Functional Properties of the Leuco Dye-Based Thermochromic Printing Inks

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Abstract

Leuco dye-based thermochromic printing inks are one of the candidates for active packaging of the future. Such an advanced application requires much more knowledge about these novel inks as it is currently provided by the manufacturers. Thermochromic inks reversibly change from colored to discolored state in a certain temperature region. Details of this change and the width of the temperature region required for it are characteristic properties of a selected ink. Inside this region the color of a sample depends on temperature and thermal history; this is a color hysteresis, which contains a sort of memory. The activation temperature, which is the only parameter given by the producer to describe the change of color, does not reveal any characteristic properties of this temperature dependent color loop. Therefore other parameters were introduced to characterize the analyzed thermochromic inks. Thermochromic material is leuco dye-based composite which is protected in round-shaped capsules. They are much larger than pigments in conventional inks. Their large size can seriously influence the appearance of very thin layers, being the size of capsules. The polymer envelopes of pigment capsules are more stable against oxidation than the binder. If these envelopes are damaged, the dynamic color is irreversibly lost. The lightfastness of thermochromic samples is low. Thicker layers retain their dynamic color up to longer light exposures. Light changes color of the fully colored and totally discolored states and of all intermediate

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states; the changes are larger in the colored state and smaller in the discolored one.

Introduction

Active and smart packaging has become very popular and widely demanded in modern packaging industry for selling goods while it enables higher added value, enhanced security and additional opportunities for marketing promotion. In most cases it may contain several elements that can protect forgery and display some invisible properties of the product in an easy recognized form. One of the most important elements on such packaging is also a temperature sensitive indicator (Kerry and Butler, 2008). Many of them are currently printed using color-changing inks in more or less simple designs; however, more sophisticated products are also used. Temperature indicators could show the current temperature of the product or could indicate its thermal history; the former requires reversible changing inks but the later should apply irreversible or semi-reversible inks.

Printed temperature indicators almost exclusively use thermochromic (TC) printing inks. In general, they consist of TC pigments and a suitable binder. Pigments can be inorganic particles or organic composite protected in polymer capsules. In inorganic TC materials, such as metal salts and metal oxides, the effect originates from changes of crystal structure and is in most cases irreversible. Temperature dependent color change occurs also in different classes of polymers; they are appearing currently almost exclusively as liquid crystalline polymers or leuco dye-based composites (Seeboth and Lötzsch, 2008). We restrict ourselves here on leuco dye-based TC inks, which currently prevail in printed TC applications.

The complex chemistry of leuco dye-based TC inks is described in very specific literature only. Any advanced application of such inks needs careful colorimetric characterization (Johansson, 2006). The temperature-dependent properties of the complex TC system, the degree of its reversibility and stability are very important. Our research group is presently focused in reversible TC inks. Temperature-dependent optical properties of several commercially available TC inks were thoroughly analyzed (Kulčar et al., 2010). Herein, we summarize main results of our research with special attention to those important for applications in graphic arts.

Thermochromic Composites

In most cases the functional part of a TC printing ink is a composite with at least three components: a color former, a color developer and a solvent (Seeboth and Lötzsch, 2008). Its color changes via two competing reactions, one between the

dye and the developer and the other between the solvent and the developer. The first reaction prevails at low temperatures where the solvent is in a solid form, therefore the dye-developer reaction prevails and gives rise to formation of the dye-developer complexes. In most cases, these complexes are colored. When at higher temperature, the solvent melts making the solvent-developer interaction dominant; thus, dye-developer complexes are destroyed and the system converts into its colorless state. The temperature at which discoloration/coloration occurs is controlled by the melting temperature of the applied solvent. Several definitions of this temperature are used in the literature, such as switching (Seeboth et al., 2007), discoloration (Maclaren and White, 2003) or activation temperature (Johansson, 2006). Here the term activation temperature (T_A) is used.

Most frequently applied color formers are the so-called leuco dyes. These electron-donating compounds, such as spirolacones, fluorans, spiropyrans or fulgides, are halochromic, i.e., they change color with pH. Most research was done applying crystal violet lactone and thymolphthalein. The second component of a TC composite is an electron-accepting developer. Frequently used developers are weak acids such as bisphenol A, gallates, phenols, hydroxybenzoates and hydroxycoumarin derivatives. The melting point of solvent controls the temperature at which the color of the composite changes (Seeboth et al., 2007, White and LeBlanc, 1999).

