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THERMOCHROMIC PRINTS ON BEVERAGES PACKAGING: THE RESISTANCE OF PRINTED LABELS UPON ETHANOL

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Abstract: *Today, the packaging industry is increasingly transforming, especially in terms of development of new sustainable materials and smart solutions in order to attract customers when choosing products, and to be competitive in the market. The use of colour changing packaging can give added value to the product since this kind of packaging can in that way interact with the consumer and provide a massage upon the product. During its lifecycle, the packaging can be exposed to the influence of various agents, for example the spilling of beverages over the printed labels. For this reason, the prints need to be resistant to certain agents, in this case, ethanol. In the end, the spill of ethanol can cause visual alterations of the print due to the colourants or the substrate itself not being resistant to the particular agent. Thermochromic inks are widely used as indicators for beverage packaging which can often be exposed to different concentrations of alcohol that may affect the functionality of that same indicator. Thermochromic inks differ in their composition from classic printing inks, which in the end results in lower stability when exposed to UV radiation and various chemicals. Thus, this study explores the influence of ethanol on the functionality of TC prints on labels. Different label papers were printed with one TC ink, with an activation temperature of 12°C. The samples were exposed to different concentrations of ethanol (8%, 12%, 25%, 35%, 42% and 96%) to simulate the real conditions in which it is possible to spill different alcoholic beverages on the thermochromic print on the packaging of an alcoholic product. It can be concluded that alcohol affects the stability of microcapsules even in the smallest concentrations because the largest changes of colour were observed at low temperature, while smaller colour changes determined at 23 ° C indicate that the classic process ink is more stable to the influence of alcohol. The results of this test showed that the chemical stability of the thermochromic print depends on both, the printing substrate and the external conditions to which the print is exposed. The results show that the proper choice of printing substrate can improve the stability of the thermochromic print in reaction with ethanol.*

Key words: thermochromic ink, packaging, labels, alcohol, ethanol, colour difference

1. INTRODUCTION

The design and colour of the packaging have been used for a long time in marketing as a tool for influencing customer purchase behaviour (Shukla et al., 2022). The stability and the quality of the prints on packaging can significantly improve the impression of the quality of the product itself. Also, the role of the colour on the packaging is very often a key factor when choosing a product, and the type of printing substrate can influence a different experience of the printed ink. Today, changes in the behaviour of consumers, are the cause of increased demand for different forms of packaging, for example due to the increase in online shopping but also the increase in the consumption of takeout food and food delivery. In order to meet consumer expectations, packaging should be functional and attractive. Recently, intelligent packaging serves as a medium that provides consumers with the necessary information about the quality and safety of packaged goods. Thermochromic printing inks, which can be applied to a variety of printing substrates, can convey a message to the consumer by changing the colour of the print they see. The use of chromogenic colours, i.e., colours that change their characteristics due to external influences, can intrigue the customer and thereby increase the price value of the product. The concept of thermochromic colours is often associated with the image of a ceramic cup, i.e., a product that uses this phenomenon, which changes colour when a hot drink is poured into it. But today, more and more applications of thermochromic colours appear on different papers and labels that have the role of indicators that provide information about the best consumption temperature of the product or as a design solution that gives the product added value.

Thermochromic materials change their colour depending on the temperature change. Colour changes can be reversible or irreversible. Materials that change colour reversibly are thermochromic pigments based on leuco dyes or cholesteric liquid crystals (Seeboth et al., 2010). Thermochromic pigments based on

leuco dyes generally change from coloured to colourless or to another colour with increase of temperature. Cholesteric liquid crystals show a "colour play effect" passing through the entire spectrum with increasing temperature (Kulčar et al., 2012). Thermochromic printing inks have a rather short shelf life and poor stability. In addition, thermochromic inks have low light fastness (Friškovec et al., 2013; Rožić et al., 2015; Vukoje et al., 2022). Very few studies so far have investigated the influence of different chemicals (chemical resistance) on the stability of the TC print. Jamnicki Hanzer et al. 2020. Showed that exposure of TC prints to ethanol caused severe damage to the prints and the bleeding of the colourants from the prints was also detected (Jamnicki Hanzer et al., 2020).
The aim of this paper is to determine the effect of alcohol ethanol on the stability of the thermochromic prints, as well as to determine whether contact alcohol - thermochromic print gives an immediate reaction of the colour change of the print. Thermochromic prints could be exposed to the effect of ethanol in real conditions during the use of products on which they are applied as indicators, for example cooling indicators for the beverages, and the effect of alcohol alone can cause irreversible changes in the colouring of the print and thus affect its functionality.

