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Stability Aspects of UV-Curable Prints on Pressure-Sensitive Labels Facestock Made from Agro-Industrial By-Products

Ivan Malenica, Marina Golik Krizmanić, Marina Vukoje *, Rahela Kulčar and Katarina Itrić Ivanda

Faculty of Graphic Arts, University of Zagreb, Getaldićeva 2, 10000 Zagreb, Croatia; marina.golik1@gmail.com (M.G.K.)
* Correspondence: marina.vukoje@grf.unizg.hr; Tel.: +385-1-2371-080 (ext. 120)

Abstract: During its life cycle, packaging comes into contact with various substances and even those it protects. Thus, for example, oil, water, and alcohol, if spilled on the packaging, can damage its functionality. In addition to exposure to chemicals, graphic products (packaging) can be exposed to moisture and UV radiation, which can negatively affect their stability during transport, storage, and handling. The choice of printing substrate can directly affect the stability of prints against different degrading influences. This paper explores the stability of thermochromic (TC) and conventional offset printing inks printed on environmentally friendly printing substrates intended for packaging applications (labelling). Results have confirmed that used printing substrates and printing inks give prints good rub resistance, but somewhat lower stability in terms of ethanol, water, and UV radiation. The choice of printing substrate can directly affect the stability of prints against different degrading influences. The resistance of prints to oil cannot be clearly defined since the samples were altered with the coloration of the oil. It can only be stated that oil reduced the functionality of the TC prints given that the samples were colored by the oil itself.

Keywords: thermochromic; cellulose; color; degradation; stability

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1. Introduction

Printing inks are liquids that are converted into solids after the printing process and form a print. This process of transition from the liquid state to the solid state (drying) is achieved by means of physical processes and chemical reactions, or by their combination. Ink drying can be achieved by absorption, oxidation, evaporation or radiation-induced drying (ultraviolet radiation, infrared, electron beam, and, experimentally, microwave and radio frequency) [1]. The composition of the printing inks is dependent on the required drying method. For UV-curable printing inks, the vehicle system in the presence of photo-initiators, and the appropriate wavelength ultraviolet (UV) light incorporated within the press, quickly produce a solid through a free radical reaction at the end of the press [1].

UV-curable printing inks consist of a colorant (pigments or dyes), photo-initiator, resins (mostly acrylate esters), and additives. Sustainable printing can include printing with UV-curable or water-based inks due to their reduced solvent content, which, in the end, results in lower VOC emissions [2]. But due to the nature of water-based inks, when the water-based prints end up in the paper recycling process, they can become a problem since they dissolve in water. The resulting printing ink particles are impossible to remove from pulp suspension due to their size and hydrophilic characteristics [3]. In the case of UV-curable prints, de-inkability aspects are much lower than in the case of conventional hydrophobic prints, but with the development of new printing technologies this problem has been surpassed, mostly with development of LED–UV curing technologies [4]. If printing inks are not completely removed from the pulp suspension in the recycling process, then the final product (recycled paper) will contain different chemical components originating from printing inks and some of them can be toxic [5]. Bearing that in mind, the use of UV-curable prints may be a better option.

Printing inks must produce a quality print, but they must also be a functional part of the product considering the design of the final product and its end use. Printing inks interact with consumers and influence consumer behavior. This means that they have to be stable during their whole life cycle. Printed products can suffer harm during transportation, storage, handling, or use by the final consumer. Such damage can lead to a noticeable decline in the product's visual appeal and the readability of the product information and thus its durability is one of the main properties. Accelerated aging tests (UV exposure) are often carried out to understand how printing substrates and inks withstand the damaging effects of UV irradiation, mainly in color change and functionality. Effective laboratory simulation tests are often performed according to standard procedures, to reproduce actual large-scale processes and resistances [6]. In accordance with quality assurance, the official specifications (weathering, abrasion resistance, lightfastness, chemical (product) resistance, and heat resistance) of the inks are agreed between the supplier and the end users. Almost all printing substrates must meet at least one critical specification.

