CELLULOSE CHEMISTRY AND TECHNOLOGY

INFLUENCE OF SOLVENT HYSTERESIS IN THERMOCHROMIC OFFSET PRINTS ON THE THERMOCHROMISM EFFECT

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The colorimetric values of prints of three thermochromic offset inks on four different paper substrates – bulky, synthetic, filter (neat cellulose) and recycled in one heating-cooling cycle – were determined. Prints that are cooled are lighter than those that are heated at the same temperature. This phenomenon is a consequence of the hysteresis of the solvent inside or outside the microcapsules. The solidification temperature of the solvent is lower than the melting point of the solvent. Due to solvent hysteresis, the concentration of solvent in the solid aggregate state at the same temperature is lower when the prints are cooled than when they are heated. Therefore, the liquid solvent prevents the interaction of dyes and developers and the formation of their colored complex, *i.e.* color development, and the prints are lighter, *i.e.* less colored. The colorimetric cooling curves are therefore shifted to the left relative to the heating colorimetric curves.

As regards certain paper substrates, for example, when the printing paper is very compressible, as in the case of bulky paper, the deformations of many microcapsules are so great that they become completely inactive in terms of color development.

Keywords: hysteresis, ink, solvent, thermochromic, thermochromism

INTRODUCTION

The reversible process of coloring or discoloration caused by changes in temperature is called thermochromism. The color change occurs at elevated temperatures, which are called thermochromic transition temperatures. When these temperatures are reached, a color change occurs.

Thermochromic colors are often used in security printing, medical thermography, food packaging. For certain applications, it is necessary for the reversible color change to be fast, which would mean that it happens at a certain temperature.

In 1929, the phenomenon of thermochromism of a colorless solution of di-β-naphthospirane was recorded, which turns blue-violet when heated, and loses color again when cooled.[1]

Indirect thermochromic systems change color when the ambient temperature changes; however, they do not use thermochromic substances, but other chrome substances. Halochromic substances sensitive to pH changes or ionochromic substances that are sensitive to specific ions are often used. As a consequence, the entire system is considered thermochromic, while the color change phenomenon itself is not thermochromism. In practice, indirect thermochromic systems are used more often than direct thermochromic systems.[2]

Organic thermochromic systems based on leuco dyes are indirect thermochromic systems. A leuco dye-based system usually consists of three components: a halochromic dye (sensitive to pH changes), a dye developer, and a solvent.[1] Many leuco dyes are of the spirolactone type. A common example is crystal violet lactone. In pure state, it is a slightly yellowish crystalline powder, soluble in nonpolar or slightly polar organic solvents. In an acidic environment, the lactone ring is broken, with the oxygen detaching from the central carbon. This single large conjugated system is a chromophore, with strong absorption in the visible spectrum, giving this compound its blue distinctive color. Color developers are usually phenolic compounds (weak acids), for example, bisphenol A.

Thermochromic inks can be reversible or irreversible, and based on liquid crystals or leuco dyes. Liquid crystal-based thermochromic inks are less applicable because they are more

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sensitive to temperature changes, compared to leuco-based thermochromic inks. They are usually used in precision applications to be able to display even small changes in temperature. Thermochromic systems based on leuco dyes contain microcapsules, in which the dye, developer and solvent are incorporated. The encapsulation of leuco dyes, solvent and developer can be carried out by emulsification, followed by polymerization. Melamine-formaldehyde, urea, melamine, gelatine-gum arabic polymers are usually used to make microcapsules during polymerization. Since the indirect thermochromic system is about 75–95 mol % organic solvent, the solvent's melting point largely controls that of the mixture. Alkyl alcohols are commonly used solvents. At low temperature, the solvent is in a solid aggregate state. When heated, it becomes liquid and then prevents any contact between the dye and the color developer. Consequently, the interaction between the dye and the color developer ceases and discoloration occurs. The melting point of the solvent determines the color change point.[3,4]

In order to expand the color palette, new colors can be obtained by mixing thermochromic inks or by mixing thermochromic inks with classic inks.

The challenge remains to produce thermochromic systems that combine good sensitivity, mechanical strength, ease of fabrication, flexibility and stability to photooxidation.[5]

In this paper, prints of three reversible offset thermochromic inks based on leuco dyes were examined. The colorimetric values of the prints at different temperatures in one cycle of heating and cooling the prints were determined. The reversibility of the thermochromic effect was monitored. The results show that the thermochromic process is reversible, but the returned colorimetric values are not the same as the initial ones. This is a consequence of the hysteresis of the solvent that is part of the mixture inside the microcapsules, as well as the same solvent that has diffused outside the microcapsules.

EXPERIMENTAL

Printing substrates and printing inks

In preparation of the experiment, four different paper samples were used: bulky paper (producer Munken Print White), recycled paper containing 33% recycled fibres (producer Evercopy+Clairefontaine), synthetic paper (producer Yupo), and filter paper (Whatman quantitative filter paper grade 589/3 blue ribbon). Filter paper was used to simulate 100% pure cellulose paper without any additives or fillers. Bulky paper contains wood-free pulp and more than 10% mechanical wood pulp. Synthetic paper is extruded from polypropylene pellets.

Thermochromic offset inks based on leuco dyes were used. One ink is produced by Chameleon®. This thermochromic ink is blue in color below 27 °C and changes to colorless when heated above 27 °C (activation temperature) according to the manufacturer. Two offset thermochromic printing inks from Chromatic Technology (CTI) were also used; the color of one of them changes from burgundy to blue at an activation temperature of 63 °C, according to the manufacturer's instructions, while the second ink is colored green below the activation temperature (T_A = 45 °C) and yellow above the activation point. CTI inks are based on vegetable oil, and Chameleon inks are based on mineral and vegetable oils.

