selected papers differ in their chemical structure and absorbency.

The prints were made with two commercially available thermochromic inks, one intended for offset printing and the other for screen printing technique. An offset thermochromic printing ink based on leuco dyes with an activation temperature of 45°C (CTI45) was used. This ink changes colour from green to yellow above the activation temperature. The other ink used was a thermochromic screen printing ink based on leuco dyes with an activation temperature of 31°C (CTI31). This ink changes colour from purple to pink above the activation temperature.

2.2 Printing

The thermochromic offset printing ink was printed on a Prüfbau MZ II multipurpose printing machine, while the thermochromic screen printing ink was printed on a semi-automatic screen printing machine Siebdruckgeräte von Holzschuher K.G., Wuppertal, through a polyester mesh 60/64Y. Both inks were printed in full tone.

The thermochromic offset printing ink dries by oxypolymerization, while the thermochromic screen printing ink dries using UV radiation, and its drying was carried out in a UV dryer Akrilprint L (Technigraf, Germany).

2.3 Conducting the Chemical Stability Test

The international standard ISO 2836 for graphic technology specifies methods for evaluating the resistance of printed materials to liquid and solid agents, solvents, varnishes, and acids. The ISO 2836 standard can be applied to all printing surfaces produced using conventional printing techniques, as well as digital methods such as inkjet, electrophotography, and others, utilizing materials suitable for the respective printing technique.

The samples were exposed to four substances – water, alcohol, oil, and alkali. Each sample was exposed to these substances according to the procedure specified in the international ISO 2836 standard in graphic technology. These substances were chosen for testing chemical stability due to their frequent contact with packaging products in everyday life (ISO, 2021).

For the chemical stability test with water, distilled water was used. The printed paper sample was placed between four layers of filter paper previously soaked in water, two on top and two on the bottom. Then the sample with the soaked filter papers was placed between two glass plates, dimensions 2.5 cm x 7 cm x 0.2 cm and weighed 1 kg. The samples were left in this state for 24 hours at room temperature.

The chemical stability tests with oil, using aromatic olive oil, and alkali, a 1% solution of sodium hydroxide (NaOH) dissolved in distilled water, were conducted in the same manner as the water stability test. The sample exposed to olive oil was left at room temperature for 24 hours under 1kg of pressure, while the sample exposed to alkali was left under 1 kg of pressure at room temperature for 10 minutes. The sample exposed to alkali was rinsed in distilled water until a neutral pH was achieved before drying.
For the ethanol resistance test, the printed samples of 6 cm^2 area were placed in the test tube filled with the solvent to half of its height, for 5 minutes at 23 ± 2°C.
After conducting the chemical stability tests, all samples were dried in a drying chamber at a temperature of 40°C. Samples exposed to water, oil, and alkali were dried for 30 minutes, while samples exposed to alcohol were dried for 10 minutes in the drying chamber.

2.4 Colorimetric Measurements

Colorimetric properties were measured using a previously calibrated Ocean Optics USB 2000+ spectrophotometer and the Ocean View software. The device uses an integrating sphere ISP-50-8-R-GT. Measurements were taken from 400 nm to 730 nm at 1 nm intervals by the (8°:di) measurement geometry. Colorimetric values were measured at temperatures of 15°C, at the activation temperature depending on the sample, and at 55°C. The measured values included CIE *L*, a*, b*,* and *C*,* from which the CIEDE2000 value was also calculated.
The samples were heated on a copper plate coated with a layer of nickel to ensure durability and even heat distribution, allowing for more precise measurements. This setup also enabled the maintenance of a constant temperature and gradual heating to the next set temperature on the device. The heater warms the liquid to the set temperature, which circulates through the system to heat the copper plate and, consequently, the sample on it. Measuring colorimetric values at different temperatures allows for the assessment of specific characteristics of thermochromic inks.