Thermochromic printing inks are inks in which the process of chromism (color change) is triggered by heat [7]. Those inks can change color within a defined broad temperature range, temporarily (reversible color change) or permanently (irreversible color change). In general, they differ from conventional inks only in the segmenting of used colorants. Instead of dyes or pigments, in thermochromic inks, the colorant is a microcapsule, which is more than 10 times larger than a conventional pigment particle.

The possibility of using thermochromic inks in labels and packaging design is an example of increasing its added values [8]. Due to their high cost compared with commercial inks, it is crucial to optimize the printing process and to increase the final product quality, i.e., stability during its whole life cycle and resistance to official specifications (weathering, abrasion resistance, lightfastness, chemical (product) resistance, and heat resistance) [1]. All of the previously mentioned elements can cause visual alterations to the print, which are mainly related to the used colorants in the inks or the substrate itself not being resistant to the particular influence [9].

In addition to the use of functional inks in packaging printing, the choice of printing substrates can also affect the quality of the final product. Apart from ensuring high quality, it is imperative to address the environmental implications of the chosen materials. Today, it is increasingly encouraged to choose recycled materials or materials that have a minimal adverse impact on the environment [10]. It is also encouraged to reduce the use of polymer materials due to their limited biodegradability and their tendency to accumulate in the environment. Cellulose-based materials not only exhibit tremendous potential in packaging advancement, but also decrease the environmental footprint of the packaging. In addition, cellulose that can be isolated from the by-products of various industries, mostly agriculture, is a promising part of the circular economy [11].

The aim of this paper is to investigate the quality of UV-curable thermochromic ink and its mixtures with conventional printing inks on environmentally friendly paper. The focus is on evaluating their resistance to various environmental conditions in order to gain insight into the fundamentals of print degradation, durability, and stability.

2. Materials and Methods

2.1. Materials

The prints were created using both UV-curable thermochromic (TC) and conventional red (WR) and yellow (Y) UV-curable offset inks on a commercial dry offset machine designed for label printing, under real and identical conditions. The applied thermochromic ink is colored blue below its activation temperature of 29 °C and colorless above this temperature. Two thermochromic mixtures were prepared by adding conventional UV-curable red (WR) and yellow (Y) offset-printing inks to the TC system in ratio 30:70, producing the effect of magenta (TC-WR) and green (TC-Y) coloration (Figure 1). All the prints were made in full tone.

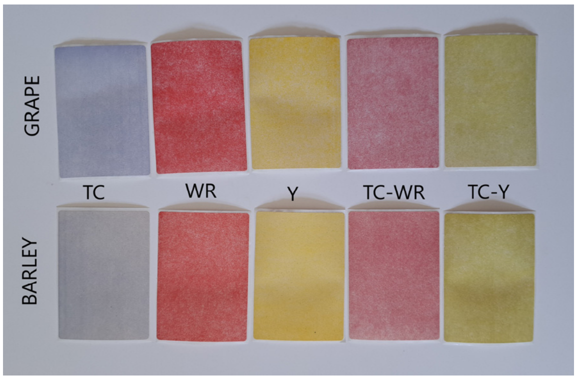


Figure 1. Two thermochromic mixtures prepared by adding conventional UV WR and Y offset-printing inks to the TC system in ratio 30:70, producing the effect of magenta (TC-WR) and green (TC-Y).

All inks were printed on two printing substrates, namely two different pressure-sensitive label (PSL) materials whose fiber-based facestock is made with 15% agro-industrial by-products (grape (G) and barley (B)), 40% recycled post-consumer paper, and 45% virgin wood pulp to form a high-quality natural paper [12,13]. Previous research showed that used PSL labels differ due to the presence of optical brighteners (OBA) in the PSL facestock, resulting in the different coloration of the papers, but the chemical composition of cellulose in facestock in both cases is almost the same [14].

2.2. Determination of Roughness

Roughness parameters (arithmetical mean roughness (Ra), mean roughness depth (Rz), and maximum roughness depth (Rmax)) of the printing substrates were determined according to ISO 16610-21:2011 [15] using the MarSurf PS 10 1.00-28 device.

