Chromatic Properties of Thermochromatic Ink

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Abstract

Dynamic pigments in combination with static pigments can be used to achieve changeable prints. For example a large billboard commercial with a message that changes over time. One type of dynamic pigments are the thermochromatic pigments, which are used in these experiments. They are characterized by their ability to undergo reversible colour changes with temperature. When heated to a specific activation temperature, the pigments change from a coloured to a transparent state. The experiments described in this paper presents some preliminary results from an investigation of the chromatic properties and color changing characteristics of thermochromatic inks alone, and in their combination with static inks.

Introduction

Thermochromatic pigments change colour when the temperature changes. The pigments in the following experiments have reversible colour changes. They are visible at room temperature and become transparent at a higher activation temperature and then return to its original colour when restored at room temperature. With thermochromatic inks in combination with electronics printed on the backside of the paper substrate, it is possible to switch the thermochromatic ink between its two states. At Acreo (the collaborator in this project), different electronic organic formulations and pastes have been developed. One is conducting polymers that can be printed on paper using different printing techniques, for instance offset-, flexo- and screen-printing. This technique makes it interesting to investigate if it is possible to print two images on top of each other and then switch between the two images. These variable images are a combination of process inks and dynamic thermochromatic inks. At the low temperature the image is a combination of the two ink types, while at the high temperature, the image mainly consists of process inks. This introduces a new general problem, the colour separation process. Dynamic

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images will demand a new set of inks, and the requirement to be able to shift between two images sets completely new requirements for the whole colour separation process. In order to know how to separate the two images to get the desired result, the properties of the thermochromatic inks must be known.

Thermochromatic Pigments

There are two types of thermochromatic ink: *liquid crystal* and *leucodye*. Liquid crystal based thermochromatic ink is sensitive to very small changes in temperature, but is fairly difficult to manufacture. This makes it perfect for use in items like thermometers were you need the sensitivity, but troublesome in an item that needs to be inexpensive and in which a large, abrupt change in temperature will occur. Leucodyes are specially formulated substances that change from a specific color to a clear state when subjected to a temperature change of about 3°C or more.

Some products printed with chemical thermochromatic inks change from one colour to another, rather than transitioning from coloured to clear. This is achieved with an ink that combines a leucodye with a permanent-coloured ink formulation. For example, green ink may be formulated by adding a blue leucodye to yellow ink. In its cool state, the printed ink layer is green, and once warmed up, reverts to yellow as the leucodye becomes clear. Leucodyes can be designed to change colour at various temperature ranges, from as low as -25°C up to 70°C.

Experimental

1. Thermochromatic Ink

The thermochromatic pigments used in our experiments are microcapsule dyes (leucodye thermochromatic inks) that reversibly change their colours under a temperature change. In its cold state the ink exhibits colour, and when the temperature increases it turns transparent, see Figure 1. The pigments *(called NCC-TM Thermochromatic Series)* come from a Taiwanese supplier, *New Prismatic Enterprise Co Ltd*.

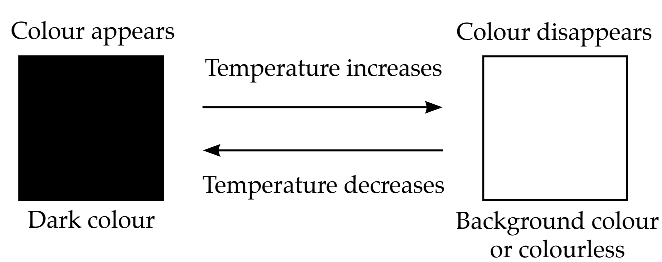

Figure 1. *Colour changing scheme for thermochromatic ink.*

According to the supplier, the colour changing temperature interval is from 0°C to 70°C. The inks used in these experiments change colour in the region from 31°C to 43°C. It takes a 2°C to 10°C shift in temperature for the inks to change colour. The activation temperatures for the 12 different pigments used in the experiments are shown in Table 1.

