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Dynamic Colour Possibilities and Functional Properties of Thermochromic Printing Inks

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Abstract:

Thermochromic printing inks change their colour regarding the change in temperature and they are one of the major groups of colour-changing inks. One of the most frequently used thermochromic material in printing inks are leuco dyes. The colour of thermochromic prints is dynamic, it is not just temperature-dependent, but it also depends on thermal history. The effect is described by colour hysteresis. This paper aims at discussing general aspects of thermochromic inks, dynamic colorimetric properties of leuco dye-based thermochromic inks, their stability and principle of variable-temperature colour measurement. Thermochromic material is protected in round-shaped capsules. They are much larger than pigments in conventional inks. The polymer envelopes of pigment capsules are more stable against oxidation than the binder. If these envelopes are damaged, the dynamic colour is irreversibly lost. Our aim is to analyse the colorimetric properties of several reversible screen-printed UV-curing leuco dye thermochromic inks with different activation temperatures printed on paper. A small analysis of irreversible thermochromic inks will be presented for comparison with reversible thermochromic inks. Moreover, so as to show interesting possibilities, a combination of different inks was made, an irreversible thermochromic ink was printed on top of the red and blue reversible thermochromic inks. Special attention was given to the characterization of colour hysteresis and the meaning of activation temperature.

Keywords:

Thermochromic Inks, Colour Hysteresis, Pigment Capsules, Variable-Temperature Colour Measurement

1. Introduction

Inks that change their colour under certain circumstances are increasingly applied in the field of security printing, brand protection, smart packaging, marketing and novelty printing. Starting with novelty items such as mood rings in 1970s, more and more applications are entering the market in which thermochromic (TC) ink become a functional part of the product. Battery testers are an example of such a product. Smart packages with an irreversible thermochromic colour change could prove the observance of the required temperature conditions during storage or transportation of sensitive goods such as heat-sensitive pharmaceuticals or frozen food *(Seeboth and Lötzsch, 2008).* Smart materials also interest artists and designers inspired by possibilities for the development of new creative design directions towards interaction, response and ultimate functionality *(Christie et all, 2007).* Colour change technology thus offers designers unique and challenging design opportunities.

The two major groups of colour-changing inks are thermochromic and photochromic, as they are presently the most easily applied colour-changing inks *(Homola, 2008).* Our work was limited to TC inks. TC inks can be manufactured as reversible or irreversible. The two types of TC inks are liquid crystals and leuco dyes. Liquid crystals are used less frequently than leuco dyes because they are very difficult to work with and require highly specialized printing and handling techniques. They are more sensitive to temperature change than leuco dyes, meaning they are used in delicate experiments where small temperature change has to be noted. The relatively complex chemistry of leuco dye-based TC inks is relatively well-known in literature *(Seeboth and Lötzsch, 2008)*. However, any advanced application of such inks requires a careful colorimetric characterization *(Johansson, 2006).* The temperature-dependent properties of the complex TC system, the degree of its reversibility and stability are very important. Temperature-dependent optical properties of several commercially available TC inks were thoroughly analyzed *(Kulčar et all, 2010).*

2. Thermochromic composites

The functional part of a TC printing ink is in most cases a composite with at least three components: colour former, colour developer and solvent *(Seeboth and Lötzsch, 2008).* Its colour changes via two competing reactions, one between dye and developer and the other between solvent and developer (see Figure 1). The first reaction prevails at low temperatures where the solvent is in solid form, therefore dye-developer reaction prevails which gives rise to formation of dye-developer complexes. In most cases, these complexes are coloured. When at a higher temperature the solvent melts, the solvent-developer interaction becomes dominating; thus, dye-developer complexes are destroyed and the system converts into its colourless state. Leuco dyes could be spirolactones, fluoranes or spiropiranes *(Burkinshaw et al, 1998);* the most research has been published on crystal violet lactone *(Maclaren and White, 2003)*, *(Burkinshaw et al, 1998), (Maclaren and White, 2005).* Typical developers are bisphenol A, gallates, phenols, hydroxybenzoates and hydroxycoumarin *(Seeboth and Lötzsch, 2008), (Seeboth et all, 2007).* Long chain alkyl alcohols, esters, ketones or ethers are applied as solvents *(Maclaren and White, 2003).* They initiate the TC effect by melting and control the decolouration process *(Maclaren and White, 2003).* The polymer envelopes of the microcapsules are mostly made from epoxy or melamine resins *(Small and Highberger, 1999).* The temperature at which discoloration/coloration occurs is controlled by the melting temperature of the applied solvent. Several definitions of this temperature are mentioned in literature, such as switching *(Seeboth et all, 2007)*, discoloration *(Maclaren and White, 2003)* or activation temperature (*Johansson, 2006).* In this paper we use the term activation temperature (T_A).

Complex chemistry of a TC composite enables the preparation of TC inks with unique dynamic colour which can be easily recognized by naked eye. The difficulty to imitate or reproduce the exact colour change makes TC inks good candidates for anti-counterfeit applications.