The printing trials with offset ink were carried out using a Prüfbau Multipurpose Printability Tester. The quantity of 1.5 cm^3 ink was applied on the distribution rollers while printing was carried out with the printing force of 600 N. All the samples were printed in the full tone.

Infrared (IR) spectroscopy

Infrared (IR) spectra of Chameleon thermochromic offset ink were recorded using the attenuated total reflection (ATR) technique. IR spectra were recorded by the ATR technique using the MIRacle ATR carrier from Pike Technologies, whose reflection element is a combination of diamond crystal and ZnSe. Spectra were recorded in the range between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1}, and the result was the average of 32 recordings.

Colorimetric values of prints

The colorimetric values of the prints were measured using an Ocean Optics USB2000+ spectrophotometer and Ocean Optics SpectraSuite Paper 695 software for the calculation of the CIELab values L^*, a^*, b^* from measured reflectance in the entire spectral range (380-730 nm in 1 nm steps). The D50 illuminant and 2 ° standard observer were applied in these calculations.

Each sample was heated by the Full Cover water block (EK Water Blocks, EKWB, Slovenia). The temperature of the copper plate surface was varied by circulation of thermostatically controlled water in channels inside the water block, which was assured to be up to 1 °C accurate in the applied temperature region. Print samples were heated and immediately cooled again.

RESULTS AND DISCUSSION

The IR spectrum of the thermochromic ink produced by Chameleon recorded at 23 °C is shown in Figure 1. Vegetable oils have bands at 1470 cm^{-1} (CH, CH_2 stretching), 1100 cm^{-1} (CO stretching) and 719 cm^{-1} (-CH_2- rocking). They also have an intense band at 1750 cm^{-1}, which is attributed to the carbonyl group of the ester. The bands at 1462 cm^{-1} (aromatic C-H bending) and 1377 cm^{-1} indicate the presence of mineral oil.

The band at 1744 cm^{-1} is attributed to the rocking of the hydroxyl groups of the microcapsule polymer. The band at 1609 cm^{-1} is attributed to the stretching of the hydroxyl groups of bisphenol A. The band at 1363 cm^{-1} corresponds to the structure of the isopropyl unit in bisphenol A,[6] and the band at 1422 cm^{-1} – to stretching of the C=C ring of bisphenol A. The stretching of the hydroxyl groups of the alcoholic solvent is marked by a band at 1556 cm^{-1}. The band at 1215 cm^{-1} indicates the rocking of the alkyl part of the alcohol, and that at 1250 cm^{-1} – the rocking of the hydroxyl groups of the alcohol.[7] Rocking of the C-C bonds of the aromatic rings of the crystal violet lactone dye is attributed to the band at 1102 cm^{-1}, while the band at 1210 cm^{-1} is attributed to the stretching of the C=C bonds of the aromatic rings of the crystal violet lactone.

The components present inside the microcapsules cannot be identified by IR spectroscopy. Only the components that are outside of the microcapsules (dye, developer and solvent) can be identified, *i.e.* those that have diffused out of the microcapsules. Based on the results of IR spectroscopy, it is possible to conclude that some microcapsules broke during the preparation of the ink and that the components that were in the microcapsules diffused.

The IR spectrum of the ink at 23 °C (blue line) does not differ from the IR spectrum of ink heated at 30 °C (red line). This means that heating the ink does not cause further diffusion.

Table 1 shows photographs of blue prints on the tested papers depending on the heating and cooling temperatures. After the process of heating the prints, the process of cooling them was carried out immediately. Table 1 shows that blue prints are lighter during cooling at all temperatures compared to the same prints during heating.

The same results were obtained with green and burgundy prints (Tables 2 and 3). This phenomenon can be explained by the solvent hysteresis process. The solidification temperature, which is the reverse of the transition from solid to liquid, is called the solidification point. For most substances, the melting point is equal to the solidification point. For some substances, the melting point and the solidification point are different. For example, organic polymer agar melts above 85 °C, and starts solidifying only when the temperature drops between 32 °C and 40 °C. This phenomenon is called hysteresis. The temperature at which a substance solidifies depends not only on the strength of intermolecular interactions, but also on how the molecules are packed in solid state. Steric hindrance of molecules can lower the solidification point even though the molecules interact strongly. Namely, due to steric interference in the solid state, some interactions between molecules that are present in the liquid state may be more difficult to perform. Molecules in the liquid state move more freely, so these interactions are carried out more easily. Due to the heavier packing of branched solvent molecules, compared to linear ones, it can be assumed that branched solvents were used in the tested inks. For such solvents, it is necessary to lower the temperature so that due to steric hindrances, all interactions are enabled and the solvents are converted into a solid aggregate state. On all paper substrates tested, the solvent in blue prints solidifies at approximately 23-24 °C and melts at temperatures of approximately 28 to 29 °C. The solvent in burgundy prints melts at approximately 63-65 °C, and turns into a solid state at temperatures of 56-59 °C. The solvent in green prints melts at temperatures between 40 °C and 45 °C, and turns into a solid state at 36 °C to 40 °C.