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

Thermochromic Pigments

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

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 usually used in interface polymerization to form a polymer envelope. The envelope should be chemically and thermally stable, must have suitable elasticity and perfect transparency for visible light. The melamine resin is almost entirely insoluble in most solvents; its porosity and elasticity can be adjusted by controlled degree of cross-linking. It is frequently applied in microencapsulation of TC composite. Epoxy resin, the alternative, has a higher transparency, and does not need surface active

compound during the encapsulation process (Seeboth et al., 2007, Seeboth and Lötzsch, 2008, Small and Highberger, 1999).

SEM micrograph of a TC pigment powder is shown in Figure 1. It shows microcapsules with broad particle size distribution. In general no aggregates or clusters are obtained. A typical size of TC pigment is more than 10 times larger than conventional pigment particles which are usually applied in printing inks. The large size causes also 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.

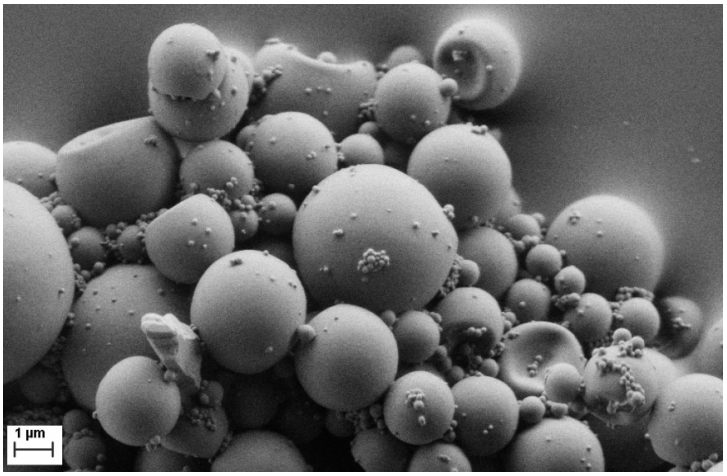


Figure 1. SEM micrograph of a TC pigment powder.
Most particles are circular-shaped capsules with diameter of several µm.
The irregular particles are non-encapsulated composite.

Thermochromic Inks

Leuco dye-based TC inks of various T_A are commercially available, from –15 C up to 65 C. However, most of current applications are limited to three standard temperature ranges, cold (~ 10 C), body-heat activated (~ 31 C) and warm (~ 43 C). The cold region is applied for checking the freshness of drinks, i.e. whether they are appropriately cooled. The body-activated region can serve for covering part of the information by a layer that can become transparent by the heat of the body. The warm region is usually applied on food packaging to inform the consumer that the food is too hot to be eaten.

TC printing inks of all basic types are available; conventional offset, water-based, solvent-based and photocuring inks for printing on paper, plastics, metal and textile. By a rule, most producers currently provide approximate color

shades of inks in their colored form, recommend appropriate printing and drying conditions; however, the T_A is the only dynamic color 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).

Materials and measurements

The results obtained for commercially available TC inks are shown here. Some of them were free samples whereas the others were bought by corresponding suppliers. The data given from the suppliers of these inks are given in Table 1.

Table 1. Basic data of the TC inks applied here: manufacturer, printing and drying methods, activation temperature (T_A), color shade at $T << T_A$ and the largest particles (obtained using a grindometer). For some inks it was not possible to determine the grindometer value.

Ink	Manufacturer	Printing	Drying	T_A (C)	Color	Largest particles (μm)
TCXb-31	Coates Screen	Screen	UV	31	Blue	12
TCXn-31	Coates Screen	Screen	UV	31	Black	12
CTIr-31	CTI	Offset	air	31	Red	1.5
CTIm-31	CTI	Offset	air	31	Magenta	1.5
CTIn-31	CTI	Offset	air	31	Black	1.5
Silitech-r-15	Silitech	Screen	air	15	Red	

Particle size distribution of TC pigment capsules in a commercial TC ink can be determined by image analysis of optical micrograph. For this purpose, micrograph of a very thin layer of a TC ink was applied. If necessary, the ink was diluted to obtain better resolved particles. In addition, the methods which are used to characterize wet paint dispersions could be applied. We applied the Hegman gauge method which measures fineness of grind and allows rapid assessment of the largest particles in wet ink. This is the so-called grindometer value. However, this method provides no information on the size distribution of particles. The grindometer values of the TC inks applied here are given in Table 1. For the purpose of our research, the TC inks were printed on different papers by the advised procedure and dried according to producer's recommendations.