2. METHODS

2.1. Materials

Six label papers (manufactured by Brigl & Bergmeister) were selected as printing substrates with properties given by the manufacturer and presented in Table 1. The used printing substrates were chosen for this application precisely because of the properties they possess. The manufacturer claims that the chosen labels are intended for applications that should be resistant to moisture and chemicals, such as alkali. This includes, for example, paper labels for beer bottles as well as many other drinks and foods (sparkling wines, spirits, liqueurs, vodka, gin, as well as for jars of vegetables, fruits or jams). The label paper must not only produce good print results in these applications, but also withstand the external influences that occur during filling, transport, storage or cooling, and use. Used label papers differ in grammage, surface properties, surface treatment, etc.

Table 1: Characteristics of the used papers according to the manufacturer

Label type	Abbreviation	Grammage, g/m^2	Thickness, μm	Cobb 60, g/m^2	Characteristics
Niklakett Special	NKS	68	61	17	functional coating on the reverse side
Niklakett Medium Fashion	NMF	70	73	17	embossed label paper, surface patterns (e.g. linen structures) in combination with the - like fine fabric -
Niklakett Premium	NP	75	64	17	highly polished surface
NiklaSelect	NS	80	65	22	Very well closed surface
Niklakett Brilliant	NB	80	64	17	high gloss and the high smoothness
Chromolux	CHR	80	84	>8	woodfree, cast coated and smooth finished paper

One UV-curing thermochromic printing ink from a commercial manufacturer was used for printing on the printing substrates. The used TC colour changes to a different colour below a certain temperature and when heated. The used TC ink is coloured orange below the activation temperature (TA = 12°C) and changes its colour to yellow when heated above it. The TC ink used is reversible, i.e., the original colour is returned by heating. This TC ink consists of two types of pigments: microencapsulated thermochromic pigments based on leuco dyes and conventional pigments. It can be assumed that the TC colour used was created by adding red leuco dyes (TC microcapsules) to conventional yellow pigments. Thus, while the print is exposed to room temperature (above TA), the thermochromic microcapsules are colourless and the colouring of the conventional yellow pigment dominates. By lowering the temperature, TC microcapsules are activated and they turn red (Figure 1). The combination of the red colouration of the microcapsules and the yellow classic pigment results in an orange colouration of the print.

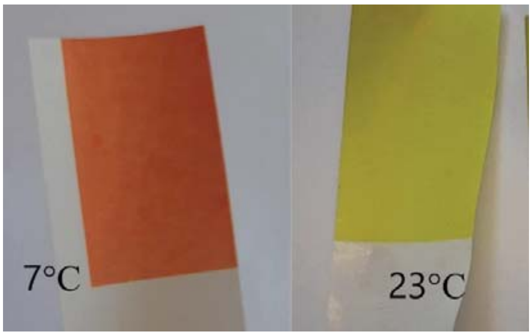

Figure 1: Visual presentation of the print colour change at temperature below TA (7°C) and at temperature above TA (23°C)

2.2. Methods

For the evaluation of printing substrate surface roughness, the MarSurf PS 10 (Mahr GmbH, Gottingen, Germany) surface roughness gauge was used. Measurements were performed ten times in fibre direction.