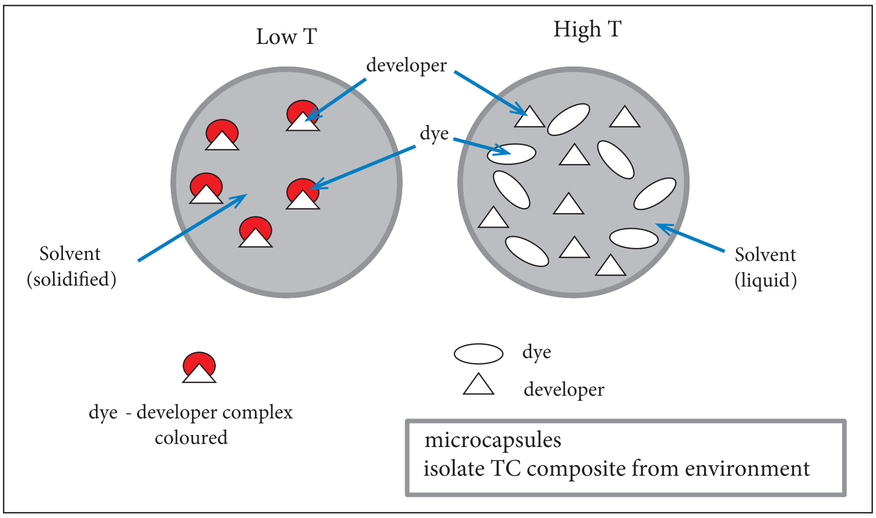

Figure 1. Schematic representation of leuco dye-developer solvent composite system

3. Thermochromic pigments and thermochromic inks

Application possibilities of leuco dye-based TC composite material are markedly enabled by microencapsulation that protects the system from reactions with their surroundings. Each microcapsule, the so-called TC pigment, contains the entire system required to reproduce the dynamic colour.

The microencapsulation process provides spherical capsules with size distribution of up to 20 μm. The actual size of TC pigments capsules is determined by the process of emulsification of TC composite, followed by interface polymerization. A melamine or epoxy resin is used in interface polymerization to form polymer envelope. The envelope should be chemically and thermally stable, it must have suitable elasticity and perfect transparency for visible light.

SEM micrograph of a TC pigment powder is shown in Figure 2. It shows microcapsules with broad particle size distribution.

The typical size of TC pigment is more than 10 times greater than that of conventional pigment particles usually applied in printing inks.

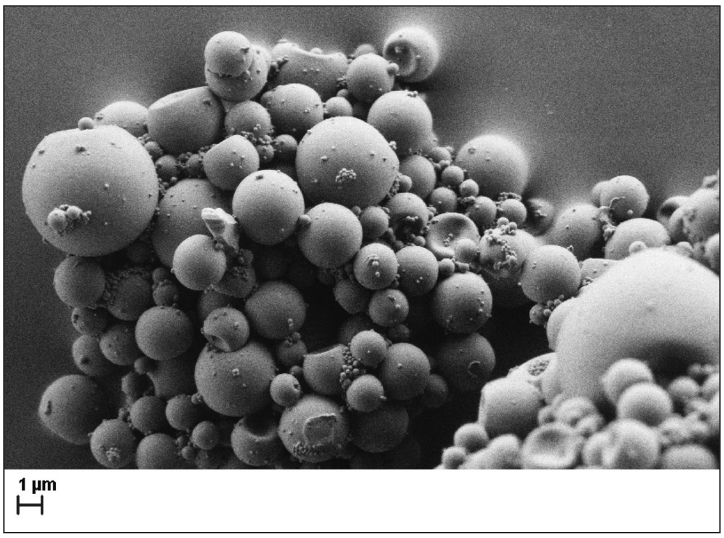

Figure 2. SEM micrograph of a microencapsulated thermochromic composite

Such a size displays some drawbacks – the capsules must withstand all standard mixing and application procedures. Typically, smaller capsules are used for offset inks and larger for screen printing. Smaller capsules have better mechanical properties than larger ones and can pass larger shearing forces.

Leuco dye-based TC inks of various T_A are commercially available, from -15 °C up to 65 °C. However, most current applications are limited to three standard temperature ranges, cold (~ 10 °C), body-heat activated (~ 31 °C) and warm (~ 43 °C). Cold region is applied for checking the freshness of drinks, i.e. whether it is appropriately cooled. Body-activated region can serve to cover some information by a layer that could become transparent by the heat of the body. Warm region is applied to indicate the customers if the food is too hot to be eaten.

TC printing inks of all basic types are available; water-based and photocuring inks for printing on paper, plastics and textile. As a rule, most producers currently provide approximate colour shade of ink in its coloured form, recommend appropriate printing and drying conditions; however, the T_A is the only dynamic colour data provided. The discoloration/coloration reactions are regarded to be reversible and it is believed that the process can be repeated several thousand times *(Homola, 2008)*.