Spectral reflectances of samples were measured using the Lambda 950 UV-VISNIR spectrophotometer (PerkineElmer) employing a 150 mm integrating sphere under (8:di) measuring geometry (diffuse geometry, specular component included). The temperature of sample was changed by heating/cooling on the Full Cover water block (EK Water Blocks, EKWB d.o.o, Slovenia), a system that was originally designed for cooling CPU's and graphic cards of power demanding computers. The base plate is made of perfectly flat electrolytic copper. A suitable liquid (water or mixture of water and ethylene glycol)

accelerates through very thin channels inside the plate which temperature was varied by thermostatic circulator. It allows adjusting the temperature of circulating liquid and thus also of the sample on copper plate surface up to tenth of degree accurately.

The reflectance spectra were measured in different heating/cooling cycles, depending on the temperature region needed to describe the entire TC color 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 otherwise. Heating/cooling rate was about 0,5 C/min. This is slow enough for measured TC samples to become thermally balanced with the copper plate and can follow the termal change. The colorimetric parameters were calculated from the reflectance data using CIELAB color space, under D50 illumination and 2 standard observer. Color differences were calculated using the CIEDE2000 total color difference formula.

The distribution of TC pigment capsules in a dry ink layer were analyzed applying weakly ionized highly dissociated oxygen plasma. It was created in a glass Pyrex tube 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 give rise to selective etching of surface material having different oxidation probability. This method is frequently used to detect distribution and orientation of particles in polymer matrix (Kunaver et al., 2003, Klanjšek Gunde et al., 2005). It was shown that polymer binder and TC pigments have different etching properties in oxygen plasma. The removal of the highest layer of the binder in TC printing inks was completed in a couple of minutes. This way the top-laying TC pigment particles become visible on SEM micrographs. The Karl Zeiss Supra 35 field emission scanning electron microscope (SEM) was used for taking the pictures.

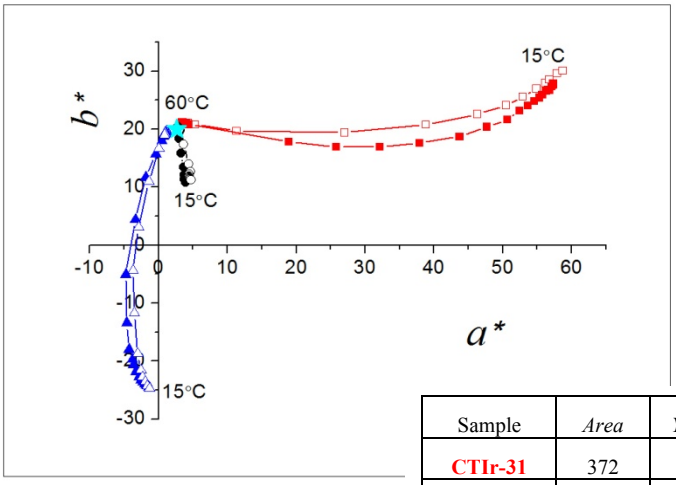
Surface appearance of TC prints was evaluated also according to their surface gloss. In particular, the influence of TC pigment capsules on the surface gloss of thin printed layer was analyzed. The specular gloss was measured at 85 angle applying the Micro-TRI-gloss µ glossmeter apparatus (Byk-Gardner, Germany). The reflectometer value related to a black glass standard with refractive index of 1.567 was applied which gives readings in gloss units (GU).

Colorimetric Properties

TC samples lose their color during heating and regain it during cooling. Both processes are continuous without any abrupt change. This could be described by a path (a color trajectory) in the CIELAB color space (Figure 2). 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, this was never obtained in praxis. Therefore, a parameter called *Area* was introduced which measures the area of the curved surface between both color trajectories. Larger *Area* shows bigger differences between colors appearing on the sample at the same temperature 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 printing material (the uncoated paper). The effect was evaluated by the *Yellowness*, the total color difference between TC sample in the completely discolored 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.



Sample	*Area*	*Yellowness*
CTIr-31	372	4.1
TCXb-31	247	3.4
TCXn-31	45	3.9

Figure 2. Color trajectories in the (a,b*) plane of CIEAB color space as obtained for three TC samples: TCXn-31 (black), TCXb-31 (blue) and CTIr-31 (red) at heating (full signs) and cooling (open signs). All applied inks have T_A=31 °C. Samples with similar layer thickness were evaluated. The value of the applied bare paper substrate (OBA free gloss coated paper, 150 g/m^2) is shown by a star. The area of the surface between the two trajectories in the CIELAB color space is given in the legend (Area) (quadratic CIELAB units). Degree of discoloration (Yellowness) is also specified (in CIELAB units).*