The assessment of the chemical resistance of TC prints was carried out in accordance with the standard method ISO 2836: 2004. The international standard ISO 2836: 2004 in the area of the printing industry defines the methods of assessing the resistance of prints to liquid and solid agents, solvents, varnishes and acids (ISO 2836, 2004). In this work, the chemical resistance of the prints to water and ethanol was evaluated. In this way, an attempt was made to simulate real conditions, i.e., the spilling of various alcoholic beverages on the print, i.e., the label. The prints were immersed in test tubes containing water and alcohol ethanol concentrations of 8%, 12%, 25%, 35%, 42% and 96%. These concentrations were chosen in order to simulated by different alcoholic beverages, from mild ones like beer and wine to strong alcoholic drinks like brandy or whiskey. The method of testing the chemical resistance of prints to ethanol was carried out by immersion of the print in the solvent in the test tube for a continuous duration of 5 minutes. After the reaction, the samples were air-dried, after which the colour change on the prints was monitored.

Determination of print's colour changes was obtained using a spectrophotometer "OceanView" and software Ocean Optics, which was additionally used for the calculation of CIELAB values, with standard observer 2° and taking into account illuminant D50. The colour of the samples was measured at two fixed temperatures (7°C and 23°C), one temperature below the activation temperature (12°C) and one above. Each sample was heated with a water block (EK Water Blocks, EKWB; Slovenia). From the obtained colorimetric parameter colour differences were calculated using the CIEab (ΔE_{ab}) colour difference formula (CIE Central Bureau, 2004).

3. RESULTS AND DISCUSSION

In order to conclude if surface properties such as surface roughness contribute to the ethanol resistance of the prints, the surface roughness of the used labels was measured. This assumption was derived from the fact that surface roughness affects the printing substrate's affinity for the ink (ink demand) and ink pigment penetration due to formation of temporary fibre-fibre gaps suitable for penetration in the printing nip and subsequent relaxation of fibres to their original state (Eriksen et al., 2007) and from the assumption that higher ink demand will result in the increased ethanol resistance of the prints.

Table 2 presents the results of measured roughness parameters R_a, R_z, and R_{max}. The R_a parameter describes absolute values of the profile heights over the evaluation length and gives a general description of the height surface variations, R_z parameter defines average value of the absolute values of the heights of five highest profile peaks and the depths of five deepest valleys within the evaluation length, R_{max} parameter, indicating the largest single roughness depth within the surface length (Rubert&Co.Ltd, 2022). From the presented results it is evident that two types of used labels (CHF and NB) significantly differ in their surface roughness from the other. NP label has higher surface roughness than the previously mentioned but lower than following NKS and NS, with similar surface roughness around 6.500 µm. NMF label with embossed surface patterns shows the highest surface roughness, as expected. The same behaviour is seen for all presented surface parameters (Table 2).

Table 2: Roughness parameters measured on used label types (printing substrates)

Label type	R_a (µm)	R_z (µm)	R_{max} (µm)
CHR	0.253±0.033	1.411±0.256	1.983±0.601
NB	0.397±0.053	2.171±0.150	2.768±0.231
NP	0.5653±0.072	3.317±0.593	5.564±1.393
NKS	0.687±0.023	4.270±0.456	5.616±1.311
NS	0.696±0.059	4.311±0.797	5.373±1.137
NMF	1.104±0.223	5.340±1.073	6.858±1.409

Figures 2-4 show the results of colorimetric difference determination. The results show a trend of colour difference increase with an increase of the EtOH concentration. At lower alcohol concentrations (8-42%), colour changes are greater at 7°C. Precisely in these alcohol concentrations, there is a higher proportion of water. This means that the stability of microcapsules is affected by water as well as ethanol. At 23°C, the colour changes are somewhat smaller, so it can be assumed that the influence of water on the stability of the yellow process colour is smaller. The high concentration of ethanol (96%) significantly affects the colour change of the print, and to a greater extent the yellow coloration of the classic process colour (measured at 23°C) than in the case when the TC microcapsules are active at 7°C. This can easily be explained by the interactive forces between materials, i.e., hydrogen (δ_H), polar (δ_p) or dispersive interactions (δ_d). The polar interactions are considerably lower compared to dispersion and hydrogen interactions. Hansen solubility parameters (HSP) can be a useful tool in the prediction of materials compatibility (miscibility) based on their interactive forces (Rožić et al., 2017). The use of HSP has a wide range of applications, such as in polymer compatibility determination, interactions at pigment surfaces, and the prediction of the chemical and solvent resistance of the coatings and films (Lambourne, 1999). Taking this into account we can assume about the print's interaction with used alcohol concentrations. Water interacts mostly with hydrogen bonding, while ethanol reacts by polar interactions (Table 3) (Rožić et al., 2017). In used ethanol solutions from 8- 42%, hydrogen interactions predominate, with somewhat lower dispersive interactions. In 96% EtOH solution, the polar interactions are dominant. Taking that in mind, we can conclude that classic process printing ink interacts mostly by high polar interactions as evident from the high colour difference measured at 23°C, while TC microcapsules interact with dispersive forces.

