The thermochromism of organic pigments dispersed in liquid phase

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Short abstract

Temperature is a known factor for colour appearance of both inks and dyes. This work investigates the temperature influence on the visible spectra of 43 organic pigments. The pigments are converted into solvent-based flexo inks and spectrally measured in transmission within a temperature range of 20–50 °C. After cooling down, up to two more heating and measuring cycles take place to assess reversibility. Significant thermochromic spectral effects and ΔE_{00} values > 1 can be observed for the majority of pigments. For most samples, spectral transmittance increases with increasing temperature. For peaks and gradients, a wavelength shift is observed usually. This leads to shifted hues and decreased chromaticities. The thermochromic effect can be described as linear with temperature increase, whereby the effect is only reversible from the second heating cycle onwards.

Keywords: thermochromism, UV-Vis spectroscopy, organic pigments

1. Introduction and background

The term 'thermochromism' describes colour changes as a function of changing material temperatures. Apart from known thermochromic effect colourants, which are subject to temperature-related changes in their crystal structure, this work is dealing with organic pigments, which are actually known as 'non-thermochromic'. Their thermochromism can be relevant for colour measurements in production processes such as printing presses using thermal dryers, coil coating or plastic injection moulding. It is known from industrial printing processes, that significant temperature differences can occur between inline and offline colour measurement. In one specific flexo print production, for example, a temperature difference ΔT of 15 °C and resulting colour differences which were of magnitudes of visual perception were measured. (Bohn, 2020)

From the perspective of thermochromics, however, it is difficult to put hard numbers on printing processes as many variables have an influence. For example, dryer temperature, substrate thickness, speed and material as well as the position of the inline colour measurement within the machine setup. For plastic injection with its ΔTs > 100 °C, Botos, et al. (2014) identified changes in colour values of up to 10 percent while measuring colour inline. Besides scientific interests, the thermochromism of organic colour pigments thus also has practical relevance.

As other factors, like concentration or solvent used, temperature is known for potentially having influence on UV-Vis measurements (Bamfield, 2001). Temperature, generally speaking, can be described as the average kinetic energy in a molecular system (Stierstadt, 2020). When energy is added to a system, it results in a stronger molecular vibration which could cause altered material properties. In an early study, Yarborough, Haskin and Lambdin (1954) have measured the absorption coefficient of various organic compounds as a function of temperature which was found to decrease with increasing temperature. Other studies were dedicated to the thermochromism of solids, started with ceramic tiles. Compton (1984) determined thermochromic effects for seven out of twelve tiles whereby red, yellow and green hues showed effects in contrast to blue and grey tiles. The effects had magnitudes of up to 0.9 ΔE_{00}/10 °C. Fairchild and Grum (1985) also investigated ceramic tiles in temperature ranges of 25–45 °C. The most intense thermochromic colour

changes were found for orange and red colours, successively decreasing with the wavelength of the main reflection for green and blue. Results that were fundamentally confirmed by Verrill, Comptom and Malkin (1986). Malkin, et al. (1997) pointed out that the reflectance decreases with increasing temperature, which affects particularly spectral bands with large gradients. For various sample materials and colours, Hiltunen, et al. (2002) marked principles for the thermochromic phenomena which can also be found in some of the sources already cited: the shift of transmittance or reflectance is described as being directly proportional to the temperature change; the greater the slope in a spectral curve the bigger the colour change; a rising edge of a spectrum tends to shift towards longer wavelength, whereby this shift became bigger with rising wavelength. Furthermore, valid for single absorption, spectral changes occur in such a way that the integrated absorption area remains constant. Piening (2006) has worked on methods for analysing art and made some statements on temperature influence in this course. Following his argumentation, the temperature-dependent distances within molecular orbitals are responsible for colour differences. Here should be remembered that the visible colour of organic materials is mostly based on electron transitions between molecular orbitals. Generally speaking, the distance between those orbitals corresponds with the necessary amount of absorbed energy and thus the absorption spectrum (Nassau, 1978). The number of possible locations and energy differences of an electron also increases with the temperature. That's what leads to sharper absorption bands of measurements on lower temperature. Griffiths (1976) and Song, et al. (2014) investigated the temperature-dependent absorption of β-carotene in a solvent. For a temperature range of 18–81 °C, they determined a spectral red shift. They attributed this to the temperature-dependent reduction in conjugation length and thus increased μ-electron delocalisation.

Che, Li and Senanayake (2016), examined ceramic tiles for a range of 10–55 °C. They found almost no thermochromism for reflections without significant slopes, only little effects for blue tiles, and distinct thermochromism for yellow, orange and red tiles with values up to 1.8 ΔE_{00}. The authors hypothesize the following: the steeper the slope, the greater the red shift for positive slopes, reflections with only negative slopes don't show thermochromic shifts, for reflections with both negative and positive slopes there is also no spectral shift. In another work, Che and Senanayake (2017) were able to confirm their previous results for a more diverse sample field with respect to colourimetric characteristics. For a temperature range of 20–60 °C, colour changes correlated linearly with the temperature change. According to them, the physical mechanism for the hue dependency of thermochromism is still unclear. Che (2018) again investigated only samples of thermochromic-sensitive hues including ceramic and plastic tiles, textile fabrics, ink-printed and paint-coated paper cards in a range of 20–60 °C. This investigation confirms the hue dependency. He locates a possible explanation for the greater temperature sensitivity of colours such as red, yellow and orange in their particle size.