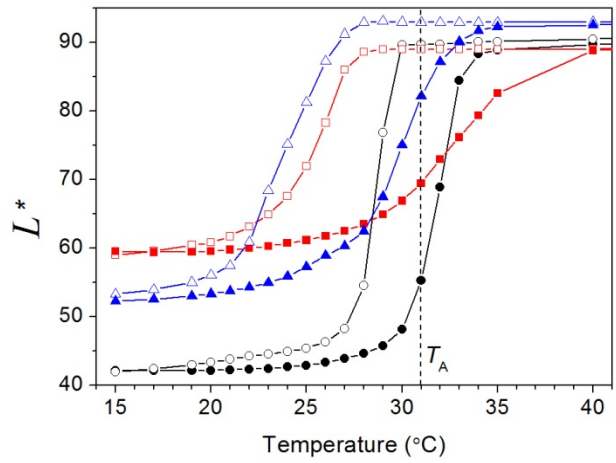
The color values of a TC sample should be shown also as a function of temperature. In such a presentation, the entire $L^*(T)$, $a^*(T)$ and $b^*(T)$ curves have a form of a loop (Figure 3). Most of the discoloration process is

accomplished already some degrees above T_A and all color values remain approximately the same with further increase of temperature. The reverse process occurs during cooling but it requires lower temperatures. Because of that, the color of a TC sample does not depend only on temperature, but also on its thermal history, i.e. whether the particular color was reached during heating or during cooling. The color 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.

The shape of color hysteresis obtained for different TC samples differs in temperatures where the loop starts and finishes as well as in its steepness and area. It can be seen that T_A, specified by the producer (T_A = 31 C for all samples shown in Figures 2 and 3), does not correspond to any of these features. It is located at temperature where the discoloration process is going on; in some samples it approaches well to initial achromic temperature where discoloration starts (e.g., TCXn-31 on Figure 3) and to final achromic temperature where the discoloration is almost completed already (e.g. TCXb-31 on Figure 3) (Kulčar et al., 2010).

An important parameter of a TC sample is efficiency of the color change that it provides. We express this property as the color difference between completely colored and fully discolored states and called it *TC contrast*. Larger *TC contrast* gives better recognizable color change. The values for some samples are given on Figure 3.

The color hysteresis can also be represented by the color difference between states during heating and states during cooling of the same sample as a function of temperature, as it is illustrated on Figure 4. This function describes a single peak with different position, intensity and width. It was found that, in general, it peaks at temperature lower than T_A. The peak is not necessarily symmetric. Its width could be used as a measure of temperature region needed for the TC sample to undergo the color change.


L*
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70
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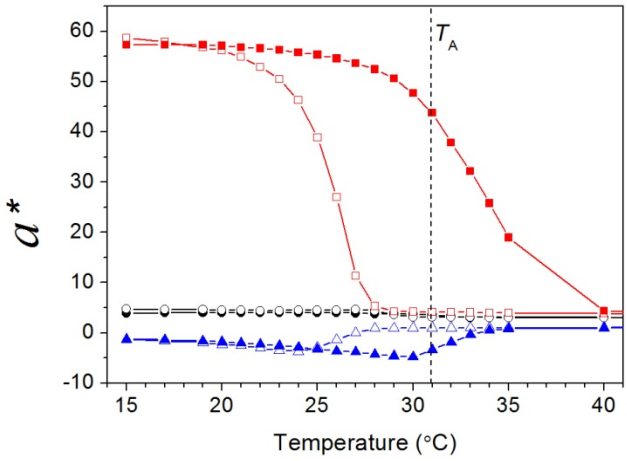
T_A
Temperature (°C)


a*
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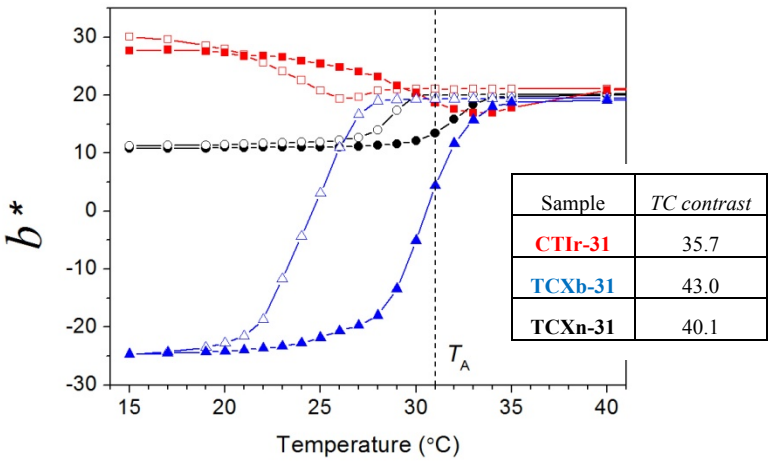


Figure 3. Color hysteresis of TC samples. CIELAB color values as a function of temperature for three TC samples: TCXn-31 (black), TCXb-31 (blue) and CTIr-31 (red) at heating (full signs) and cooling (open signs). All inks have T_A = 31 °C. Samples with similar layer thickness were evaluated. Efficiency of color change is expressed by TC contrast, the total color difference between totally colored (15 °C) and discolored states (60 °C) and is given in the legend (in CIELAB units).