INK	COLOUR (low temperature)	COLOUR (high temperature)	ACTIVATION TEMPERATURE
1	Magenta	Transparent	43°C
2	Red	Transparent	31°C
3	R-Red	Transparent	31°C
4	Vermillion	Transparent	31°C
5	Yellow	Transparent	31°C
6	Yellow-Green	Transparent	43°C
7	Blue	Transparent	31°C
8	Sky Blue	Transparent	31°C
9	Violet	Transparent	31°C
10	T-Blue	Transparent	31°C
11	Green	Transparent	31°C
12	Black	Transparent	43°C

Table 1. *Colours and activation temperature for the thermochromatic pigments.*

The sensitive polymer based pigments are mixed with a transparent screen printing base, Encres Dubuit. The amount of pigments is about 20-30%.

2. Screen Printing

The ink film is applied to an uncoated white card. The card is opaque which eliminates the effect of the colour of the backing substrate on which the print is measured. The printing method was screen printing, and the printing parameters are collected in Table 2.

The measurements of the test prints were made using a 0/45 spectrophotometer under a D50 illuminant and 10° standard observer. To transform the thermochromatic inks to the warm state a radiator was used together with an aluminum plate to separate the test prints from the radiator and make the heat distribution more even. The temperature was set to 50°C with a precision of ±1°C. The temperature was measured against the paper on top of the plate.

SCREEN PRINTING PARAMETERS	
Line screen	60 lines per inch (lpi)
Mesh	120 threads/inch, 15 mm thread diameter
Ink	UV Process Cyan, Magenta, Yellow and Black with base, *Encres Dubuit* Thermochromatic pigments mixed with base, *Encres Dubuit*
Substrate	Uncoated cardboard, *Opalin*, 220g
Press	Semiautomatic flatbed, *American*

Table 2. *Screen printing parameters.*

Results and discussion

1. Chromatic Changes at High and Low Temperature

In order to get an overview of how each thermochromatic ink changes chromatically within the CIELAB colour space the a*b*-values of the inks in the two different states are visualized in an a*b*-plot, see Figure 2. The plot shows how the chromaticity changes. The black dots represent the inks in the cold state, and the grey dots represent the inks in the warm state. The measured value for the paper is also indicated in the figure.

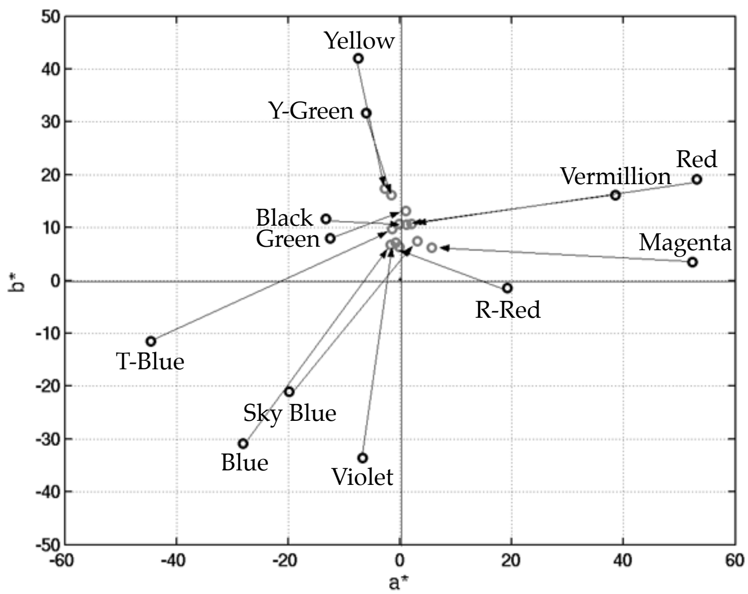

Figure 2. *CIE a*b*-values for the thermochromatic inks in the cold state (black dots) and in the warm state (grey dots). The CIE a*b*-values for the paper substrate in indicated by the small black dot in the middle.*

The figure shows that the thermochromatic inks do not become completely transparent in the warm state. All of the inks still exhibit a colour. It is also clear that the hue and chroma for the different colours vary for the different pigments. The thermochromatic inks that become least transparent are the yellow, y-green and green inks. And closest to the colour of the paper are the blue, sky blue, violet and r-red inks. The CIE a*b* difference between the inks in the warm state is unfortunately rather high. The majority of the inks in the warm state lie in the first quadrant, and thus have a slight yellow-redish tint. The results can also be plotted as ΔE, i.e. the difference between the thermochromatic ink in the warm state and the paper substrate. The results are shown in Figure 3.