Table 3: Hansen's solubility parameters for water and ethanol (EtOH)

Solvent	δ_d	δ_p	δ_H
Water	15.6	16.0	42.3
Ethanol	15.8	8.8	19.4

The biggest difference in the colour change of the print at a temperature of 7°C is shown by the prints on the CHR, NB and NP substrates (Figure 1), which points to the degradation of the microcapsules because they are active at that temperature. The used labels (CHR and NB) have the smoothest surface in comparison to other printing substrates (Table 2). With the increase of surface roughness, the resistance of prints to ethanol slightly increases. The biggest changes in the colour of prints at a temperature of 23°C are shown by all prints treated with 96% alcohol in all cases. Since a rougher printing surface has higher ink demand, the resistance of prints to ethanol is greater.

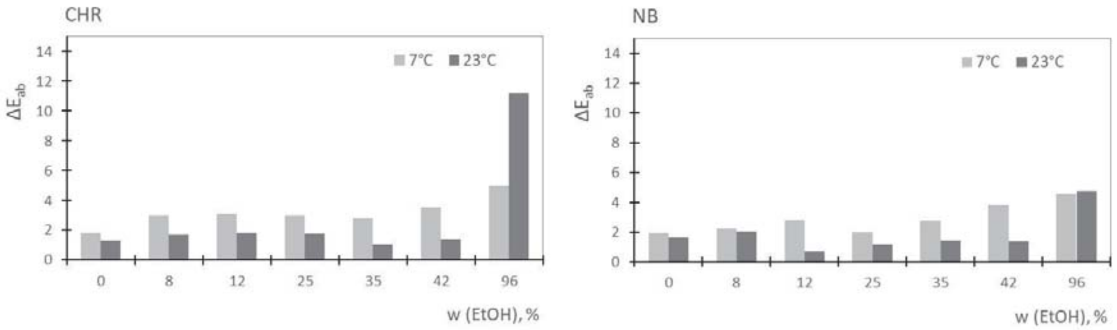

Figure 2: Total colour difference (ΔE_{ab}) of TC prints on CHR and NB labels, measured at 7 and 23°C after their exposure to different concentrations of ethanol

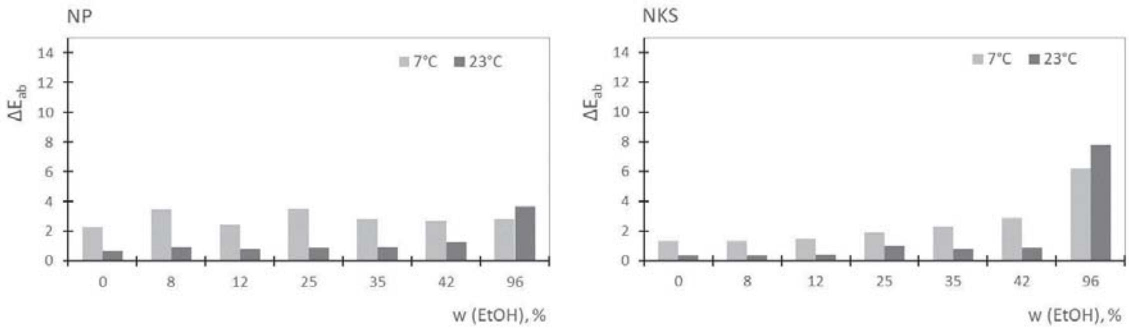

Figure 3: Total colour difference (ΔE_{ab}) of TC prints on NP and NKS labels, measured at 7 and 23°C after their exposure to different concentrations of ethanol