Post-print functionality can be adversely affected by UV light, temperature in excess of 140 °C and aggressive solvents. The lifespan of these inks is normally very limited because of the degradation caused by exposure to the UV light. However, some manufacturers nowadays offer a range of UV protected TC inks with a longer lifespan. In addition to reversible TC inks, there are irreversible TC inks that are invisible until exposed to a high temperature, when an intense colour develops. Once the colour has appeared, it will not disappear. Or they change from one colour to another leaving a permanent indication about temperature change. Typically the colour of the ink starts to develop at 65 °C and is fully developed at 90 °C although higher temperature inks give a stronger and more stable colour change *(Williams, 2003)*. Classic applications for this are indicators that a medical package has been properly sterilized.

4. Experimental part

We tested six commercially available TC inks. Some of them were free samples, whereas the others were provided by the suppliers. In this paper we will present a short overview of five reversible and one irreversible TC ink. Two reversible inks were a product of Coates Screen Inks GmbH, Germany (red TCX R-31 and blue TCX B-31) and three of Sicpa, Switzerland (SicpaRed-33, SicpaGreen-33 and SicpaBlue-45). These inks reversibly change their colours under a temperature change. In its cold state the ink exhibits colour and when temperature increases, it turns transparent. Irreversible TC ink is water-based "Thermoprint" colour-change ink (Siltech LTD, England) that changes colour irreversibly when threshold temperature is exceeded. This ink is changing from yellow-to-red, and it starts to develop at65 °C. The inks were screen printed over gloss coated paper (150 g/m²) by the universal screen printed machine for flatprinting SD 05 (RokuPrint Germany) applying SEFAR® PET 1500 high-modulus monofilament polyester mesh 120/34Y. Printed samples were cured applying UV dryer Aktiprint L (Technigraf, Germany) by UV energy of approximately 0,83 W/cm² at 8 m/min speed of conveyor belt, where the curing energy on sample surface is approximately 400 mJ/cm² as measured by the UV integrator (Technigraf, Germany). The thickness of dry layers was measured by the profilometer Talysurf (Rank Taylor Hobson Series 2).

Spectral reflectance of samples was measured by means of the Lambda 950 UV-VIS-NIR spectrophotometer (Perkin-Elmer), employing a 150 mm integrating sphere under (8:di) measuring geometry (diffuse geometry, specular component included). Sample temperature was changed by heating/cooling on the Full Cover water block (EK Water Blocks, EKWB d.o.o, Slovenia), a system which was originally designed for cooling CPU's and graphic cards of power demanding computers. The base plate is made of perfectly flat electrolytic copper. Suitable liquid (water or mixture of water and ethylene glycol) accelerates through very thin channels inside the plate whose temperature was varied by thermostatic circulator. It allows accurate adjustment of circulating liquid temperature of the sample on copper plate surface up to the tenth of degree.

The reflectance spectra were measured in different heating/cooling cycles, depending on the temperature region needed to describe the entire TC colour change of selected sample. In each cycle the sample was heated from the lowest to the highest temperature and then cooled back to the lowest one. Reflectance spectra were measured in suitable temperature intervals, narrower in rapid-changing regions and coarser outside. Heating/cooling rate was about 0,5 °C/min. This is slow enough for all measured TC samples to be thermally-balanced with the copper plate and able to follow the change. For irreversible ink the reflectance spectra were measured from 35 °C to 85 °C, where between 60 °C and 75 °C the reflectance spectra were measured in 1 °C intervals and 5 °C elsewhere. Moreover, the combination of inks was made with irreversible TC ink printed on top of the TCX R-31 and TCX B-31 reversible TC inks. Colorimetric parameters were calculated from the reflectance data using CIELAB colour space, under D50 illumination and 2° standard observer. Colour differences were calculated using the CIEDE2000 total colour difference formula.

The stability of TC pigment capsules inside dry samples was analyzed applying weakly ionized highly dissociated oxygen plasma. It was created in a Pyrex tube glass with an inductively coupled RF generator at a frequency of 27.12 Hz and an output of 200W. The oxygen pressure was 75 Pa. Activated gaseous particles in oxygen plasma gave rise to selective etching of surface species having different oxidation probability. This method is frequently used to detect distribution and orientation of particles in polymer matrix *(Kunaver et all, 2003), (Klanjšek Gunde et all, 2005).* It was proved that polymer binder and TC pigments have different etching properties in the oxygen plasma. The removal of the highest layers of polymer binder in UV-cured TC printing inks was executed in a couple of minutes. This way the top-laying TC pigment particles become visible on scanning electron micrographs. The Karl Zeiss Supra 35 field emission scanning electron microscope (SEM) was used for taking these pictures.

5. Results and discussion

5.1 Colorimetric properties

TC samples lose their colour during heating and regain it during cooling. Both processes are continuous without any abrupt change. This could be described by a path (a colour trajectory) in the CIELAB colour space (see Figure 3). Our measurements show that the trajectory obtained by heating is not completely equal to that obtained by cooling. When trajectories are identical, the area of the surface defined by the two trajectories is zero. However, in practice it was never obtained. Therefore, a parameter called *Area* was introduced, which measures the area of the curved surface between both colour trajectories. Larger *Area* shows bigger differences between colours appearing on the sample when it is heated compared to those when it is cooled.