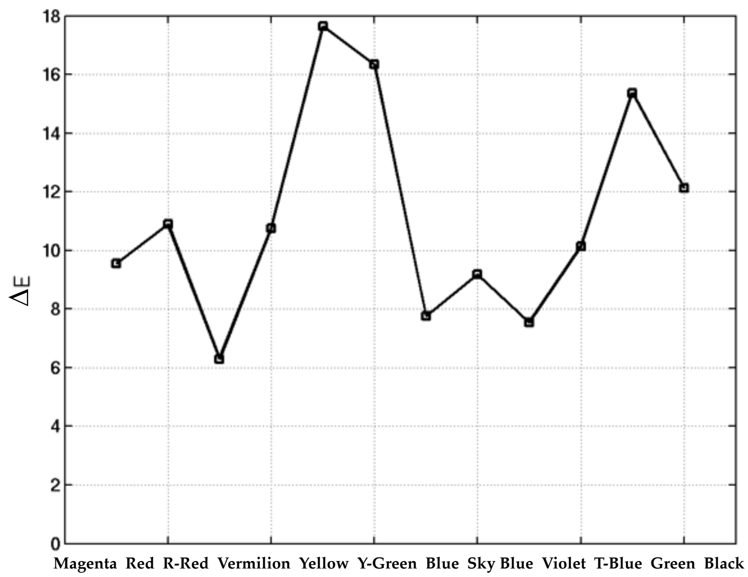

Figure 3. *Colour difference between the paper substrate and the twelve thermochromatic inks in the warm state.*

As can be seen in the figure, the yellow and green inks have the largest colour differences, and the r-red, blue and violet inks have least colour difference. The mean colour difference is near ten, which is very high and clearly noticeable. Note that ΔE values above ten are not of interest for comparison purpose.

3. Transparency of Thermochromatic Ink

The transparency of the thermochromatic inks in the warm state is also important because most process inks are over printed, therefore one ink has to be seen through another. The transparency of the ink is evaluated using the cyan (t-blue), magenta, yellow and black thermochromatic inks. The thermochromatic ink is heated to its specific activation temperature. The tints measured are from 10% to 100% with increasing steps of 10%. The difference in ΔE between the unprinted and the printed card is calculated. The ΔE for the thermochromatic ink is plotted versus percentage ink, see Figure 4. The slope of the graph gives the change in ΔE per percentage change of ink strength.

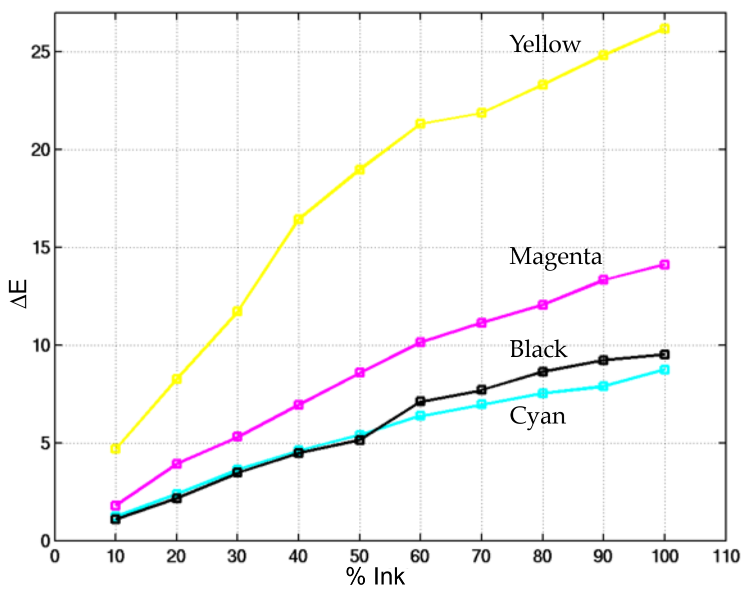

Figure 4. *Colour difference between the paper substrate and the ten tint percentages for the four thermochromatic inks cyan, magenta, yellow and black.*