By heating the prints, a gradual melting process of the solvent occurs. As the solvent gradually melts, it gradually destroys the complex of dye and developer, so the transition from one color to another (or to colorless in the case of blue prints) is gradual. Colorimetric values were determined for all the prints, at all heating and cooling temperatures: L^*, a^* and b^*. When a color is expressed in *CIELab*, L^* defines lightness, a^* denotes the red/green value and b^* – the yellow/blue value. The a^* value (axis) goes from left to right. The movement of the color measurement in the $+a^*$ direction shows a shift towards the red color, and in the $-a^*$ direction – towards the green color.

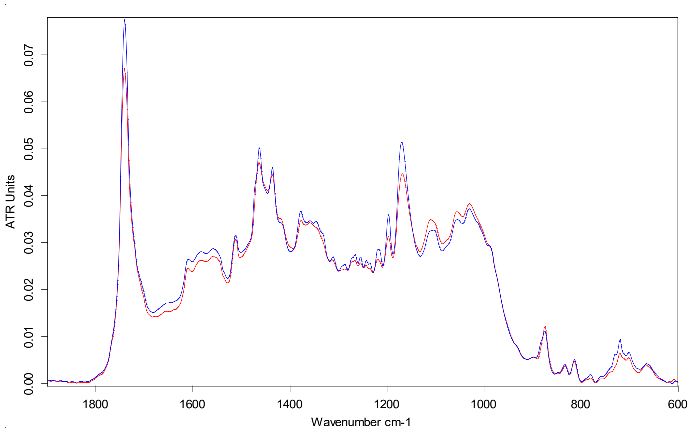
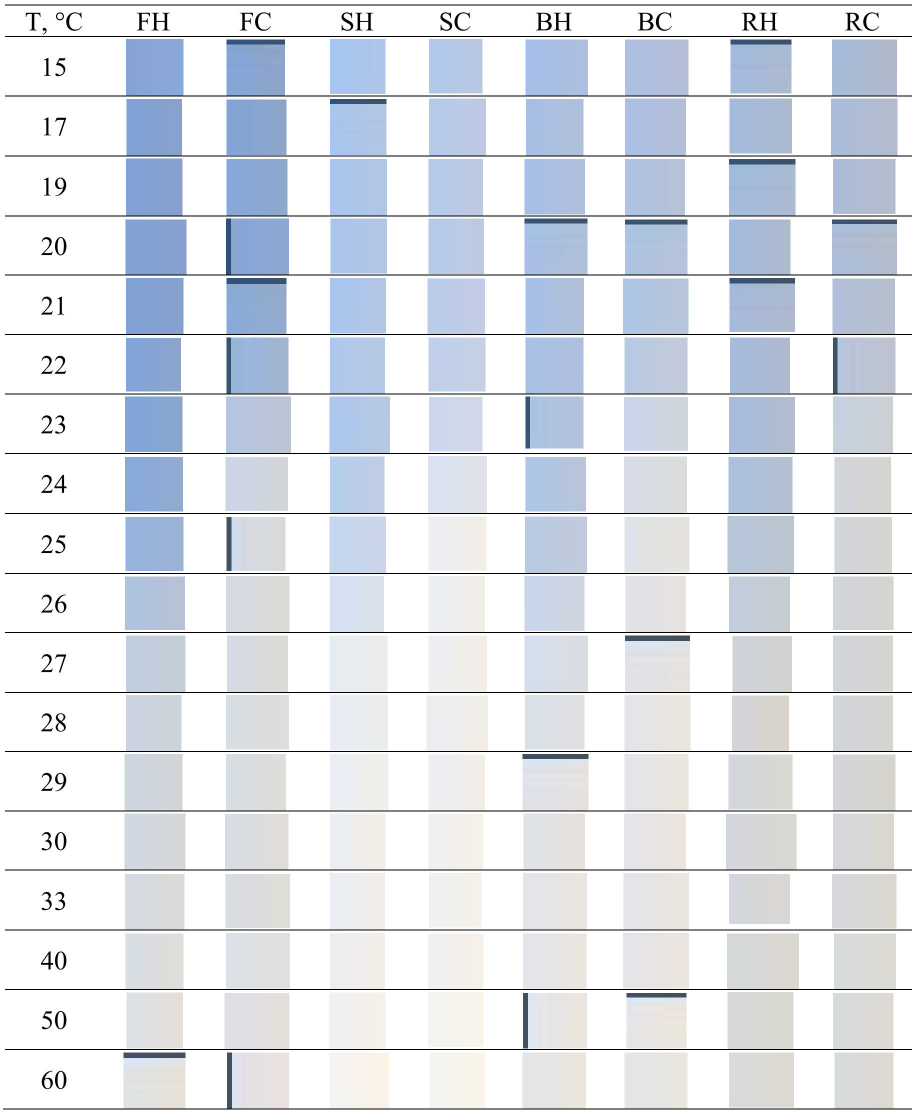


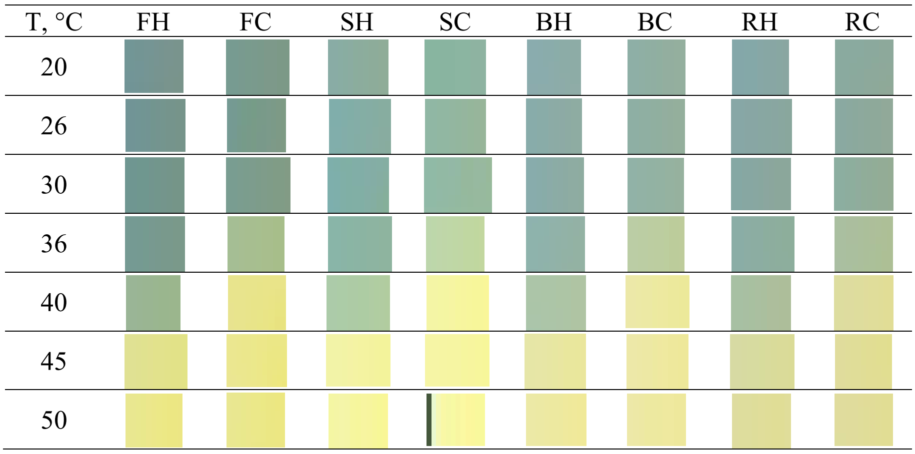
Figure 1: ATR spectra of blue ink samples (Chameleon) at 23 °C (blue line) and heated at 30 °C (red line)