2.3. Rub Resistance Test

For the purposes of the research, the Hanatek RT4 Rub and Abrasion Tester tribometer device was used to test the resistance of the prints to rubbing. When examining a dry print, there is some removal of the paint due to friction. The white offset paper and the test print are placed on the discs. The discs driven by electric motors rotate at the same angular speeds. By placing a weight of different masses on the upper disc, the pressure between the sample and the paper is regulated. The pressure can be 0.5, 1.0, and 2.0 psi, while, in the SI system, it is 3.5, 6.9, and 13.8 kPa. The ink is removed from the sample during rubbing and transferred to the white paper. A pipe with an air supply removes dust particles that accumulate in the sample during testing. After turning the selected number of times (10, 20 or 40), the device stops.

2.4. Chemical Resistance Test

The chemical stability test of the samples was carried out in accordance with the international standard ISO 2836:2004 [9] and experimental conditions presented in Table 1. In this work, the chemical stability of the prints on alcohol (96% ethanol), water, and oil was tested. These agents were chosen to simulate the real contact conditions of labels with various liquid products (alcoholic and other beverages, olive oil).

Table 1. Test conditions for used liquids.

Test Agent	Receptor Surface	Test Duration	Contact Condition
Water (distilled)	filter paper	24 h	Contact pressure
Olive oil	filter paper	1 h	Contact pressure
Ethanol (v/v = 96%)	test tube	5 min	Immersion

2.5. Determination of Lightfastness

The Solarbox 1500e (CO.FO.ME.GRA) was used for the accelerated aging of prints. The device can simulate outdoor or indoor environmental conditions and provides temperature and radiation control. In this work, the samples were exposed to filtered xenon light for 12 h at a temperature of 50 °C, with a radiation intensity of 550 W/m^2 according to standard procedures [16,17]. A UV filter was used to change the spectral curve from the xenon to the ultraviolet range.

2.6. Determination of Color Difference

To measure the spectral reflectance of the samples, an Ocean Optics USB2000+ spectrometer was used, which uses an integrating sphere with a width of 30 mm in accordance with the (8°: di) measurement geometry. The measurement geometry (8°: di) indicates the diffuse illumination of the samples and the detection of reflected light at an angle of 8 ° relative to the vertical with a deviation of ±5°. An Ocean Optics LS-1 tungsten halogen light source with a radiation range from 360 to 2000 nm was used. The samples were measured at room temperature and heated to 20 °C, 29 °C, and 40 °C. The samples were heated using a temperature-changing device (EK Water Blocks, EKWB d.o.o., Komenda Slovenia), which consists of a control panel, a liquid that is heated/cooled and circulated through the system, and a metal plate on which u-samples are placed. The advantage of this device is the constant temperature. The spectral reflectance was measured in the visible range of the electromagnetic spectrum (400 to 750 nm) with a step size of 1 nm. Samples were measured before and after exposure to chemicals or to the accelerated aging process. In addition to the spectral reflection curves, the colorimetric parameters C^*, h^*, L^*, a^*, and b^* were measured, which were used to calculate the CIEDE2000 colorimetric difference according to Equation (1) [18]. The interpretation of the calculated color difference (CIEDE2000) was performed in relation to the conditions presented in Table 2. The ideal target result is CIEDE2000* < 1, but the tolerance standard in print shops is usually CIEDE2000* < (2–3) [19].

$$\Delta E^*_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}} \quad (1)$$

Table 2. Subjective assessment metric based on the CIEDE2000 color difference [6,20].

Value of Color Difference	Description of Color Difference	Tolerance for Printing Industry
<0.2	not visible	Acceptable
<0.5	negligible	
0.2–1.0	noticeable	
1.0–3.0	visible, but small	
3.0–6.0	clearly visible, obvious	Unacceptable
6.0–12.0	extremely large	
>12.0	unacceptable	