The figure shows that the color difference increases almost linearly for increasing ink percentage. The color difference, ΔE, between the low ink percentages and the paper is hardly noticeably for cyan and black (ΔE<5,4 for ink percentages up to 50%). However, as the ink percentage increases the colour difference increases to ΔE≈9 for 100% ink coverage. The magenta thermochromatic ink has a higher increase of ΔE for increasing ink percentage. The fulltone gives a ΔE=14 which is clearly noticeable. Yellow thermochromatic gives the highest colour difference. It starts with ΔE=4,7 for 10% ink coverage and ends with ΔE=26,2 for fulltone. One measure for the thermochromatic ink transparency in the warm state is 1/slope, where a higher value gives a higher transparency. This gives cyan=12, magenta=7, yellow=4 and black=11. Note that ΔE values above ten are not of interest for comparison purpose.

The measured data is collected in Table 3 where also a mean value for the color difference is calculated. The high values indicate that the visible colour of the thermochromatic ink in the warm state has to be compensated for when separating the variable images.

ΔE BETWEEN THE PAPER SUBSTRATE AND THE THERMOCHROMATIC INK IN THE WARM STATE				
Ink %	**Cyan**	**Magenta**	**Yellow**	**Black**
10%	1.23	1.79	4.67	1.10
20%	2.37	3.92	8.25	2.16
30%	3.62	5.30	11.72	3.46
40%	4.60	6.93	16.43	4.49
50%	5.39	8.58	18.97	5.14
60%	6.38	10.15	21.32	7.10
70%	6.96	11.13	21.87	7.69
80%	7.54	12.06	23.31	8.63
90%	7.88	13.33	24.82	9.28
100%	8.72	14.12	26.18	9.53
Mean ΔE	***5.47***	***8.73***	***17.75***	***5.85***

Table 3. *ΔE between the paper substrate and the cyan, magenta, yellow and black thermochromatic ink in the warm state.*

In order to get an overview of how the inks change chromatically within the CIELAB colour space, the a*b*-values of the tints in the two different states are visualized in an CIE a*b*-plot, see Figure 5. The cyan, magenta, yellow and black plots show the tints for the different thermochromatic inks at low temperature, and the grey plots show the tints at high temperature.

All of the thermochromatic inks become more yellow as the ink percentage increases. This is indicated by the increased b*-values in the plots. It is also clear that the difference in CIE a*b* values between the tints is larger for yellow thermochromatic ink compared to cyan, magenta and black. The plot for the yellow tint in the warm state also follows the plot for the yellow tint in the cold state, which indicates that the ink still preserves much of its original colour even in the warm state. The thermochromatic magenta also deviates towards the cold state colour for the higher ink percentages, while cyan and black completely turns to a new colored state when heated to their specific activation temperatures.