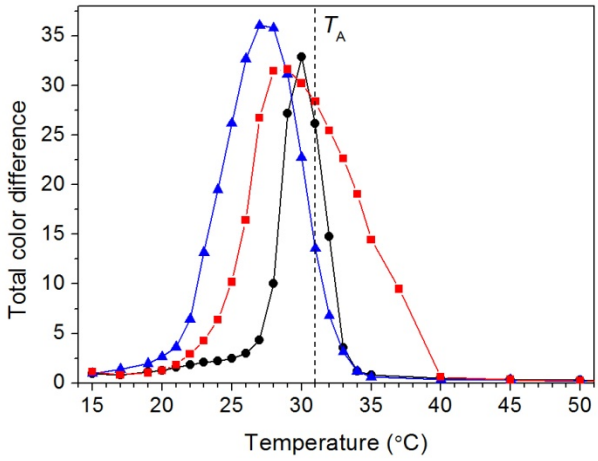


Figure 4. The total color difference between heated and cooled states of the same TC sample as a function of temperature, as measured for TCXn-31 (black), TCXb-31 (blue) and CTIr-31 (red) samples. All inks have T_A = 31 °C. Samples with similar layer thickness were evaluated. See also figures 2 and 3.

The colored dye-developer and colorless solvent-developer complexes are metastable and long-lived (Seeboth et al., 2006). Colored complexes prevail at low temperatures and colorless ones at high temperatures, regardless of composite's thermal history. At intermediate temperatures competitive dye-developer and solvent-developer reactions occur causing the system to change its color 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 color hysteresis of all reversible TC samples are stable when the temperature was kept constant for more than 10 h. After testing for such a long time, the color continued to change practically on the same path as if there would be no stability testing (Kulčar et al., 2010).

Physical Properties

The size of TC capsules is much larger than that of conventional pigments. It is obvious, that the μm-sized capsules could influence considerably on the appearance of prints, especially if layer thickness is of the order of μm or less. This effect was evaluated for offset-printed samples where typical thickness in usually small compared to the size of TC capsules inside the printing ink. For this reason the specular gloss of offset TC prints was measured in dependence on layer thickness.

To evaluate the above-mentioned effect, offset TC inks (CTIr-31, CTIm-31 and CTIn-31) were printed on four paper substrates: gloss-coated (250 g/m^2, PPS roughness 1.31 μm), matt (250 g/m^2, PPS roughness 1.56 μm), label (80 g/m^2, PPS roughness 1.68 μm) and metal-coated ones (PPS roughness 2.03 μm). The IGT Printability Tester C1 (IGT – C1) with printing speed of 0.3 m/s and different printing force was applied for printing. It was impossible to measure the thickness of printed layers; instead we used the amount of wet ink applied on substrate by printing (in g/m^2). The specular gloss of all three inks applied on the four papers is shown in Figure 5. Similar phenomena were observer in all cases. The thinnest printed layer has considerably smaller gloss as the corresponding substrate. It shows that pigment capsules, which are larger than layer thickness, make print surface very uneven. Scattering of collimated light on such a surface is large which gradually diminishes specular gloss. Approximately equal gloss was measured on the thinnest ink layer of all inks if printed on gloss, matt or metal-coated papers but somewhat smaller for those on the label substrate. This effect could be due to the small gloss of label paper (which has the smallest gloss) but the effect is not yet completely understood. Similar gloss measurements for the thinnest layers on smooth papers confirm that the applied TC capsules have similar sizes.