3. Results and Discussion

3.1. Roughness of the Samples

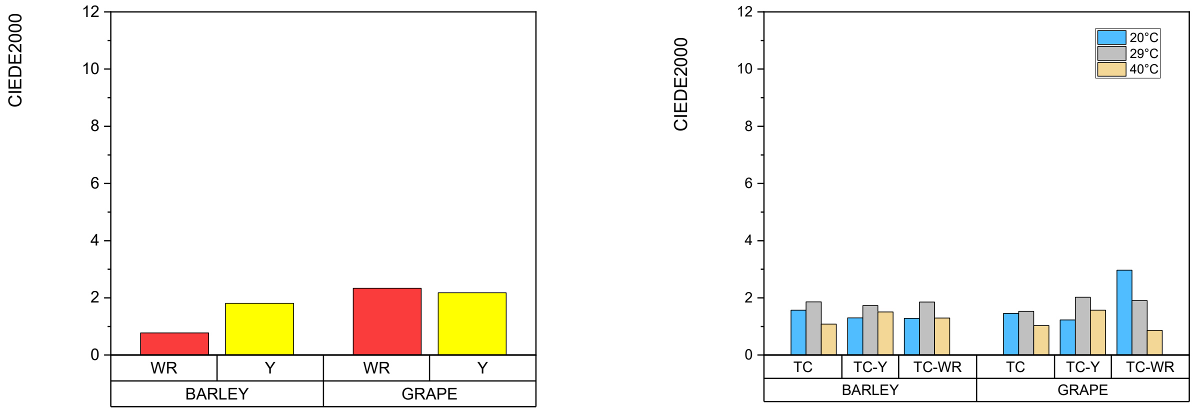
Table 3 shows the determined roughness parameters. It can be seen that a higher roughness profile (Ra) is observed in the PSL facestock made from grape. This can influence the ink demand on the paper substrate during printing and, consequently, the print quality. Eriksen et al. showed that the ink pigment penetration, ink demand, and ink coverage correlate well with printing substrate roughness, and that the ink demand and ink pigment penetration increases with increasing surface roughness, due to the formation of temporary fiber–fiber gaps [21].

Table 3. Surface roughness parameters.

Substrate	Ra (µm)	Rz (µm)	Rmax (µm)
Grape	2.860	17.725	22.918
Barley	2.853	15.782	18.930

3.2. Rub Resistance of the Prints

Figure 2 shows the results of color difference between the samples obtained before and after the rub resistance test according to the CIEDE2000 formula. The rub resistance of prints refers to the degree of scraping and removal of the ink film under the action of rubbing, and is most often influenced by the basic properties of the paper (roughness, absorbency, etc.), ink composition, and printing conditions [22]. Zhou et al. showed that the ink rub resistance of print on coated paper is mainly influenced by the absorbance of coated paper and that better absorption properties of paper result in good ink rub resistance [22].



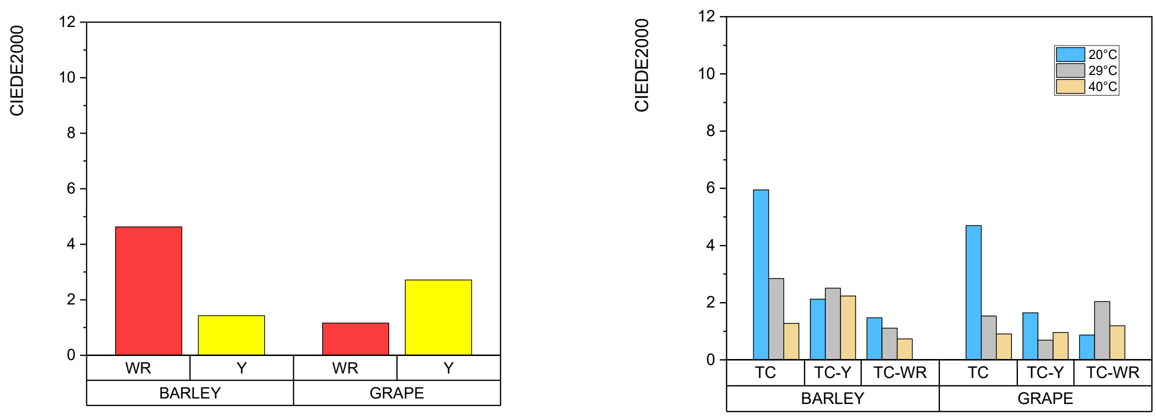
(**a**) (**b**)

Figure 2. CIEDE2000 of the prints after rub resistance test of (**a**) prints made from conventional inks and (**b**) prints made from TC ink and mixture of TC and conventional inks.