Table 1
Photographs of blue prints on the tested papers depending on heating and cooling temperatures



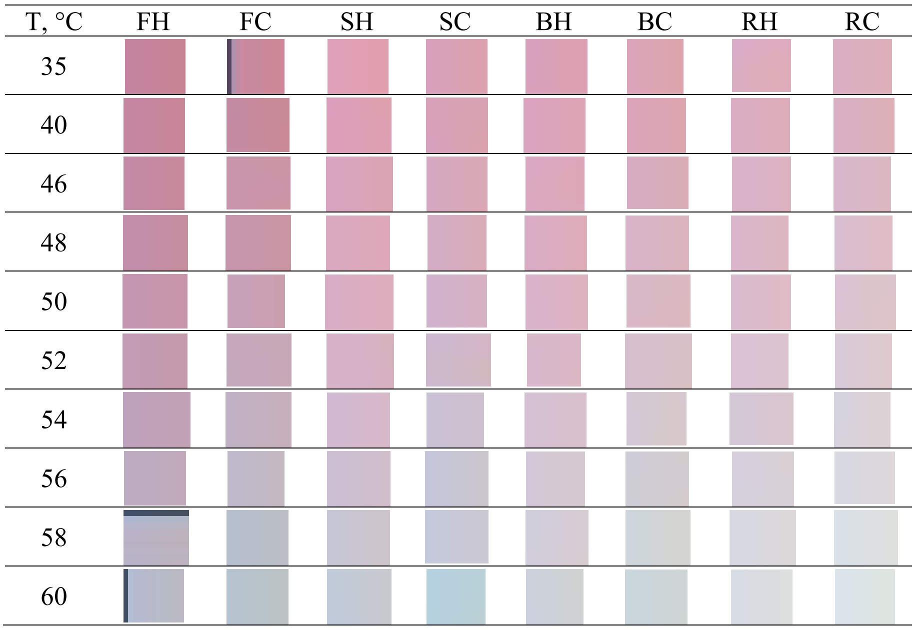
T, °C	FH	FC	SH	SC	BH	BC	RH	RC
15								
17								
19								
20								
21								
22								
23								
24								
25								
26								
27								
28								
29								
30								
33								
40								
50								
60								

Table 2
Photographs of green prints on the tested papers depending on heating and cooling temperatures



T, °C	FH	FC	SH	SC	BH	BC	RH	RC
20								
26								
30								
36								
40								
45								
50								

Table 3
Photographs of burgundy prints on the tested papers depending on heating and cooling temperatures



T, °C	FH	FC	SH	SC	BH	BC	RH	RC
35								
40								
46								
48								
50								
52								
54								
56								
58								
60								

Along the b^* axis, the movement $+b^*$ represents a shift towards yellow, and $-b^*$ – towards blue. The L^* coordinate of *CIELab* represents the brightness of the color ($L^* = 0$ gives black, and $L^* = 100$ indicates diffuse white).

L^* values of prints as a function of temperature in the heating–cooling cycle are shown in Figure 2.

On all the prints, the cooling curves (open symbols) are shifted to the left, which means that the prints at the same temperature are lighter in the cooling process than in the heating process. It is obvious that by cooling the prints at the same temperatures, fewer dye–developer complexes are formed, because the excess solvent in the liquid aggregate state prevents the interaction of the dye and the developer and the formation of a colored complex.

Figure 3 shows the change in the b^* value of the blue (a) and green (b) prints, and the change in the a^* value of the burgundy prints (c) in one heating–cooling cycle depending on the temperature and paper substrate. Blue offset ink consists of blue colored microcapsules at lower temperatures. Under the influence of elevated temperature, blue prints change color to colorless (b^* tends to zero). The more negative the b^* value of the prints at lower temperatures, the greater the shift towards blue in the *CIELab* space, which means that the concentration of microcapsules in the print is higher. At the lowest temperature, the most negative *b** value of the print is on pure cellulose paper (filter), followed by synthetic paper. The least negative *b** value was obtained for the print on recycled paper. It can be assumed that the blue microcapsules have the highest concentration on the surface of the filter paper.

Green ink consists of microcapsules colored blue at lower temperatures and classic yellow pigments. Blue colored microcapsules and yellow pigments give green color. By raising the temperature, the blue colored dye–developer complex becomes colorless and the yellow color of the pigment remains (*b** coordinate becomes positive). This phenomenon of color transition from green to yellow according to Figure 3 occurs in a temperature interval from 32 °C to 45 °C.