The very low gloss of prints slowly increases when layer gets thicker; the effect occurs up to a limiting value. Simultaneously, also the color of corresponding sample stopped changing with increasing amount of ink transferred on a

substrate by printing. The similarity of these processes against layer thickness most likely confirms almost equal sizes of pigment capsules in the three inks. The dependence of gloss on layer thickness shows also some additional properties which could be understood as combined effects of particle size distribution, layer thickness and surface properties of applied papers. The gloss of prints also depends on the applied papers, which could be understood as a combined effect of TC ink and surface roughness of papers

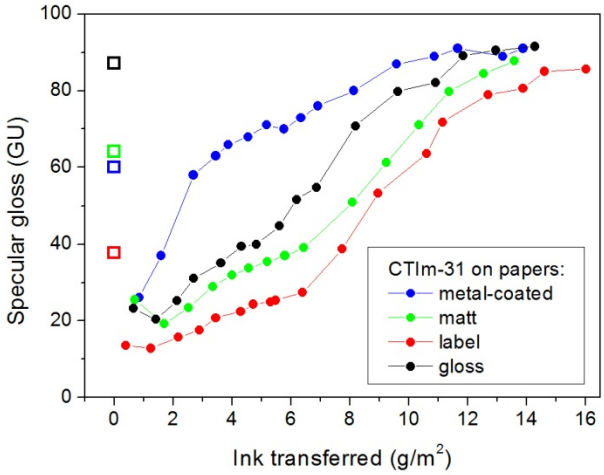


Figure 5. Specular gloss of prints made with magenta (CTIm-31) offset TC inks in dependence on the amount of ink transferred by printing. Data for papers are represented by squares at 0 g/m^2. The black, red, green and blue colors denote prints on gloss, label, matt and metal papers, respectively. Approximately the same dependence was obtained for the other offset TC inks, CTIr-31 and CTIm-31.

The size distribution of TC capsules dispersed in a TC ink could be obtained applying image analysis of photomicrograph made by an optical microscope. A typical example is shown on Figure 6. Here, asymmetric particle size distribution was obtained. It has 26% of particles between 3.5 and 4.5 µm, the maximum of size distribution at 4 µm and the mean value at 5.0 µm. The largest particles were observed at around 9.5 µm in diameter. This size is smaller than the corresponding grindometer value (see Table 1, TCXn-31). We concluded that transparent envelopes of TC capsules cannot be recognized as a part of TC capsules. Such an assumption would contribute a couple of µm to the TC capsules, which could be recognized as the thickness of the capsule's shell.

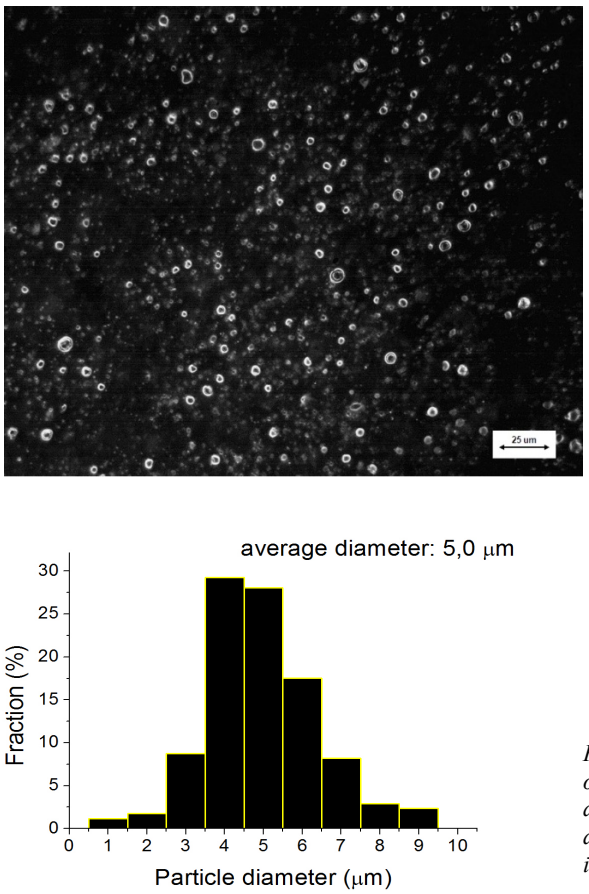
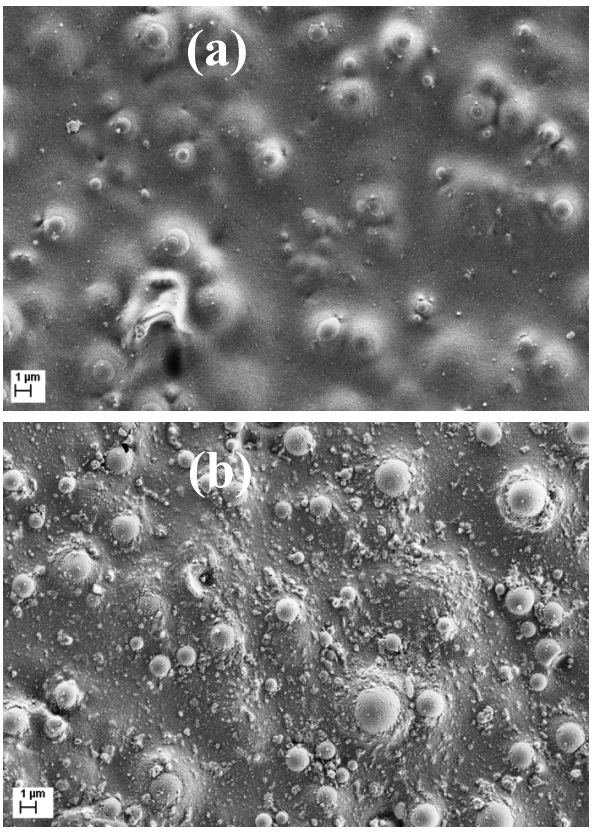