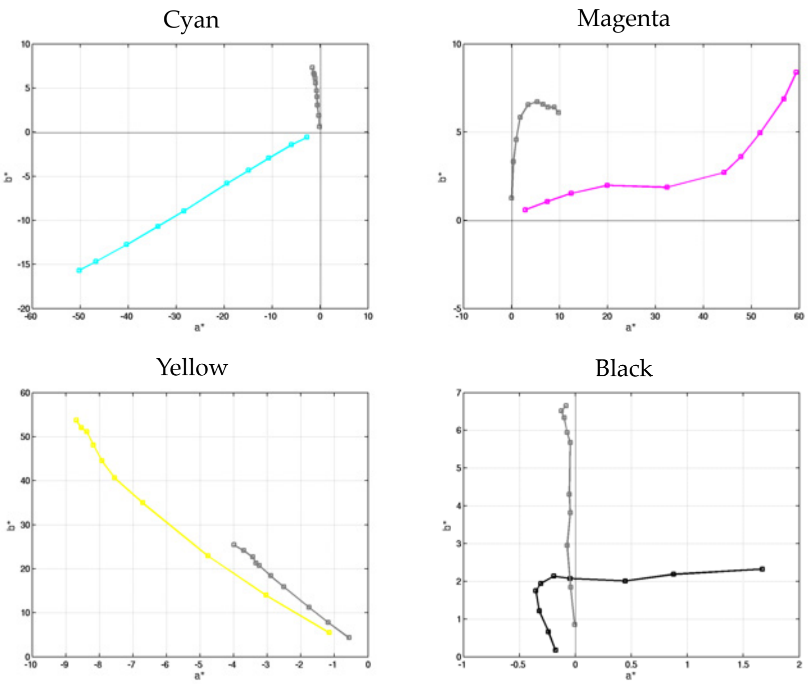

Figure 5. *CIE a*b*-values for the cyan, magenta, yellow and black thermochromatic tints in the cold state (cyan, magenta, yellow and black dots) and warm state (grey dots).*

The transparency of the thermochromatic ink layer is also evaluated in the cold state. Process cyan, magenta, yellow and black were printed from 10% to 100% with increasing steps of 10%. On top, a fulltone layer of thermochromatic blue ink was printed. The CIE a* b* values are shown in Figure 6. The figure shows that the thermochromatic ink layer has a high transparency and never can cover static ink printed beneath except for the low cyan tints. This indicates that the colours in the variable images has to be formed as an optical colour mixture of static and dynamic halftoning dots.

4. Dot Gain

Another interesting thermochromatic ink characteristic is the dot gain, which has to be compensated for during the color separation. The density measurements were performed on 80 samples, eight tonal strips with ten different tints for each strip from 10% to 100% with increasing steps of 10%. The eight tonal strips represent process C, M, Y and K and thermochromatic C, M, Y and K. Every sample was measured four times in order to obtain reliable values. From these measurements a mean value was calculated. The area coverage was calculated using the Yule Nielsen

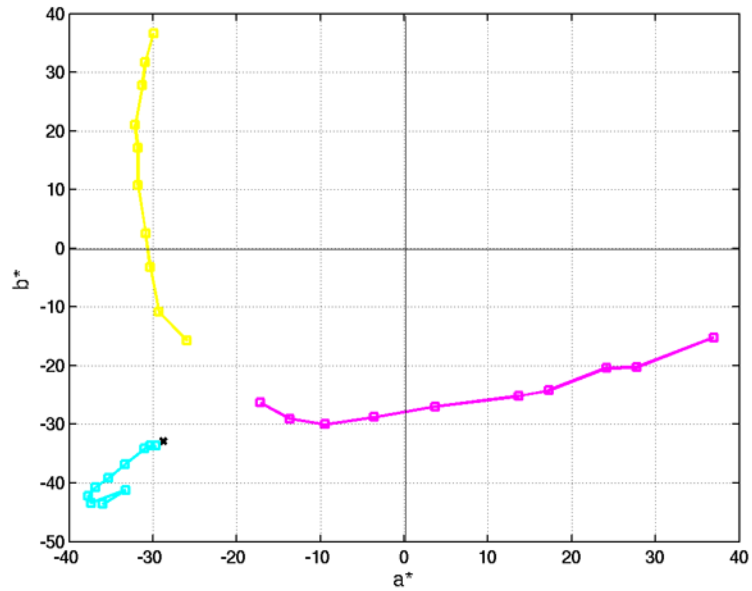

Figure 6. *CIE a* b* values for thermochromatic blue (indicated by x) printed on cyan, magenta and yellow process ink strips from 10% to 100% with increasing steps of 10%.*

equation, and the correction factor for the internal light scatter, n was set to 1,7. Then, eight different dot gain curves were plotted; four curves for the process inks and four curves for the thermochromatic inks, see Figure 7. The graphs in the figure show the variation in dot gain throughout the tonal range resulting from the two ink types under the specified conditions. The graphs with dashed lines represents the dot gain curves for the thermochromatic ink, and the graphs with solid lines represent the dot gain curves for the process ink. The graphs show that the dot gain for the thermochromatic inks show opposite results from the process inks. The thermochromatic inks produce a high dot gain for magenta (maximum dot gain=18,9 for 60% dot area) and yellow (maximum dot gain=25,9 for 50% dot area) and a low dot gain for cyan and black. The process ink produces a high dot gain for cyan (maximum dot gain=15,1 for 60% dot area) and black (maximum dot gain=21 for 40% dot area) and a low dot gain for magenta and yellow. Additionally, thermochromatic cyan, process magenta and thermochromatic black show dot loss. For thermochromatic cyan the dot loss occurs in the highlight to midtone range, for process magenta the dot loss occurs in the highlight to shadow range, and for thermochromatic black there is a dot loss in the highlight to midtone range. This dot loss is probably due to an excessive stencil thickness that prevents an efficient transfer of ink from the screen to the substrate.