From the results, it can be observed that the CIEDE2000 values are lower than 3, indicating the acceptable color change and good rub resistance of the prints. In addition, the smallest color difference is obtained for prints made on barley substrate using conventional WR ink (Figure 2a). The prints made on the grape substrate show lower rub resistance using conventional WR ink (Figure 2a). Furthermore, the TC–WR ink mixture on grape substrate shows a lower rub resistance measured at 20 °C. This points to the conclusion that both substrates make different chemical bonds since different behavior for the ink-printing substrate combination can be noticed. In addition, the TC prints show low rub resistance due to the presence of microcapsules that are active below 29 °C and colored in blue (Figure 2b). Therefore, the TC prints made on both substrates show the highest changes in color at 29 °C, when the change from the colored to the decolorized state occurs. The smallest color difference among all the samples was obtained in the TC ink and mixture of TC–conventional ink at a temperature of 40 °C, when the TC microcapsules are inactive (decolorized). At this point, the color of the printing substrate becomes dominant (Figure 2b). Nevertheless, the use of conventional printing inks in TC mixtures does not improve the rub resistance of the studied prints. From the results, it can be concluded that a better rub resistance shows a smoother printing substrate (barley). These results are not in agreement with previous research, in which a better resistance to rub was achieved on printing substrates with a higher surface roughness [22,23]. This different behavior probably occurs due to the different compositions of the printing ink used in this study. UV-curable printing inks contain polymers (prepolymers, monomers, and photoinitiators) that enable UV drying. Compared to conventional printing inks, UV-curable inks give thicker films on printing substrates and dry faster than conventional offset-printing inks [24]. In addition, due to a higher surface roughness, the ink sets between the surface irregularities and forms a heterogeneous film, in comparison to on a smoother surface where the ink forms a more even ink film. An evenly distributed ink film results in higher rub resistance.

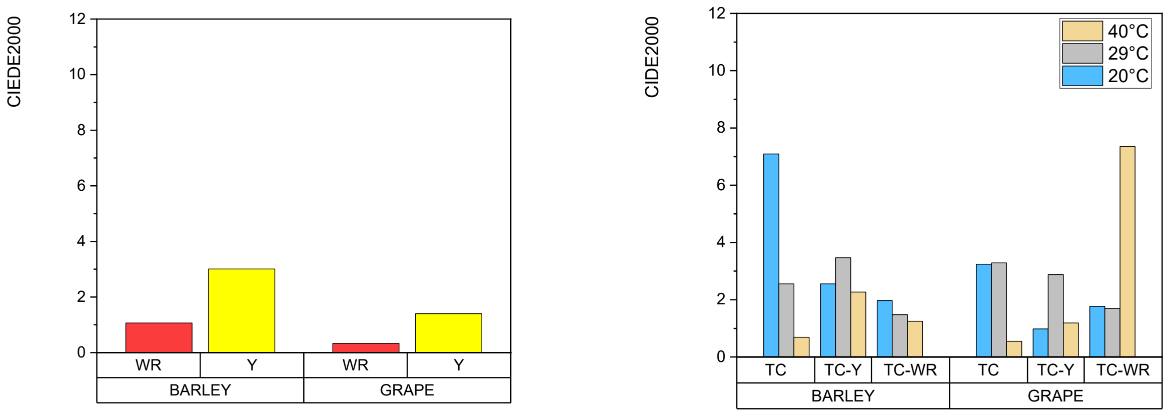
3.3. Chemical Resistance of the Prints

Figures 3–5 show the colorimetric differences obtained for the evaluation of prints' resistance to water, ethanol, and oil, measured at temperatures of 20 °C, 29 °C, and 40 °C, or only 20 °C for conventional inks.