3. RESULTS AND DISCUSSION

Spectral reflectance curves were measured at three different temperatures: 15°C, the activation temperature depending on the sample (31° or 45°C), and 55°C. Reflectance was measured on two printing substrates, synthetic and bulky paper, and on samples exposed to alkali, ethanol, water, and oil, compared to unexposed original samples. Samples marked as CTI31 on the graph transition from purple to pink at an activation temperature of 31°C, while samples marked as CTI45 on the graph transition from green to yellow at an activation temperature of 45°C. Based on the results, the spectral curves were obtained and are shown in Figures 1 to 4.

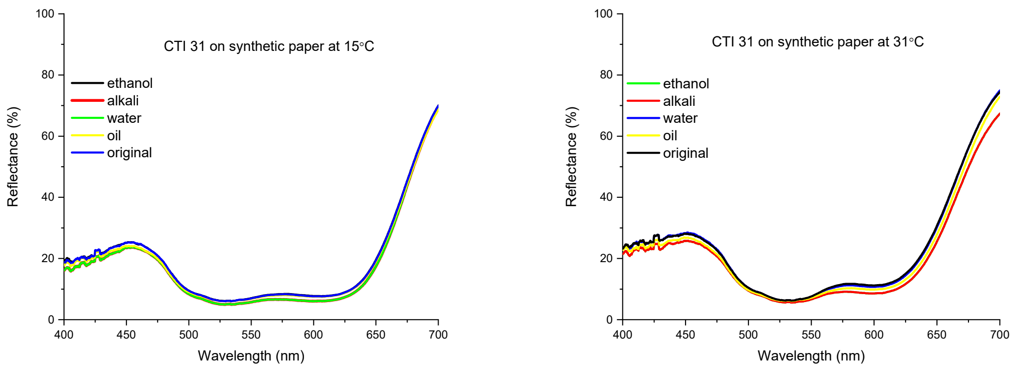

Figure 1 (part 1): Spectral reflectance curves of CTI31 measured at three different temperatures on synthetic paper

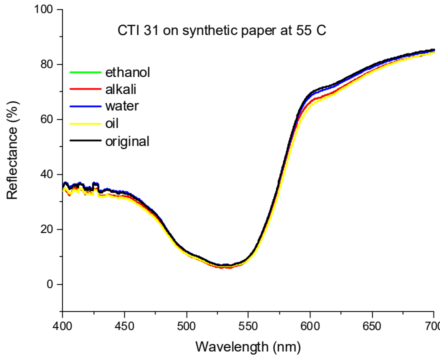

Figure 1 (part 2): Spectral reflectance curves of CTI31 measured at three different temperatures on synthetic paper