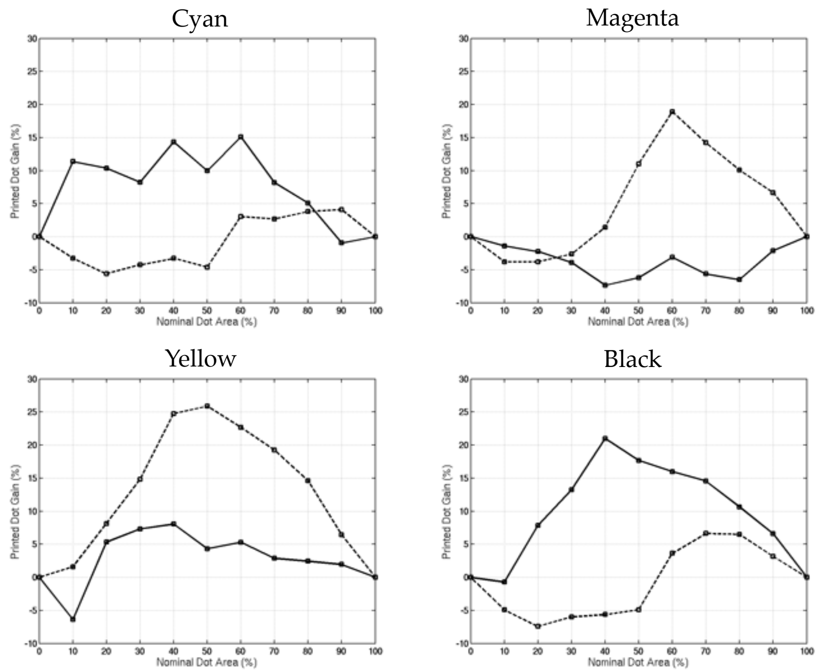

Figure 7. *Dot gain curves for process cyan, magenta, yellow and black (solid lines) and thermochromatic cyan, magenta, yellow and black (dashed lines).*

5. Two-Layer Case: Process Ink and Thermochromatic Ink

Another test print made was one fulltone thermochromatic ink layer printed on top of a fulltone process ink layer in order to see how the inks interact. The process inks used were cyan, magenta and yellow, and the thermochromatic ink used was blue. The spectral reflectance was measured for the ink layers alone and printed on top of each other.

A simple model of the static and dynamic ink layer combination is that the spectrum for the process ink multiplied by the spectrum for the thermochromatic ink in the warm state equals the process-thermochromatic ink combination in the warm state, i.e:

$$P(\lambda)\cdot PI(\lambda)\cdot TI(\lambda)^{WS}=PPITI(\lambda)^{WS} \quad (1)$$

$P(\lambda)$= spectrum of the paper
$PI(\lambda)$= spectrum of the process ink layer
$TI(\lambda)^{WS}$= spectrum of the thermochromatic ink layer in the warm state
$PPITI(\lambda)^{WS}$ = spectrum for the paper-process-thermochromic ink layer in the warm state.

The calculated spectral reflectance together with the corresponding measured spectral reflectance for thermochromic blue printed on cyan, magenta, yellow and black respectively in warm state are shown in Figure 8. The dashed line represents the calculated spectrum and the solid line represents the measured spectrum.