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

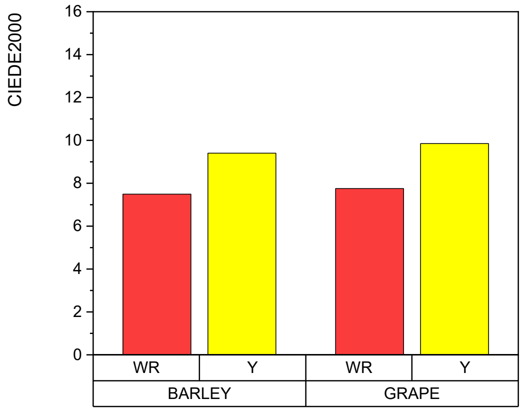
Figure 3. CIEDE2000 of the print after water resistance test of (**a**) prints made from conventional inks and (**b**) prints made from TC ink and mixture of TC and conventional inks.



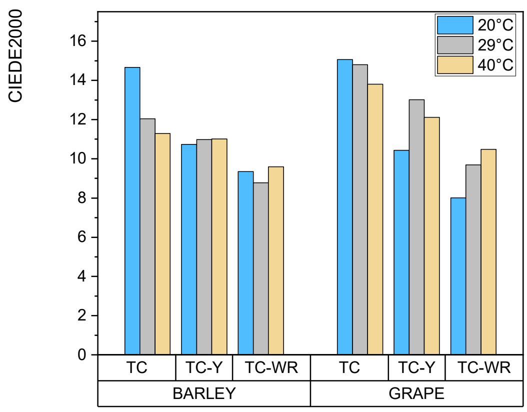
(**a**) (**b**)

Figure 4. CIEDE2000 of the prints after ethanol resistance test of (**a**) prints made from conventional inks and (**b**) prints made from TC ink and mixture of TC and conventional inks.

In the case of prints' resistance to water, it can clearly be seen that the conventional WR ink on the barley substrate and the TC ink on both substrates, have lower stability to water, resulting in a higher value of CIEDE2000 (CIEDE2000 > 3) (Figure 3a). In the case of TC prints and TC–WR and TC–Y mixtures, some variations in behavior were observed, with better resistance in the TC–WR ink mixture. When the prints were made from mixtures of TC with conventional inks, the CIEDE2000 value was below 3, indicating acceptable color changes. However, this was not the case for pure TC prints on both substrates where the CIEDE2000 value exceeded 5. Changes in the surface of the receptor (filter paper) that has been in contact with print were not detected.



(**a**)



(**b**)

Figure 5. CIEDE2000 of the print after oil resistance test of (**a**) prints made from conventional inks and (**b**) prints made from TC ink and a mixture of TC and conventional inks.

In the case of prints' resistance to ethanol (Figure 4), it can clearly be seen that Y ink has lower stability, resulting in a higher CIEDE2000 value for both printing substrates (Figure 4a). Despite that, it can be concluded that prints made from the conventional inks, WR and Y, show good resistance to ethanol since the CIEDE200 values are below 3. For pure TC prints, TC–WR, and TC–Y mixtures, somewhat varied behavior was observed, without a consistent pattern, probably due to heterogeneity of the prints and the PSL facestock surface (Figure 4b). Nevertheless, it can be concluded that TC prints, TC–WR, and TC–Y mixtures on both printing substrates have notably lower resistance to ethanol. Changes in the receptor (liquid ethanol) that has been in the contact with the print were not detected.

Water is a polar solvent, while, with organic molecules in a hydrocarbon chain, such as CH_2CH_3–in ethanol, this influence is reduced. Water interacts primarily with hydrogen bonding, while ethanol reacts through polar interactions [25].

Different behaviors were observed for the conventional prints with Y and WR; specifically, a higher color difference was observed in response to water compared to ethanol (Figures 3 and 4). Considering this, it can be concluded that used printing inks Y and WR, primarily interact through hydrogen interactions. Probably due to the lower adhesion properties of the barley substrate, the CIEDE2000 value is higher in comparison to grape substrate. This can be attributed to the higher roughness of the grape substrate, i.e., better mechanical adhesion occurring due to the penetration of the printing ink into the surface irregularities (pores) of the printing substrate [26]. Slightly higher CIEDE200 values were obtained for the TC print in reactions with ethanol, indicating that TC ink interacts with polar interactions [1]. The results confirm previous research findings and confirm that TC prints are unstable to the action of ethanol [6,25,27]. In addition to pigments and binders, the composition of the paper can have a significant influence on the chemical stability of prints [6,27–29].