Discoloration of analyzed TC samples is not complete. At the highest temperature applied in our experiment all samples retain a yellow shade which differs from the uncoated paper. The effect was evaluated by the *Yellowness*, the total colour difference between TC sample in the completely discoloured state and the bare paper. It could be a result of several effects, the incomplete transparency of the TC composite inside capsules at high temperature, the scattering of light on capsule's polymer envelopes, and of the blue-light absorption in the binder.

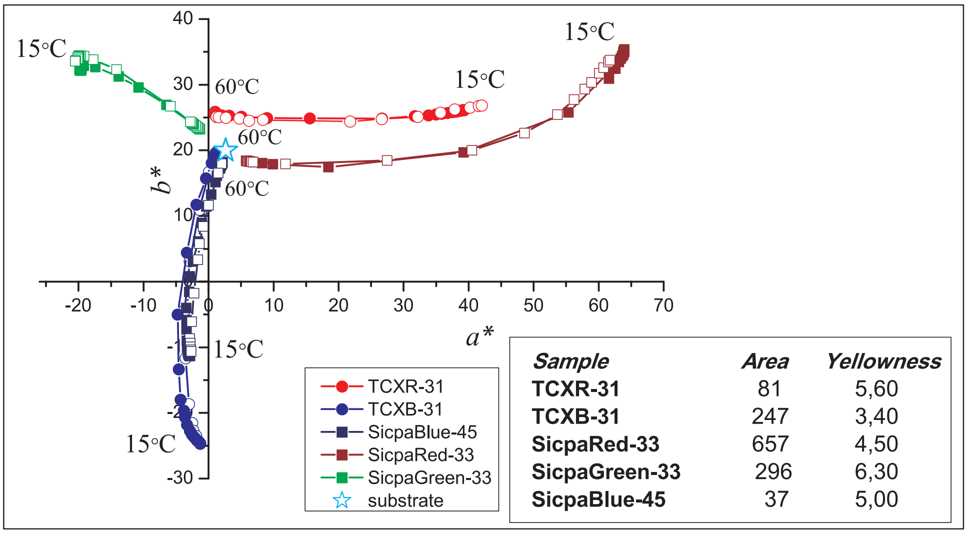

Figure 3. Colour trajectories in the (a,b*) plane of CIELAB colour space as obtained for five TC samples at heating (full signs) and cooling (open signs). The value of the applied bare paper substrate (OBA free gloss coated paper, 150 g/m²) is marked with a star. The area of the surface between two trajectories in the CIELAB colour space is shown in the key (Area) (quadratic CIELAB units). The degree of discoloration (Yellowness) is also specified (in CIELAB units).*

On the contrary, irreversible TC inks change from one colour to another leaving a permanent indication of a temperature change. In Figure 4. it is evident that irreversible yellow ink, after being exposed to high temperature, changed from orange to red without returning to the original colour.

Colour values of a reversible TC sample should also be shown as a function of temperature. In such a presentation, the entire $L^*(T)$ curve has a form of a loop (see Figure 5). The discoloration process is almost finished when the temperature reaches T_A and all colour values remain approximately the same with further increasing of temperature. The reverse process occurs during cooling but it requires lower temperatures. Because of that, the colour of a TC sample does not depend only on temperature, but also on its thermal history, i.e. whether the particular colour was reached during heating or during cooling. The colour of such a sample cannot be characterized only by temperature. It shows that TC systems have a sort of memory – their output is not possible to predict without knowing the path which was followed before the current state was reached. Such a phenomenon is called hysteresis. TC materials belong to several physical systems with hysteresis.

Temperature-dependent curves obtained during heating and cooling can vary significantly in their symmetry and steepness. If they are far apart, the hysteresis loop is wide, but if they are close together, the loop is narrow. The T_A lies somewhere within this loop but its position does not reveal any of its characteristic properties *(Kulčar, 2010), (Klanjšek Gunde et all, 2011).*

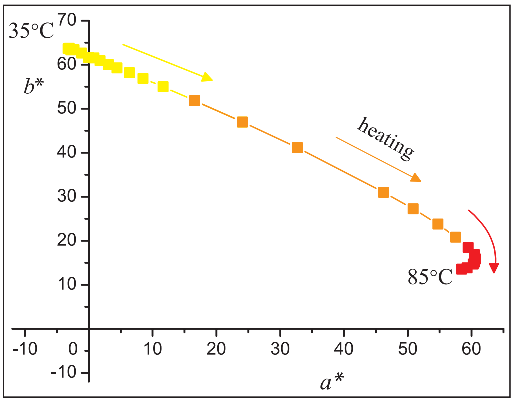

Figure 4. Changing of CIELAB values of irreversible Yellow-to-red TC sample in (a,b*) plane at heating.*