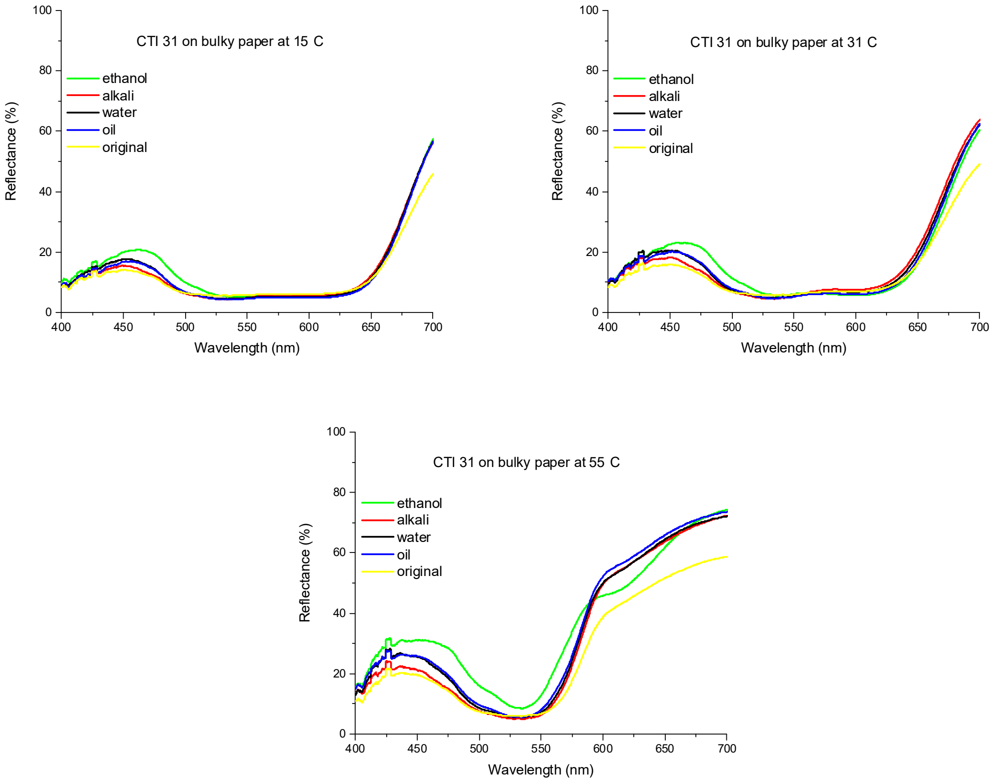

Figure 2: Spectral reflectance curves of CTI31 measured at three different temperatures on bulky paper

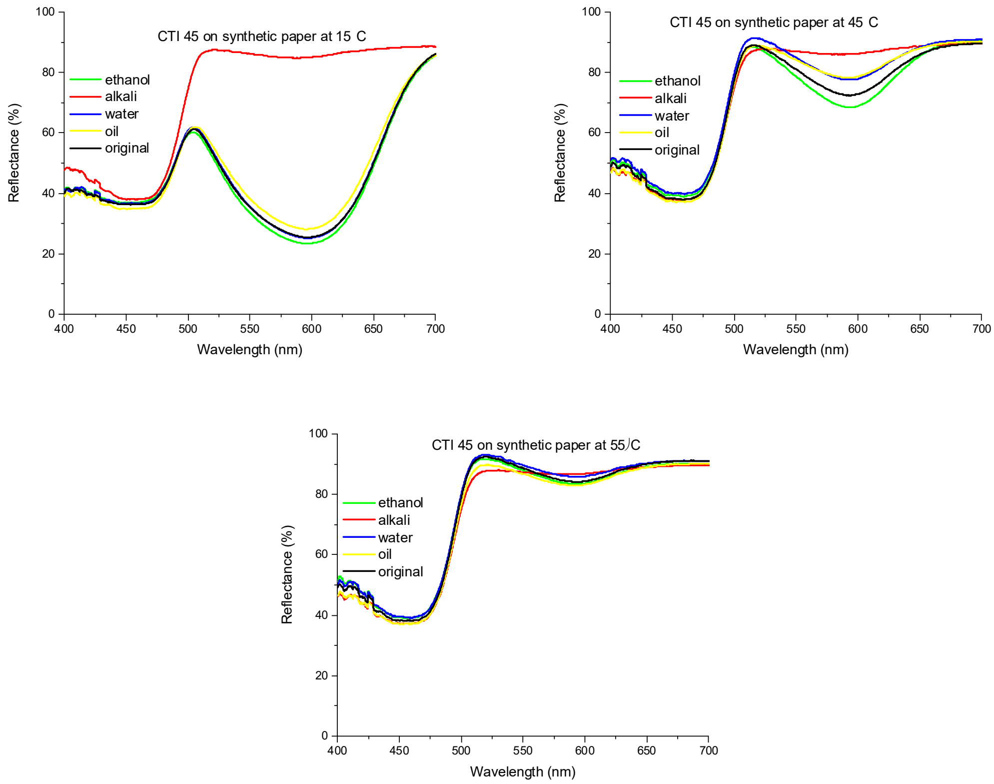

Figure 3: Spectral reflectance curves of CTI45 measured at three different temperatures on synthetic paper