The greatest color change, i.e., the lowest resistance of prints to the action of oil was observed for all studied samples (Figure 5). None of the ink and substrate combinations in the test met the standard color deviation tolerance. This can be partially attributed to the color of the oil used, which has been noticed to change the color of the paper, which then ultimately affects the color of the print itself. In all other tests, thermochromic ink on the barley substrate at a temperature of 20 °C shows the greatest difference. On the grape substrate, the deviations of the thermochromic ink are slightly smaller, but still exceed the permitted standards described in Table 2. From the result presented, we cannot make a clear conclusion about the pigment deterioration, considering that the color of the oil prevailed on all samples. However, we can claim that the functionality of the print is completely destroyed.

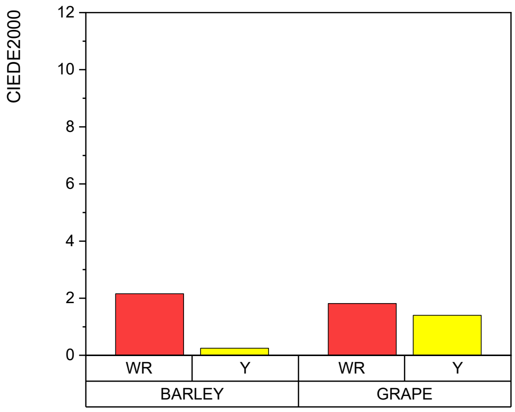
From Figures 3–5, it can be seen that the CIEDE2000 results are significantly higher when thermochromic colorant is active, i.e., when measured below its activation temperature (20 °C). Based on the previously presented findings, it can be inferred that the CIEDE2000 values acquired at temperatures below the activation temperature stem from a combination of TC microcapsules and conventional pigment. In the case of ink mixtures, TC–Y and TC–WR, the CIEDE2000 values obtained at temperatures above the activation temperature (40 °C) mainly result from the deterioration of the color of the conventional pigment. In the case of the TC–Y and TC–WR, the CIEDE2000 values obtained at temperatures above the activation temperature (40 °C) result mainly result from the deterioration of the color of the conventional pigment, as confirmed in recent studies [6].

3.4. Light Fastness of Printing Inks

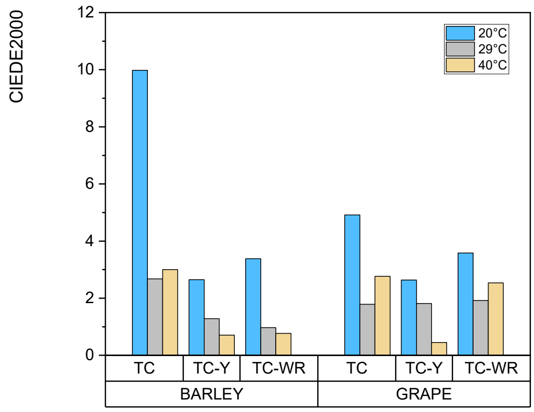
Light fastness of printing inks, defined as the resistance of inks to fading under the influence of a light source, is one of the most important ink properties, especially in the packaging and advertising industries [30]. As described earlier, the UV stability of prints is generally a complex photochemical reaction, resulting from the numerous reactions occurring due to the interactions of light (radiation) and printing ink components (binders, solvents, colorants, and additives) [6,30]. In general, photooxidation as a consequence of UV radiation is higher with the presence of chromophore groups due to their high capacity for UV absorption, resulting in increased material degradation [31].