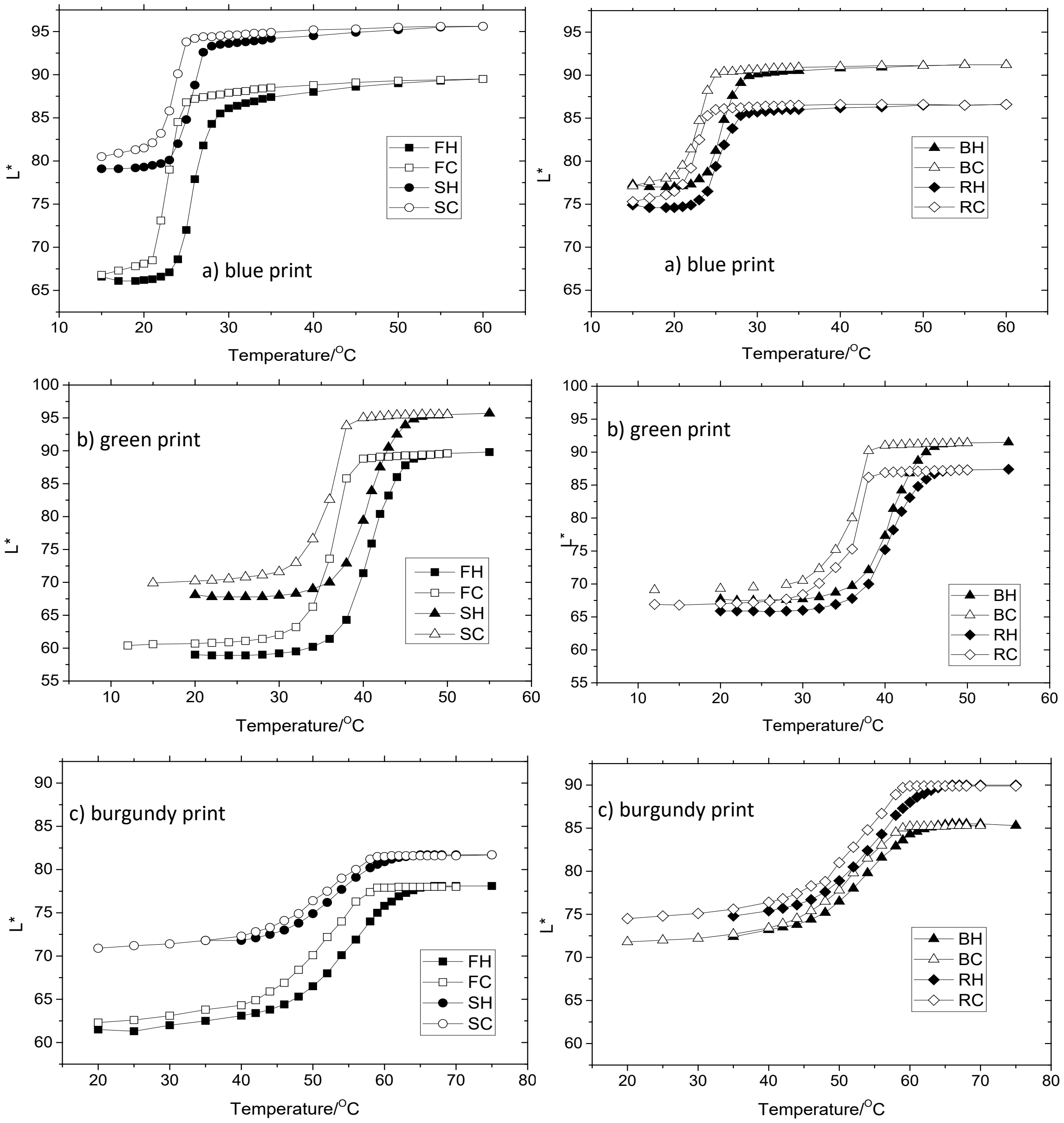


Figure 2: *L** values in heating and cooling cycles of blue (a), green (b) and burgundy (c) prints; F – neat cellulose (filter paper), S – synthetic paper, B – bulky paper, R – recycled paper; H – heating, C –cooling

Since burgundy offset ink consists of red microcapsules (at lower temperatures), the *a** coordinate of *CIELab* was taken as a measure of microcapsule concentration. In addition to microcapsules colored red at lower temperatures, the burgundy ink also consists of classic blue offset pigments. Blue-colored classic offset pigments and red-colored microcapsules give a burgundy color at lower temperatures. When heated, the red color of the microcapsules is lost (a^* coordinate decreases), and the blue color of the classic pigment remains. The biggest changes in a^* colorimetric values of burgundy prints were obtained in the temperature interval from 40 °C to 60 °C. Concentrations of microcapsules on paper surfaces follow the trend of concentrations of blue dye–developer complex in blue prints. At the lowest temperature, the a^* value of prints is the most positive on pure cellulose paper (filter), followed by synthetic, bulky and recycled paper.