Figure 6. Photomicrograph of TC sample (TCXn-31) in dark field and particle size distribution obtained by its image analysis.

Stability

The surface of a typical dry TC ink layer is covered by the binder and only very few TC capsules can be seen on SEM micrograph. In general, capsules are covered by the binder so that no clear boundaries can be seen. During exposure to weakly ionized oxygen plasma, the topmost material with the lowest oxidation probability is etched away first. Our experiments show that during the removal of the top layers, the upper TC capsules become visible and their envelopes don't appear to be damaged. Such a sample has different appearance because of the lack of the cover binder; however it still retains original color shade and responds well to temperature changes. When such a sample is exposed to oxygen plasma for a longer period, its color is lost and temperature response continuously disappears. SEM micrograph of this 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 in the inside (Figure 7). The dynamic color of such a sample is irreversibly lost. However, the described experiment confirms that polymer envelopes have higher stability against oxidation than the binder.



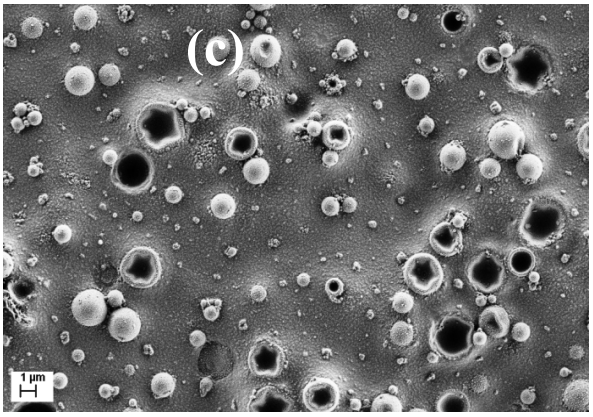


Figure 7. SEM micrograph of the TC sample (Silitech-r-15 without oxygen plasma treatment (a), after 30 s exposure to oxygen plasma (b), and after 60 s exposure to oxygen plasma (c).

Light with enough photon energy has a detrimental effect on color and appearance over longer periods of time. Conventional printing inks have usually an acceptable lightfastness, mainly because of the high stability of applied pigments. On the contrary, 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) In many cases additional protection is applied which could help in solving these drawbacks.

Light stability of TC inks applied in different thickness was tested with special attention to their dynamic color. Some tested samples were also additionally protected by a transparent lacquer. For testing purposes, part of the samples was exposed to quartz-filtered Xenon Arc Radiation (Suntest XLS+, Atlas Material Testing Technology) for 1.5, 6 and 24 hours, corresponding to radiation dose of 2700, 10800 and 43200 kJ/m^2, respectively. The stability of prints against light was evaluated by the total color difference between fully colored states of exposed and unexposed samples and by the *TC contrast*, i.e., the total color difference between fully colored and totally discolored states. The ability of sample to be discolored was followed by the *Yellowness*, i.e., the total color difference between the applied paper substrate and the TC sample in fully discolored state. The fully colored state was measured at 8 C and completely discolored at 40 C.

When a TC sample is exposed to UV light, its color changes in the fully colored and totally discolored state. With longer exposures the change of color of both states also increases. However, the effect is larger in colored state and smaller in discolored one. Thicker samples give smaller color change in colored state but larger in discolored one (Figure 8). This can be explained by the loss of color

and by increasing damage inside the layer. The first effect prevails in the colored state. It increases with exposure time but lowers with layer thickness. Most likely, the light continuously destroys the composite inside TC capsules. However, visible light penetrates deeper in the layer than the more energetic UV light. The color of thicker layers could therefore come from deeper undamaged parts of the TC layer. In fully colored form a smaller total color difference between exposed and unexposed samples was obtained when thicker layers were examined (Figure 8, left). In completely discolored state the increase of the yellowish effect upon light exposure was detected (Figure 8, right). The effect gets larger at longer exposure and is larger for the thicker layers.