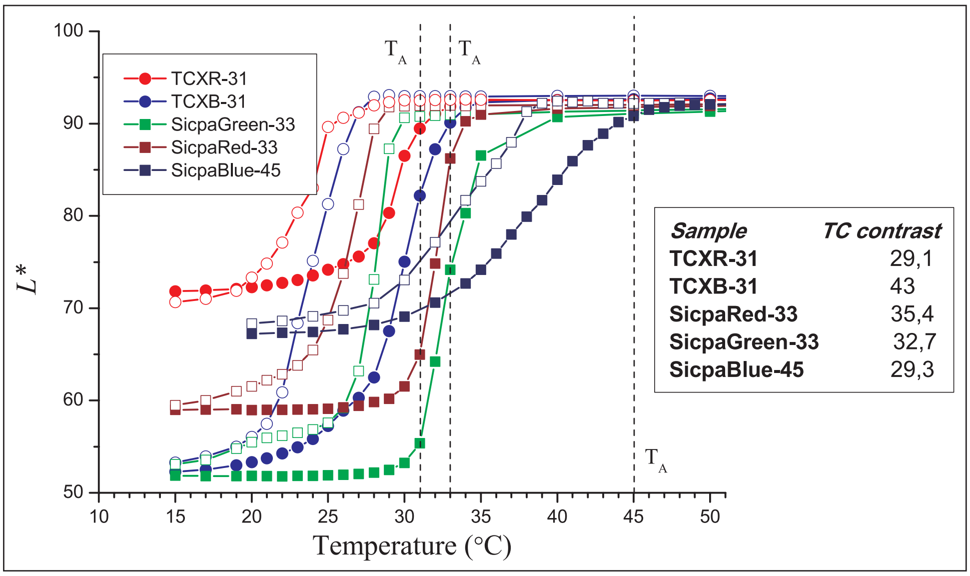

Figure 5. Colour hysteresis of TC samples. CIELAB colour values as a function of temperature for five TC samples: TCXR-31, TCXB-31, SicpaRed-33, SicpaGreen-33 and SicpaBlue-45 at heating (full signs) and cooling (open signs). Samples with similar layer thickness were evaluated. Efficiency of colour change is expressed by TC contrast, the total colour difference between totally coloured and discoloured states and is given in the key (in CIELAB units).

An important parameter of a TC sample is efficiency of colour change that it provides. We expressed this property as the colour difference between completely coloured and discoloured states and called it *TC contrast*. Larger *TC contrast* gives better ability to recognize colour change. The values for some samples are given in Figure 5.

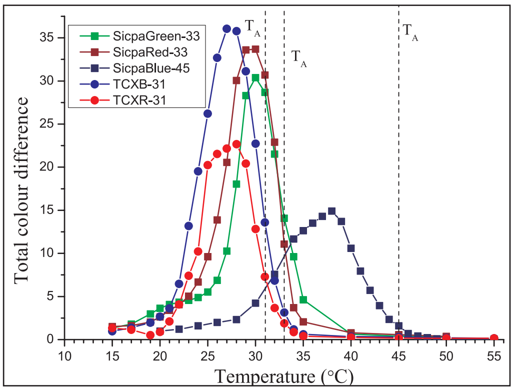

Figure 6. Total colour difference between heated and cooled states of the same TC sample as a function of temperature, as measured for TCXR-31, TCXB-31, SicpaRed-33, SicpaGreen-33 and SicpaBlue-45.

The colour hysteresis could also be represented by colour difference between heated and cooled states of the same sample as a function of temperature, as it is illustrated on Figure 6. This function describes a single peak with a different position, intensity and width. It was found that, in general, it peaks at a temperature lower than T_A. The peak is not necessarily a symmetrical one. Its width could be applied as a measure of temperature region needed for the TC sample to accomplish the colour change.

The coloured dye-developer and colourless solvent-developer complexes are metastable and long-living *(Seeboth et all, 2006)*. Coloured complexes prevail at low temperatures and colourless at high, regardless of composite's thermal history. At average temperatures competitive dye-developer and solvent-developer reactions occur, thus causing the system to change its colour in accordance with its thermal history. The temporal stability of such a competitive mixed system is not obvious. However, it was confirmed that all states within colour hysteresis of all reversible TC samples are stable when the temperature remained constant for more than 10 h. After such a long testing period, the colour continued to change practically the same path as if there had not been any stability testing *(Kulčar et all, 2010).*

Interesting effect and spectra were obtained with combination of different inks, irreversible TC ink printed on top of the blue and red reversible TC ink (see Figure 7 and Figure 8). In such a case, printed sample is not completely irreversible because of the reversible TC ink under irreversible ink. The interesting thing with such mixing is that during heating one colour play occurs and during cooling the other one. After the first heating/cooling cycle, changes will stay the same all the way up and down. On Figure 8., open signs are showing the reversible colour path, were the change will continue. Applications with a combination of these inks can provide information on temperature changes that are occurring in their environment.