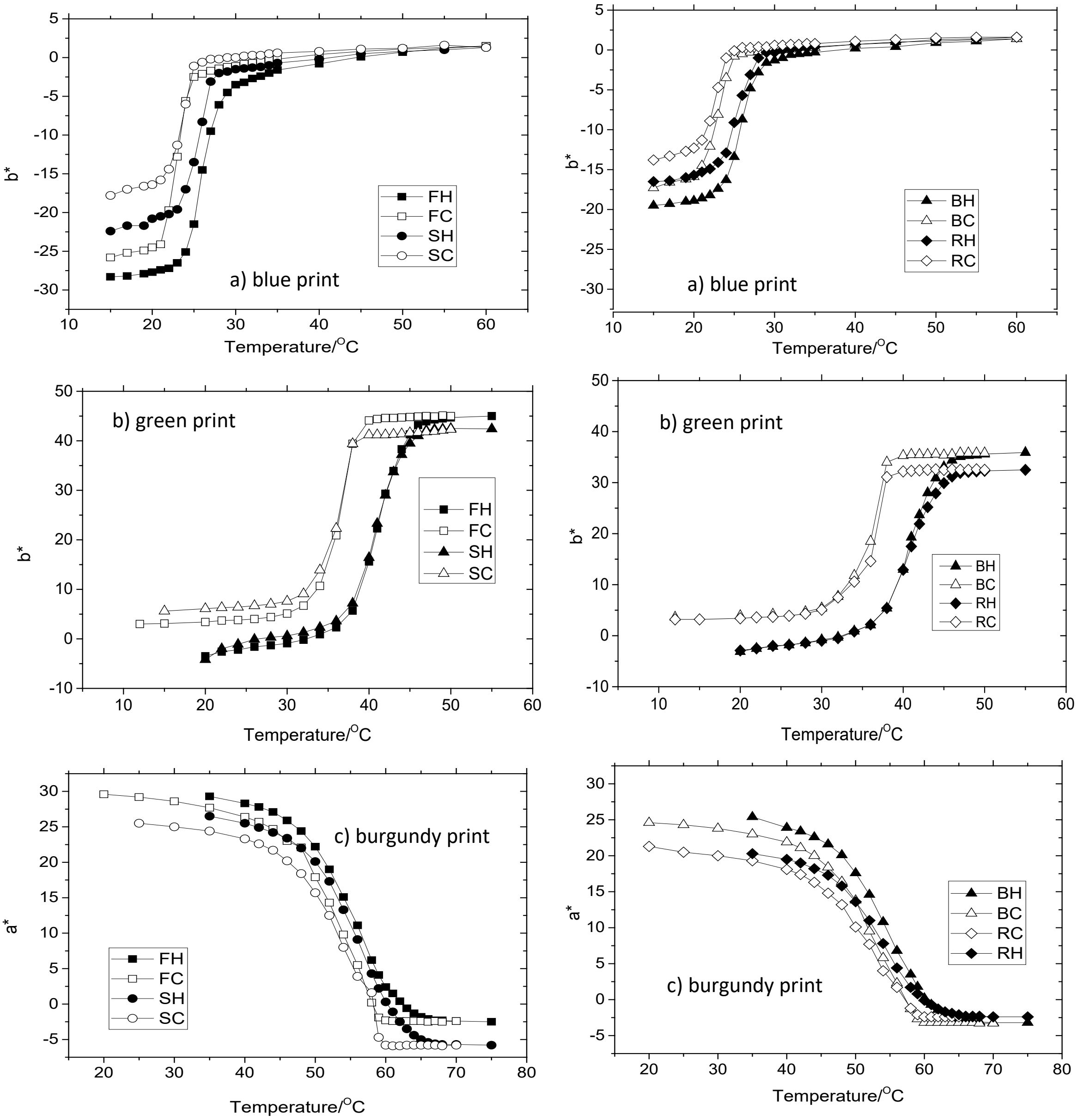


Figure 3: b^* values in heating and cooling cycle of blue (a) and green (b) prints and a^* values in heating and cooling of burgundy prints (c); F – neat cellulose (filter paper), S – synthetic paper, B – bulky paper, R – recycled paper; H – heating, C –cooling

All the cooling curves in Figure 3 are shifted to the left due to solvent hysteresis. It is interesting that in the case of green colored prints, the b^* values of the prints on all paper substrates, at the lowest temperatures, are approximately the same (black colored symbols, Fig. 3b). This would mean that unlike the previous two inks, where the concentration of microcapsules depended on the physicochemical properties of the paper substrates, by printing the tested green ink, the concentration of microcapsules does not depend on the physicochemical properties of the paper substrates. The concentrations of blue-colored microcapsules on all paper substrates before heating are almost equal.

By heating the green prints, the *b** values take on large positive values due to the resulting yellow color. However, from the final different *b** values of the prints (after heating), it can be concluded that the concentration of the classic yellow pigment is not equal on the surfaces of all papers.