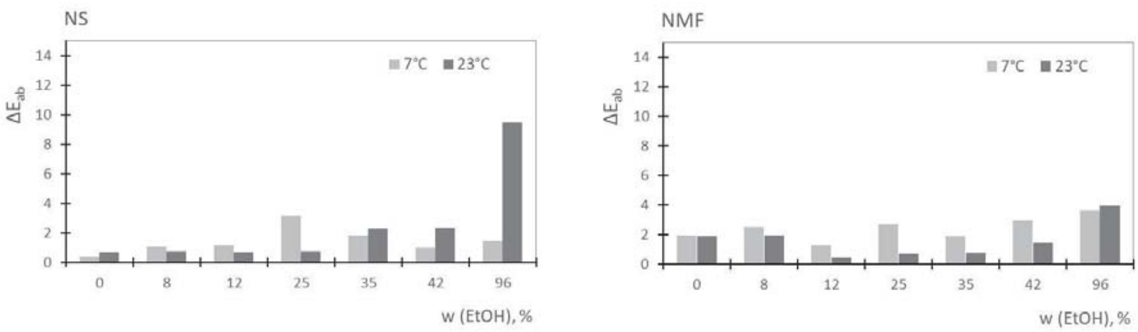

Figure 4: Total colour difference (ΔE_{ab}) of TC prints on NS and NMF label, measured at 7 and 23°C after their exposure to different concentrations of ethanol

Despite the negative impact of ethanol on TC prints, one interesting observation was made during the experiment. When thermochromic prints were exposed to ethanol, the colour of the TC print changed from yellow to orange at room temperature. The orange colouration of the TC print indicates a low temperature (below 12°C). In that case, the sample was not exposed to low temperature even though it was coloured orange (Figures 5 and 6). This indicates that the alcohol evaporation reaction leads to an endothermic reaction, which creates a lower temperature on the surface of the print and changes its colour. Also, this fact indicates that the evaporation of ethanol on the surface of the TC print creates a temperature lower than 12°C. This reaction of the alcohol can give a false colour response of the print when spilling alcohol over a thermochromic print. Due to the heating of the spectrophotometer, this change of the print colour due to the endothermic evaporation reaction, was impossible to record, so only a visual assessment was recorded (Figures 5 and 6). This phenomenon was recorded on all samples, for all ethanol concentrations. In addition, this points to the conclusion that thermochromic printing inks with low activation temperature (cold-activated) can be a useful indicator for endothermic reactions.

Figure 5: Change in the colour of the print as a result of the ethanol endothermic evaporation reaction on the CHR sample at room temperature (23±2°C) indicating a temperature below 12°C in areas where coloured in orange

Figure 6: Change in the colour of the print as a result of the ethanol endothermic evaporation reaction on the NMF sample at room temperature (23±2°C) indicating a temperature below 12°C in areas where coloured in orange

4. CONCLUSIONS

The aim of this study was to determine whether the chemical stability of thermochromic prints depends on the printing substrate on which the thermochromic ink is printed and to determine how different concentrations of alcohol (ethanol) affect the stability of thermochromic print. From the obtained results, it is evident that the chemical stability depends on the substrate on which the thermochromic ink is printed, and that with an increase in the alcohol concentration to which the thermochromic ink is exposed, the chemical stability of the TC print decreases, i.e., TC print loses the properties it had before exposure to ethanol. The samples were exposed to pure water (0% ethanol) and six different concentrations of ethanol: 8%, 12%, 25%, 35%, 42% and 96% to simulate the real conditions in which it is possible to spill different alcoholic beverages over the thermochromic print on the packaging of an alcoholic product. Moreover, it was concluded that besides ethanol, water affects the stability of the prints. The results of this test showed that when choosing a printing substrate for the printing thermochromic ink for alcoholic beverages packaging applications, the printing substrate with higher surface roughness should be considered. An additional benefit of this research was the fact that a TC print with a low activation temperature can be used as an indicator of endothermic reactions.

5. ACKNOWLEDGMENTS

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