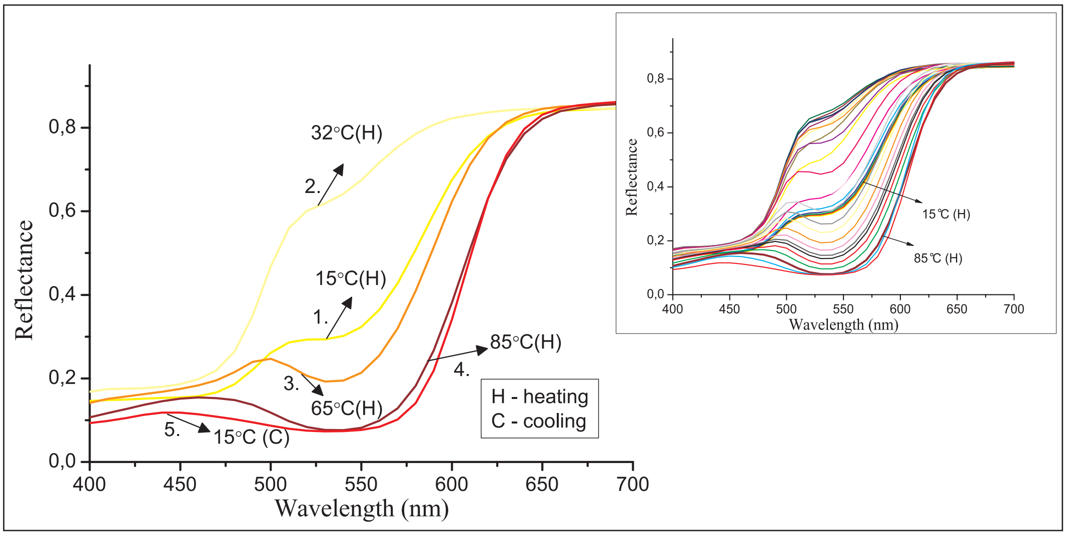

Figure 7. Reflectance spectra of irreversible TC ink printed on top of the red TC ink (H signs – temperature, in °C, reached by heating, C signs – temperature, in °C, reached by cooling).

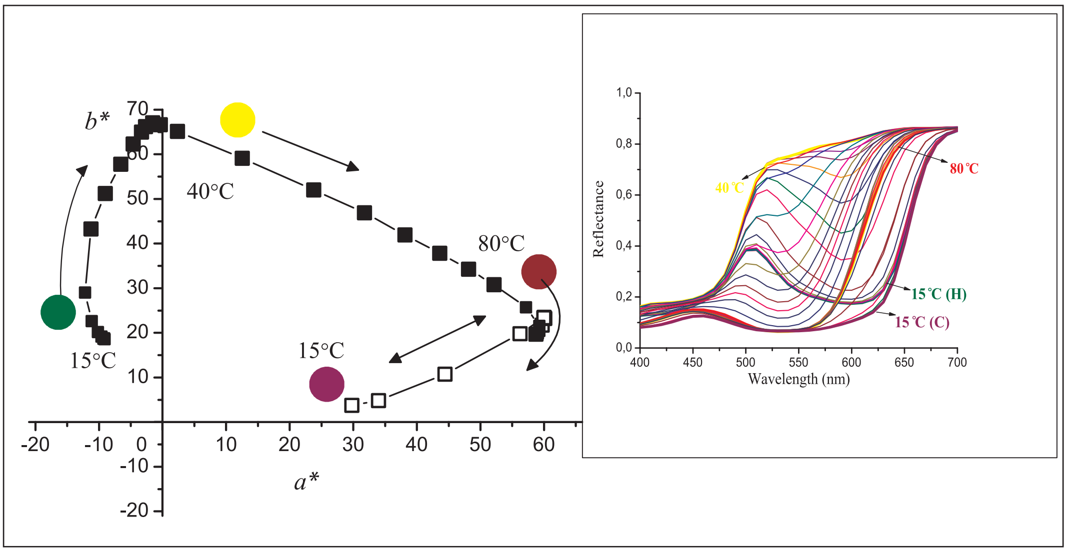

Figure 8. Changing of CIELAB values of irreversible TC ink printed on top of the blue thermochromic ink in (a,b*) plane at heating, irreversible change, (solid signs) and cooling, reversible change, (open signs). Small figure represents reflectance spectra of irreversible TC inks printed on top of the blue TC ink.*