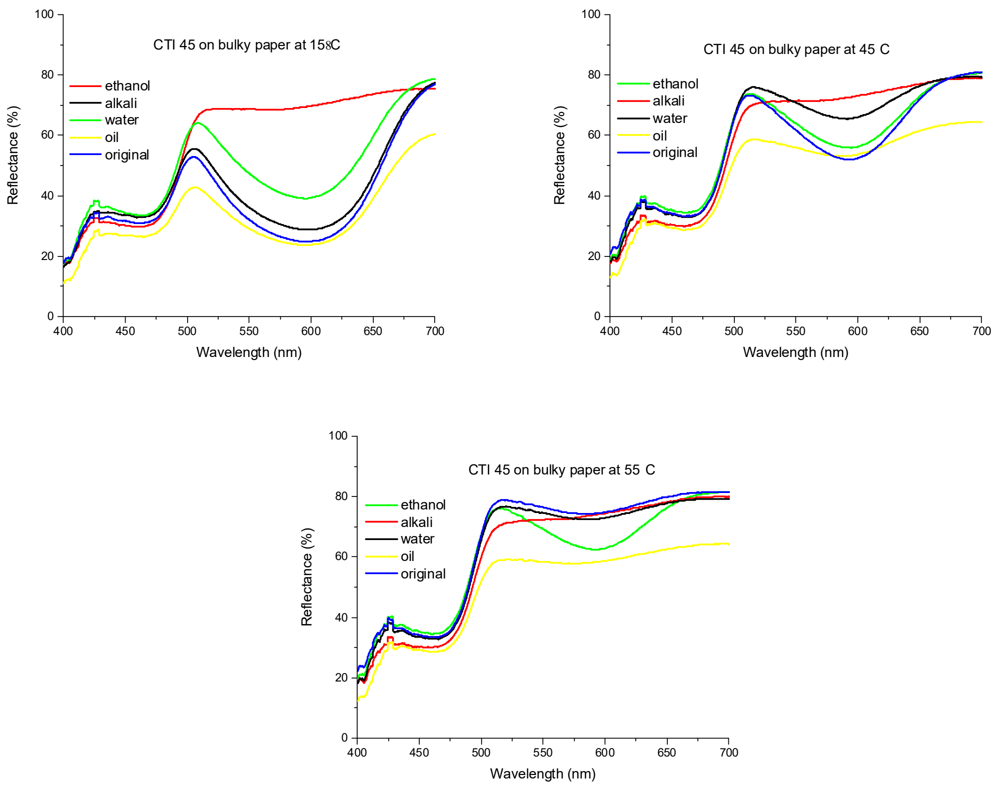

Figure 4: Spectral reflectance curves of CTI 45 measured at three different temperatures on bulky paper

Samples printed with screen printing thermochromic ink at an activation temperature of 31°C transition from purple to pink (Figures 1 and 2), and at 55°C they completely exhibit a pink coloration.
Samples printed with screen printing thermochromic ink on bulky paper show greater deviations in samples exposed to oil (Figure 2, yellow), whereas samples printed on synthetic paper show no significant deviations compared to the original samples (Figure 1). Greater deviations are also observed in samples exposed to ethanol and printed with screen printing thermochromic ink on bulky paper (Figure 2, green) compared to those printed on synthetic paper (Figure 1, green).
Samples printed with offset thermochromic ink at an activation temperature of 45°C transition from green to yellow (Figures 3 and 4). The greatest deviations were observed in samples exposed to alkali (Figures 3,4, red) and at the activation temperature (Figure 3,4, red), suggesting that the alkali may have degraded the thermochromic ink properties. Deviations are also noticeable in samples exposed to oil on bulky paper at the activation temperature (Figure 4, yellow) and above the activation temperature (Figure 4, yellow).
It can be observed that the spectral reflectance curves differ between synthetic and bulky paper. Samples printed with screen printing thermochromic ink on bulky paper (Figure 2) exhibit lower reflectance than samples printed on synthetic paper (Figure 1). This observation is also noted for samples printed with offset thermochromic ink (Figures 3 and 4).
The results suggest that the printing substrate affects the stability of the thermochromic ink. Samples printed with screen printing thermochromic ink show greater stability after exposure to certain chemicals than samples printed on bulky paper.