From the presented results (Figure 6a,b), it can be seen that the highest changes are in the case of TC prints on both substrates at 20 °C (when the TC microcapsules are active and colored in blue). This clearly shows that the TC pigments in the TC printing ink have low stability to UV irradiation. The mixture of TC–Y ink results in better color stability than the mixture of TC–WR ink obtained on both substrates, due to the higher stability of conventional Y ink (Figure 6a). In addition, it is evident that the choice of printing substrate can increase the stability of a print. In this case, the barley substrate shows better UV stability. Previous research has indicated that barley substrate exhibits higher stability compared to grape substrate, attributed to the presence of optical brighteners (OBA) in the grape-based printing substrate. With the action of UV irradiation, the OBA degrades and, therefore, influences the coloration of the paper [14]. This research showed that the OBA in the paper influences the stability and color performance of the prints. In both cases, previous research confirmed that short exposure to ultraviolet irradiance does not significantly oxidize the surface, and that the photooxidation of the surfaces is not the reason for color degradation. The color degradation of both printing substrates is only a consequence of the OBA degradation [14]. In addition to the absence of the OBA, the better stability of prints made on the barley substrate can also be attributed to the homogeneous distribution of the ink layer resulting from a smoother surface in contrast to the heterogeneous distribution of the ink layer on the surface of the grape paper resulting from a rougher surface (Table 3). This is also related to the fact that pigments in an ink layer are evenly distributed over a smoother surface, in contrast to a rougher surface. It is generally known that the color of the pigment ink is more stable if the concentration on the surface is evenly distributed [32].

For the conventional inks Y and WR on both printing substrates (Figure 6a), the CIEDE2000 $\leq$ 2, which is acceptable for the graphic industry (Table 2). In the case of TC prints (CIEDE2000 determined at 20 and 29 °C) the value is $\geq$3, which is not acceptable for the printing industry and indicates the low stability of TC print in terms of UV radiation. At a temperature of 40 °C, the CIEDE2000 results were found to be $\leq$3, which indicates good color stability. However, it is crucial to emphasize that the color of the print at 40 °C is influenced by both the discolored TC ink, the conventional ink, and the printing substrate.



(**a**)



(**b**)

Figure 6. CIEDE2000 of the print after UV aging test of prints made from (**a**) conventional inks and prints made from (**b**) TC ink and mixture of TC and conventional inks.

4. Conclusions

The objective of this study was to examine the stability of UV-curable offset thermochromic ink printed on two different substrates. The study aimed to examine how the type of substrate influences the stability of prints under various environmental conditions and whether mixing thermochromic ink with conventional printing inks can improve the stability of prints. The rub resistance, chemical stability, and lightfastness of prints were investigated. Blue TC printing ink and two conventional offset inks (red and yellow) were used on substrates made from the agricultural residues of barley and grapes. A visual assessment of the samples before testing showed that the substrate affects the appearance of the print. The prints on the barley substrate had a saturated and more uniform tone. This can be attributed to the different surface properties of the printing substrate used. All tested samples show good rub resistance, considering that the color degradation monitored via the CIEDE2000 value is less than 3. The results of the chemical stability test revealed that the prints have a lower stability to ethanol than to water. In general, TC prints have low stability in terms of both water and ethanol. In all cases, for TC prints and TC-conventional ink mixtures, the most significant changes occur at 20 °C, when the TC microcapsules are active (colored blue), resulting in a change in coloration. The chemical stability of the prints is influenced by the mechanical adhesion occurring due to the penetration of printing ink into the surface irregularities (pores) of the printing substrate, i.e., the rougher the surface, the better stability. In addition, the nature of the pigments determines their solubility in a specific media. The conclusion cannot be derived for the determination of the print's resistance to oil. It can only be stated that oil adversely affects the color of all tested prints, resulting in high CIEDE2000 values. Additionally, it can be concluded that oil significantly reduces the functionality of TC prints, but a clear conclusion about prints degradation cannot be derived from these results. The UV stability of the studied samples is influenced both by the stability of the pigments and the stability of the printing substrate. In this case, conventional pigments have a higher stability in terms of UV irradiation than TC pigments. Moreover, evenly distributed ink (pigments) on a smoother surface will result in better UV stability. This research contributes to our understanding of the fundamental aspects related to print degradation, durability, and stability. The used printing substrates and inks can be used for different packaging applications, but for oil packaging it should be avoided, as well as for packaging which is intended for longer UV exposure.

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editing, R.K. and K.I.I.; visualization, M.V.; supervision, M.V.; project administration, M.V. All authors have read and agreed to the published version of the manuscript.

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