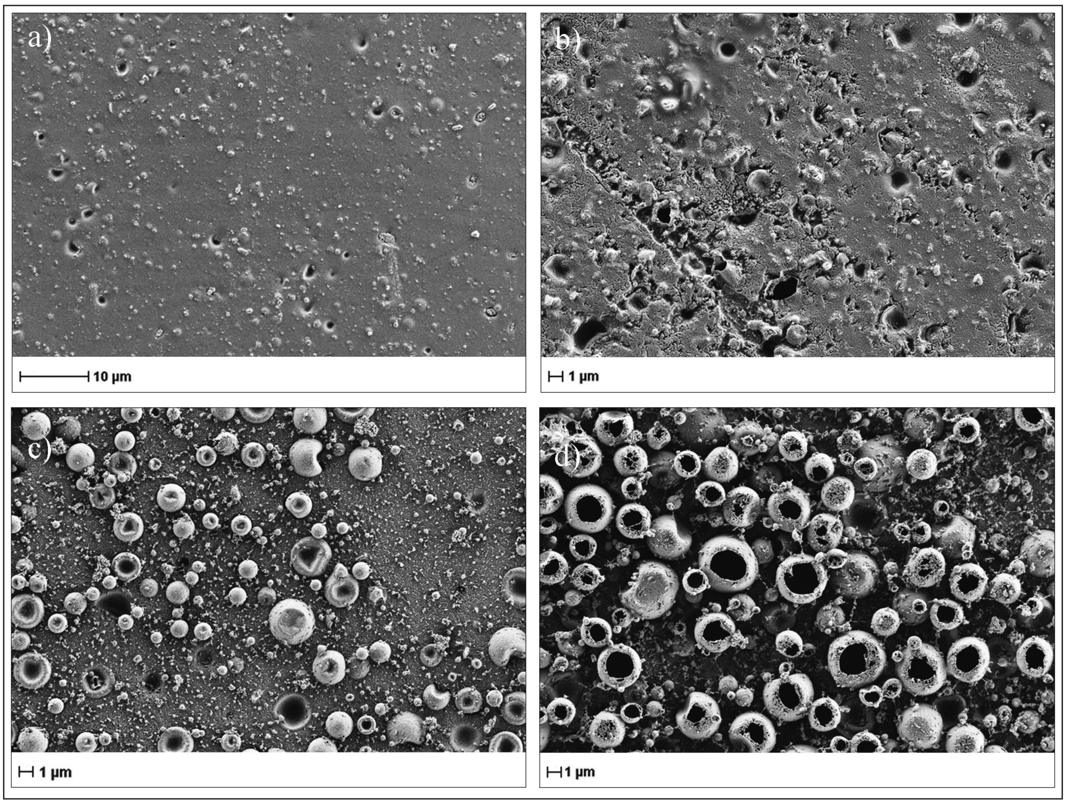

Figure 9. SEM micrograph of the TC sample SicpaGreen-33 without oxygen plasma treatment (a), after 30s exposure to oxygen plasma (b), after 60s exposure to oxygen plasma (c) and after 120s exposure to oxygen plasma (d).

5.2 Physical properties

The surface of a typical dry reversible TC sample is covered by the binder and only very few TC capsules could be seen on a SEM micrograph. In general, such capsules are obliterated by the binder so that no clear boundaries can be seen (see Figure 9a). During exposure to weakly ionized oxygen plasma, the topmost material with the lowest oxidation probability is etched away first. This can be seen in Figure 9b and Figure 9c, where the TC surface layer after 30s and 60s treatment with plasma is shown. Our experiments show that during the removal of the top layers, the upper TC capsules become visible and their envelopes do not appear to be damaged. Such a sample has a different appearance because of the lack of cover binder; however it still retains original colour shade and responds well to temperature changes. When such a sample is exposed to such oxygen plasma for a longer period, its colour is lost and temperature response continuously disappears. SEM micrograph of such a sample shows that the binder is extensively etched so that many more TC capsules are lying on its surface. Polymer envelopes of several TC capsules are destroyed and cannot protect the composite inside (see Figure 9d). The dynamic colour of such a sample is irreversibly lost. However, the described experiment confirms that polymer envelopes have higher stability against oxidation than the binder.

Conventional pigments are relatively stable against activated neutral oxygen radicals which are responsible for selective etching in weakly ionised oxygen plasma *(Mozetič, 2003), (Vesel et al., 2007).* The situation is different in systems with TC pigments: exposure time required to etch enough binder away is too long for particles polymer shells. When they are destroyed, pigment particles change simultaneously, so the method cannot be applied to evaluate the particle size distribution. However, this experiment shows that polymer envelopes are much more stable against selective etching than the binder itself, whereas the binding energy of the molecular species in the polymer protecting capsule is much larger than it is inside the binder.

Light with enough photon energy has a detrimental effect on colour and appearance over longer periods of time. Conventional printing inks usually have acceptable lightfastness, mainly because of the high stability of applied pigments. On the other hand, TC inks have sophisticated pigments which are not crystalline and therefore have a low resistance to light, high temperatures and some chemicals *(Small and Highberger, 1999), (Friškovec et all, 2010).* In many cases additional protection is applied which could help in solving these drawbacks.

6. Conclusion

The aim of this paper was to provide a short overview of colorimetric and physical properties of TC inks. Interesting effects and spectra were obtained with a combination of different inks thus demonstrating that TC inks offer lots of interesting possibilities.