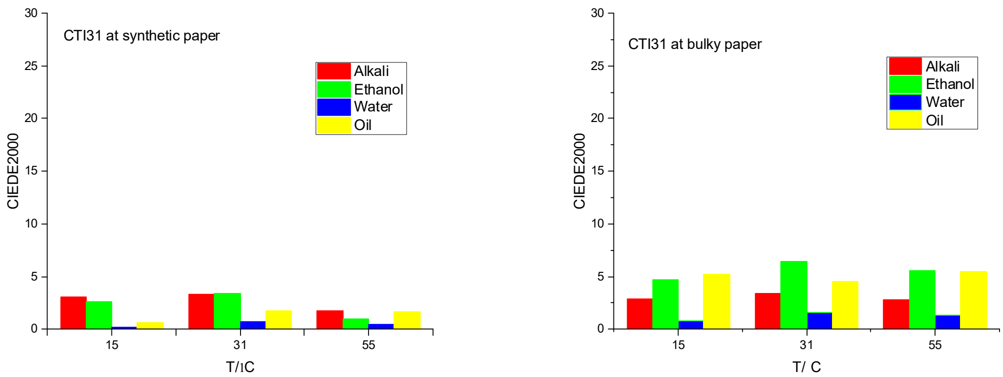

Figure 5: CIEDE2000 colour difference observed on CTI31 samples when exposed to different chemicals

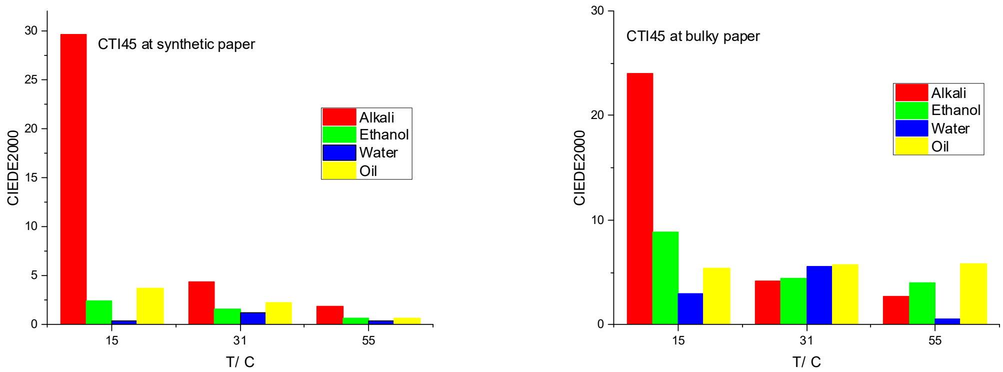

Figure 6: CIEDE2000 colour difference observed on CTI45 samples when exposed to different chemicals

For samples printed with purple thermochromic ink (CTI31), the greatest colour difference was observed in samples exposed to ethanol and alkali, while the smallest colour change was noted in samples exposed to water (Figure 5). For green thermochromic ink (CTI45), the most significant change was observed in samples exposed to alkali, whereas smaller changes were noted in samples exposed to oil (Figure 6).

Greater colour differences were observed in samples printed with green thermochromic ink compared to purple, and in samples printed on bulky paper compared to synthetic paper.
Based on the results, it can be concluded that the printing substrate significantly impacts the stability of thermochromic inks. Samples printed on bulky paper were found to be less stable compared to those printed on synthetic paper. This instability is attributed to the paper's structure, which allows the bulky paper to absorb more of the ink and the chemicals to which it is exposed, leading to faster and easier degradation of the thermochromic ink.

4. CONCLUSION

The objective of this study was to determine which type of paper is preferable and to assess which types of dyes are chemically more stable given their different chemical compositions.
The samples were exposed to four substances: water, oil, ethanol, and alkali. The greatest impact on the thermochromic ink was observed in samples exposed to alkali and printed with offset thermochromic ink, while a slightly smaller impact was noted in samples printed with screen printing thermochromic ink and exposed to oil and ethanol. This is likely due to the drying method of the thermochromic ink. UV-cured inks showed better stability against the exposed substances compared to inks dried by oxy polymerization, as the microcapsules are protected by a polymeric binder.
UV thermochromic inks require specific drying conditions and units, while thermochromic inks that dry by oxy polymerization demand less air supply and fewer conditions, making them more cost-effective. All these parameters ultimately define the cost of the product and the efficiency of the printing process. The results of this investigation suggest that the type and purpose of the product must be considered when selecting the appropriate thermochromic ink and substrate for printing.

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