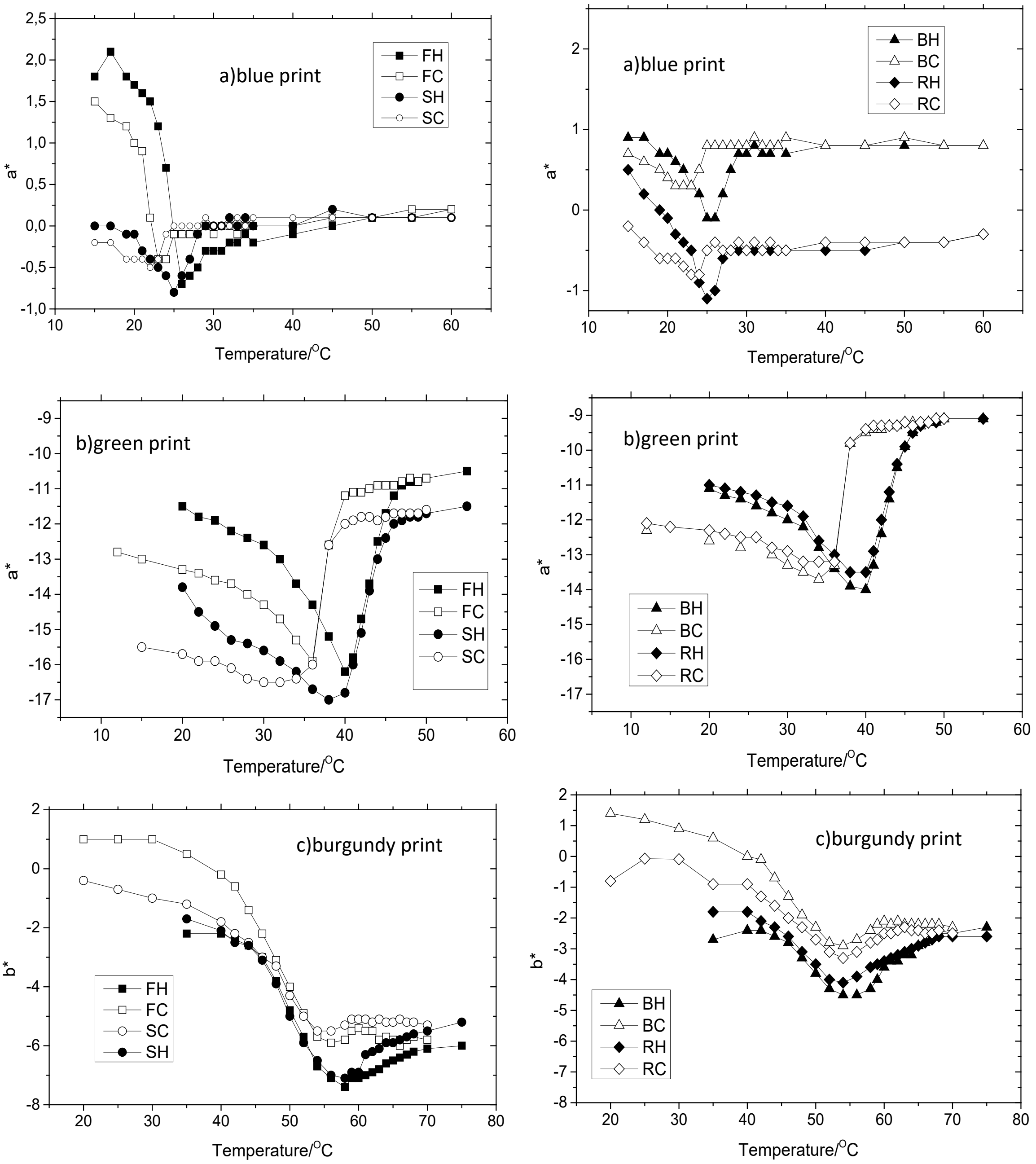


Figure 4: *a** values in heating and cooling of blue (a) and green (b) prints and *b** values in heating and cooling cycle of burgundy prints (c); F – neat cellulose (filter paper), S – synthetic paper, B – bulky paper, R – recycled paper; H – heating, C –cooling

Based on the size of the *b** value, the concentration of the classic yellow pigment is highest on the surface of filter paper (the most positive *b** values), then on the surface of synthetic paper, and then on the surface of bulky paper. The lowest concentration of yellow pigment is on the surface of recycled paper (least positive *b** values). Since the concentration of the yellow pigment is different from paper to paper, and the concentration of the blue-colored complex does not depend on the type of paper, this means that the yellow pigment is first sorbed on the surface of the paper, and then the microcapsules are sorbed on the pigment surface.

Figure 4 shows the dependence of *a** values of blue and green prints and *b** values of burgundy prints. Since the color in the *CIELab* space is determined by the value of all coordinates (*L**, *a**, *b**), the displayed values reflect the overall change in the color of the prints and cannot be said to refer to a specific ink component. As in the previously considered colorimetric values (Figs. 2 and 3), it can also be seen here that the colorimetric cooling curves are shifted to the left in relation to the heating curves.

A previous study[8] presents some physical and chemical properties of the used papers. Filter paper is pure cellulose that contains many hydroxyl groups and is therefore polar from this point of view. Synthetic paper consists of polypropylene and calcium carbonate. The mass concentration of calcium carbonate in synthetic paper is 44.5 wt%. The bulky paper contains a high percentage of calcium carbonate filler (33.9 wt%). In addition to calcium carbonate, bulky paper contains cellulose as a basic component. The high content of calcium carbonate in bulky paper is probably due to the fact that the bulky paper is made of mechanical cellulose, which has a lower whiteness compared to papers made from chemical cellulose. Calcium carbonate increases the whiteness of the paper, which is reduced due to the low content of lignin. Recycled paper is the surface sizing and therefore has a smaller number and diameter of pores (lowest porosity). The addition of sizing agents reduces the absorbency and porosity of the paper and the free surface energy.

If we consider the polar functional groups of microcapsules and paper substrates, then we can assume that the strongest attractive force is between the polar groups of microcapsules and the hydroxyl groups of cellulose (hydrogen interactions) and between the polar groups of microcapsules and ionic fillers (ion-dipole interactions). The highest concentrations of blue and red microcapsules can be assumed on the surface of pure cellulose, and then on the surface of synthetic paper.

On the surface of bulky paper, hydrogen interactions of cellulose fibers with the surfaces of microcapsules and ion-dipole interactions with calcium carbonate are possible. However, according to the chemical composition, bulky paper could have a higher amount of blue colored microcapsules at least compared to synthetic paper. Synthetic and bulky paper types have similar proportions of calcium carbonate, but bulky paper contains cellulose as a basic component in addition to calcium carbonate. This does not mean that there was no adsorption of microcapsules on its surface, but during offset printing, considerable damage occurs to the microcapsules (Figs. 5, 6). The SEM image (Fig. 6) shows that the microcapsules are significantly flattened after printing on bulky paper.