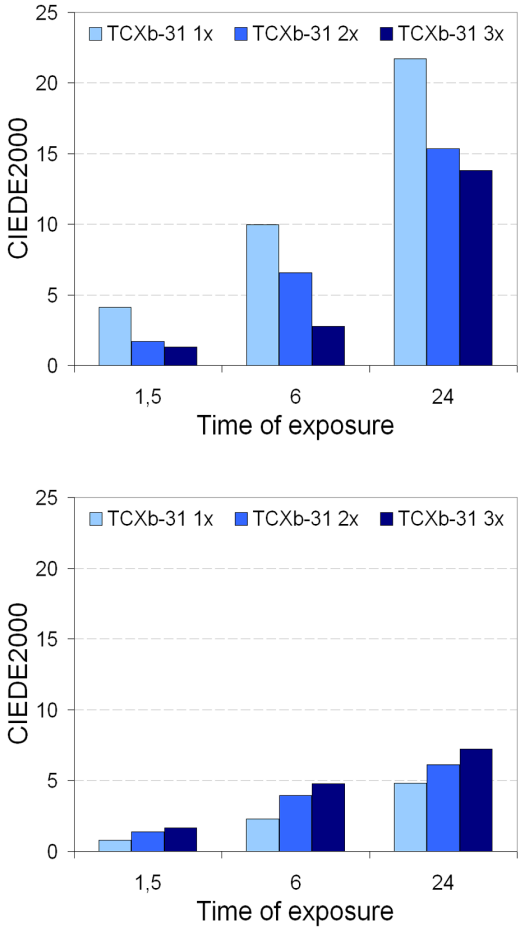


Figure 8. Total color change of TC samples because of exposure to light. It was calculated between unexposed and exposed samples in dependence on exposure time in fully colored (left) and totally discolored states (right). The results were obtained for samples printed with TCXb-31 ink in single (1x), double (2x) and triple (3x) layers. No protective layer was applied.

Conclusions

The dynamic color and stability properties of several commercial reversible TC inks were studied. They are colored at temperatures well below the activation temperature and discolor when heated well above. The colors developed during heating are not completely the same as those appearing when the same sample is cooled. The temperature region where the color changes, is characteristic for a selected ink. Inside this region the color of a sample depends on temperature and thermal history. All individual color states were confirmed to be stable up to at least 10 hours at fixed temperature. Thus the temperature alone cannot describe the color of a TC sample. Additional information is needed—whether the sample is being heated or cooled. The phenomenon is called color hysteresis; all color values in dependence on temperature describe hysteresis loops.

The activation temperature, which is the only parameter given by the producer to describe the change of color, lies somewhere in the color loop; however, its position does not reveal any of the characteristic properties of this temperature dependent loop. Other parameters were therefore introduced to characterize the analyzed TC inks; *Area*, *Yellowness*, and *TC contrast* are presented here in more detail. The first parameter measures the similarity of the colors at the same temperature when the sample is being heated and cooled. The larger the *Area* the more different colors are observed. The ability of a TC sample to become discolored was evaluated by *Yellowness*, the color difference between its totally discolored state and the bare substrate. The *TC contrast* measures the color difference between totally colored and fully discolored states; the larger the *TC contrast* the easier it will be to recognize the TC change.

All analyzed reversible TC inks contain leuco dye-based composite which is protected in pigment capsules. The capsules are round-shaped with sizes of several micrometers. No aggregation of these particles was observed in the inks. Typical size of TC pigments is much larger than that of pigments in conventional printing inks. However, different size of TC pigments is applied for different printing method; smaller pigments are used in offset inks but larger are allowed for screen printing. The size of TC capsules is important for appearance of prints, especially for very thin layers made with offset printing. When the average layer thickness is smaller than the size of capsules, the specular gloss is very low; it gets larger in thicker films and becomes the limiting value at the thickness where the color of the sample is clearly observable. We conclude that all TC prints must be thicker than the size of TC capsules.

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 color properties are irreversibly lost when the envelopes get damaged.

The lightfastness of TC samples is low. It was shown that the color changes in both end states, the fully colored and totally discolored. Larger effect was obtained in colored state and smaller in discolored one. Thicker layers retain their dynamic color to longer light exposures.

Advanced applications of TC inks in smart packaging area needs further research. Most problems concerning application of commercial TC inks which are currently on the market were addressed already. We were able to introduce the majority of important parameters and to understand some of serious problems. Further research is going on. Special attention is devoted to preparation of better/novel TC composites and capsules with suitable properties.

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