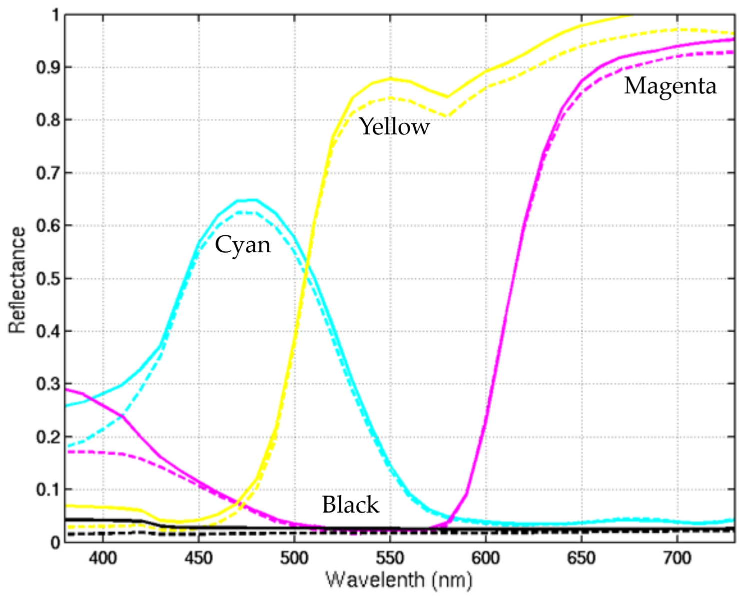

Figure 8. *Calculated spectrum for cyan, magenta, yellow and black (dashed lines) and measured spectrum for cyan, magenta, yellow and black (solid lines).*

As can be seen the simulations correspond well to the measured data. This gives an indication that the simple multiplicative model holds. The highest deviation from the calculated spectra lies in the violet-blue part of the spectrum. This can be due to the effect of the FWA (Flourescent Whitening Agents) in the paper.

INK COMBINATION IN WARM STATE	ΔE
Process Cyan (100%) + Thermochromatic Ink (100%)	14,9
Process Magenta (100%) + Thermochromatic Ink (100%)	15,4
Process Yellow (100%) + Thermochromatic Ink (100%)	10,6
Process Black (100%) + Thermochromatic Ink (100%)	9,3
Mean ΔE	*12,6*

Table 4. *ΔE between the calculated spectral reflectance combinations and the measured spectral reflectance.*

Even though the spectral reflectance curves have a high correlation, calculation of the colour difference, ΔE, between the two spectra shows that the visual colour difference is still high, see Table 4. Note that ΔE values above ten are not of interest for comparison purpose.

Conclusions

In this study the chromatic properties of thermochromatic inks have been investigated. Dynamic thermochromatic ink alone and in combination with static process ink was printed using screen print. The results show that thermochromatic inks do not become completely transparent in the warm state. All of the inks still exhibit a colour even at the high temperature and the chromaticity vary for different pigments. The colour difference, ΔE, between the paper and the thermochromatic inks in the warm state is high with a mean value near ten. The inks with the highest colour difference lie in the yellow-green part of the CIELAB colour space, and the inks with the lowest colour difference lie in the red-blue part.

The measurements show that the transparency of the thermochromatic ink layer in the warm state varies between different thermochromatic pigments. In addition, ΔE increases linearly with increasing ink percentage. The colour difference between the low ink percentages and the paper is hardly noticeably for cyan and black, while the magenta thermochromatic ink has a higher increase of ΔE with increasing ink percentage and yellow thermochromatic ink gives the highest colour difference. The high colour difference values indicate that the visible colour of the thermochromatic ink in the warm state has to be compensated for when separating the variable images. The reference white for the image in the warm state will preferably be the measured values for the thermochromatic ink layer in the warm state, instead of the paper white. The measurements also show that the thermochromatic ink layer has a high transparency in the cold state and never can cover static ink printed beneath. This indicates that the colours in the variable images have to be formed as an optical colour mixture of static and dynamic halftoning dots.

The measurement of the dot gain for the process inks and the thermochromatic inks show that the dot gain for the thermochromatic inks gives opposite results from the process inks. The thermochromatic inks produce a high dot gain for magenta and yellow and a low dot gain for cyan and black. Additionally, thermochromatic cyan, process magenta and thermochromatic black show dot loss.

In addition, a simple multiplicative model of the static and dynamic ink layer combination has been tested. The simulations of the spectra showed a fairly good agreement with the measurement, even though the colour difference shows that the visual colour difference is still high. But for most applications, like a billboard commercial, this colour difference is probably acceptable.

Acknowledgements

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