Bulky paper has a voluminous, compressible structure that causes significant paper compaction during offset printing.[9] Compressibility refers to the extent to which the thickness of the paper is reduced due to pressure applied perpendicularly to the surface of the sheet. The compressibility of paper depends on its hardness, density and properties of mineral fillers and fiber flexibility. Bulky paper is usually highly porous and can absorb the ink pigment along with the carrier. The high compressibility of the used bulky paper is the reason for the significant damage of the microcapsules on its surface and their flattening. It can be assumed that paper compression changes the physical properties of the paper, such as the pore diameter, the strength of the adhesive/substrate interaction. The microcapsules can be drawn into the pores and compressed together with the paper. In this case, when the microcapsules have completely flattened (Fig. 6), they become inactive (they no longer have the ability to have competitive interactions between dyes, developers and solvents). Such compression reduces the colorimetric values of prints. Ion-dipole forces are stronger than hydrogen interactions because the ion charge is greater than the dipole charge.[10] Since ion-dipole bonds are stronger than hydrogen bonds, the ions and the oppositely charged ends of the dipoles of the polar groups of microcapsules are much closer in the ion-dipole bond than in the hydrogen bond. It can be assumed that microcapsules that are bound to cellulose, due to weaker attractive forces with cellulose, are located predominantly on the surface of the paper compared to microcapsules that are bound to calcium carbonate by stronger ion-dipole forces. Because of this, they deform more easily and quickly during offset printing.

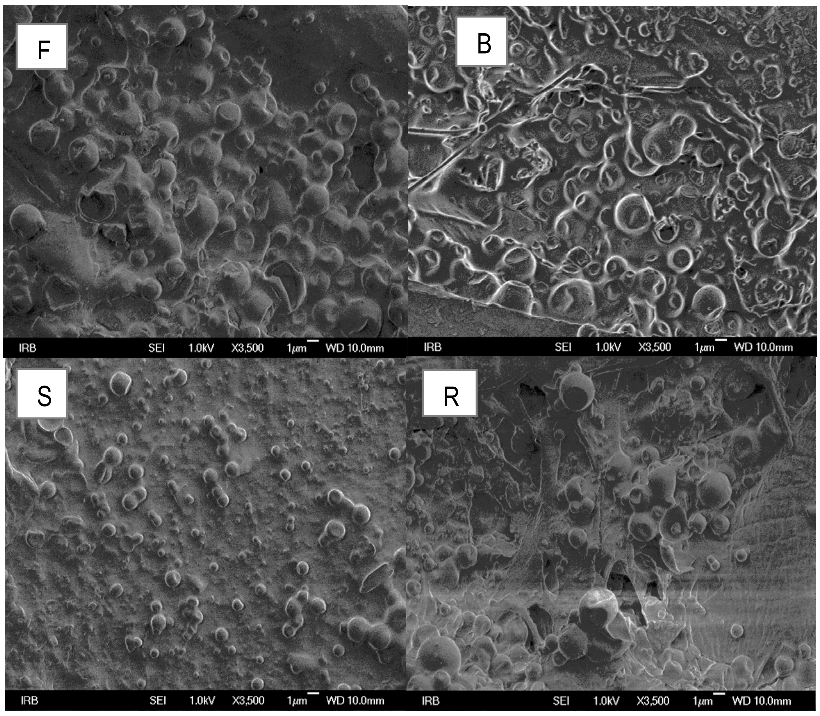


Figure 5: SEM micrographs of blue prints; F – filter paper, S – synthetic paper, B – bulky paper, R – recycled paper; Magnification 3500x

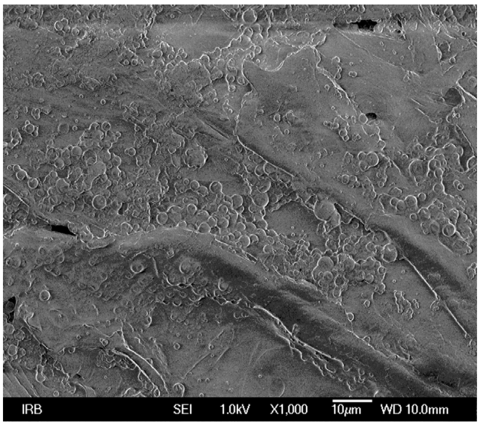


Figure 6 SEM micrograph of blue prints on bulky paper; Magnification 1000x

Microcapsules attached to inorganic fillers are not damaged during printing. This is the reason why the microcapsules on the surface of the synthetic paper are not damaged during the ink printing on its surface (Fig. 5). Damage to the microcapsules is also visible on the surface of the filter paper (Fig. 5). Filter paper is not compressible like bulky paper, so the microcapsules are much less damaged.

It is also evident that the microcapsules are unevenly distributed over the surface of the synthetic paper. They are adsorbed only in areas rich in calcium carbonate. Polypropylene-rich sites interact with the binder.

CONCLUSION

The present work was based on examining the process of reversibility of thermochromic offset prints on four types of paper under the influence of temperature. There are deviations in the colorimetric values of the prints after the cooling cycle is completed. The observed differences can be attributed to the hysteresis of the solvent contained in the microcapsules and/or diffused through the microcapsules.

Due to solvent hysteresis, the colorimetric curves are shifted to the left. The melting and solidification temperatures of the solvent in any ink are not exactly determinable, but the melting and solidification of the solvent occurs in a certain temperature interval.

On certain types of paper during offset printing, the microcapsules can be deformed to such an extent that they, *i.e.* the mixtures inside them, become completely inactive in terms of color development.

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