The activation temperature, which serves as the only parameter given by the producer to describe the change of colour, lies somewhere in the colour loops; however, its position is arbitrary and thus does not reveal any of the characteristic properties of these temperature dependent loops. Consequently, other parameters were introduced to characterize the analyzed TC inks. *Area*, *Yellowness*, and *TC contrast* are presented here in more detail. The first parameter measures how the sample develops when heating and cooling are compared. The larger the *Area* is, the more different colours are observed. The ability of a TC sample to become discoloured was evaluated by *Yellowness*, colour difference between its totally discoloured state and the bare substrate. The *TC contrast* measures the colour difference between totally coloured and discoloured states; the larger the *TC contrast* is, the easier it will be to recognize a TC change. Applications with a combination of reversible and irreversible inks can provide information on temperature changes that occur in their environment.

The stability of inks against oxidation was analyzed by weakly ionized oxygen plasma. It was confirmed that polymer envelopes of pigment capsules are more stable than the applied binder. Such envelopes protect the TC composite from unwanted influences of the surroundings. The dynamic colour properties are irreversibly lost when the envelopes get damaged.

Researches in TC colour technology will provide knowledge necessary to accomplish the expectations in technology and creative design. It can be expected that in the next few years the commercialisation of TC inks will make a giant step forward. Step-by-step, new developments will establish new areas of commercial application.

References

Burkinshaw S.M., Griffiths J. & Towns A.D. (1998) Reversibly thermochromic systems based on pH-sensitive spirolactone –derived functional inks. *Journal of Materials Chemistry*; vol. 8, pp.267-83.

Christie R., Robertson S. & Taylor, S. (2007) Design concepts for a temperature-sensitive environment using thermochromic colour change, *Colour: Design & Creativity*, 1 (1) 5: 1-11.

Friškovec M., Kulčar R. & Klanjšek Gunde M. (2010) Light stability of thermochromic prints, *Advances in Printing and Media Technology, Proceedings of the 37th International Research Conference of iarigai*, pp.147-153.

Homola J. (2008) Color-changing inks. http://www.screenweb.com/index.php/channel/6/id/1425/, http://www.mhest.com/suppar-ticles/Color-changinginks.pdf. Reprinted from McGraw-Hill Yearbook of Science & Technology.

Johansson L. (2006) *Creation of printed dynamic images*. Linköping Studies in Science and Technology; Thesis No. 1234., Norköpping, Sweden.

Klanjšek Gunde M., Kunaver M., Hrovat A. & Cvelbar U. (2005) Bonding process efficiency and Al-flake orientation during the curing of powder coatings, *Progress in Organic Coatings*, vol. 54, pp.113-119.

Klanjšek Gunde M., Friškovec M., Kulčar R., Hauptman N., Kaplanova M., Panak O. & Vesel A. (2011) Functional properties of the leuco dye-based thermochromic printing inks, *Proceedings of the TAGA Conference*, Pittsburgh, USA.

Kulčar R., Friškovec M., Hauptman N., Vesel A. & Klanjšek Gunde M. (2010) Colorimetric properties of reversible thermochromic printing inks, *Dyes and Pigments*, vol. 86, pp. 271-277.

Kulčar R., (2010) *Colorimetric analysis and stability parameters of UV-thermochromic printing inks",* Thesis, Faculty of Graphic Arts, University of Zagreb, Croatia.

Kunaver M., Klanjšek Gunde M., Mozetič M. & Hrovat A. (2003) The degree of dispersion of pigments in powder coatings, *Dyes and Pigments*, vol. 57, pp.235-243.

Maclaren D.C. & White M.A. (2003) Competition between dye-developer and solvent-developer interactions in a reversible thermochromic system, *Journal of Materials Chemistry*, vol. 13, pp. 1701-1704.

Maclaren, D.C. & White M.A. (2005) Design rules for reversible thermochromic mixtures. *Journal of Materials Chemistry*; vol. 40 pp. 669-76.

MOZETIČ M. (2003) Controlled oxidation of organic compounds in oxygen plasma. *Vacuum*, 71:237-40.

SEEBOTH A., LÖTZSCH D., POTECHIUS E. & VETTER R. (2006) Thermochromic effects of leuco dye studied in polypropylene, *Chinese Journal of Polymer Science*, vol. 24, pp. 363-368.

SEEBOTH A., KLUKOWSKA A., RUHMANN R. & LÖTZSCH D. (2007) Thermochromic polymer materials, *Chinese Journal of Polymer Science*, vol. 25, pp. 123-135.

SEEBOTH A. & LÖTZSCH D. (2008) Thermochromic Phenomena in Polymers, Shawbury: Smithers Rapra Technology Limited, 17.

SMALL L.D. & HIGHBERGER G. (1999) Thermochromic ink formulations, nail lacquer and methods of use, US patent no. 5997849.

Vesel A., Mozetič M., Hladnik A., Dolenc J., Zule J. & Milošević S. (2007) Modification of ink-jet paper by oxygen plasma treatment, Journal of Physics D: *Applied Physics*, 40:3689-96.

WILLIAMS C. (2003) Colour change inks, *Print and Paper Europe*, Vol 15 (No 9): 22.