Summarizing the main findings of past studies, it can be stated that the thermochromism intensities depend both on the particular colour material and the wavelength range of the main absorption region of a colourant. In this context, the degree of slope of a spectral curve also seems to be relevant. Moreover, the physical background of thermochromism is declared as unknown by some researchers, whereas others mention the temperature-dependent excitation energies as key factor.

Thermochromism is to be systematically investigated as part of an ongoing research project. For this purpose, a laboratory UV-Vis spectrometer for reflected light measurements of solid samples has been extended by a temperature-controlled sample holder, including an infrared thermometer for continuous monitoring of the sample temperature. However, in order to first examine the pigments without substrate influence, this work wants to characterise the thermochromic effect for organic pigments dispersed in liquids by conducting absorbance measurements. A special feature of absorption measurement is the need to dilute the samples so heavily that they appear only slightly coloured to human perception. In combination with the high layer thickness of 10 mm resulting from the cuvettes path length, this leads to very distinctive spectra.

2. Materials and methods

2.1 Organic pigments and ink components

An organic pigment is classified by its chemical type and identifiable through the established Colour Index (C.I.), following the listing in Hunger and Schmidt (2018). 43 pigments are obtained to cover a wide range of different types. Table 1 contains all pigments and Table 2 all components and respective concentrations used for the preparation of inks.

Table 1: All organic pigments used, listed following the systematic of the Colour Index, polymorphic modifications are characterised with additional Greek letter, P.V. 55 exists in dark (d) and bright (b) shade

C.I.		C.I.		C.I.	
P.B.	15:1	P.R.	122	P.Y.	83
	15:3		144		109
	15:4		168		110
	15:6		175		129
	60		176		139
P.Bl.	1		177		150
P.Gr.	7		179		151
	36		206		213
P.O.	61		254	P.V.	19 (α)
P.R.	9		254		19 (β)
	3		264		19 (γ)
	83	P.Br.	23		37
	83		25		55 (b)
	122	P.Y.	3		55 (d)

Table 2: Components and concentrations for ink and sample preparation

Component	Function/Type	Concentration (%)
Kraemer ERKAMAR 3120 (EK)	binder / maleic resin	28.5
BYK DISPERBYK-2013	dispersing agent	3
1-Methoxypropan-2-ol	diluent / solvent	37
Ethanol	diluent / solvent	28.5
Pigment	colourant	3
Kraemer ROKRAPOL 7495 (RK)	binder / polyester resin	only for dilution

2.2 Methods

A Cary 60 UV-Vis Spectrometer is employed to determine absorbance spectra of liquid samples which are filled in cuvettes made of optical glass. Cuvette path length is 10 mm. According to the usual procedure, it is assumed that the measuring device works with standard light D65. To enable temperature-variable spectral measurements in transmission, it is necessary to convert the inks in stable suspensions, as it is not suitable to measure the pigments in pure solvent only. Stability here means to minimise potentially absorbance-influencing phenomena such as sedimentation, agglomeration and other particle interactions.

Stability is even more important as the suspensions are heated up twice within the spectrometer, which lasts approx. 90 minutes for each sample. Eight suspensions are heated even three times.

The pigments are dispersed manually using a glass muller in a binder mixture of EK 3120, 1-Methoxypropan-2-ol and dispersing agent (ratio: 0.485 : 0.485 : 0.03). The resin is completely soluble in organic solvents and, according to the manufacturer, has good pigment wetting properties. The 1-Methoxypropan-2-ol with its high evaporation number (22 to 8, compared to ethanol) is used, to minimise solvent evaporation during dispersion. Ethanol is then used to reduce the pigment pastes viscosity, although the final viscosity of the inks produced in this way is never identical – due to the respective pigment properties.

For absorbance measurements, each suspension must be brought to an absorbance strength appropriate for the measuring instrument ($A < 1$) by means of a dilution series. Depending on the specific absorption strength of the pigments, dilution rates between 1 : 1 000 and 1 : 10 000 are generated. The experiments have shown that dilution with ethanol only leads to unstable samples. Therefore, the samples are diluted with a 1 : 1 mixture of Ethanol and RK 7495. RK is used here because, unlike the slightly yellowish EK, it has no inherent colouring. The mixing ratio of 1 : 1 has proven to be well suited to keep the samples stable for an adequate period of time. The relatively high viscosity η of the mixture should also contribute to this and is provided by Table 3. It is determined in shear tests deploying a cone-plate viscometer Anton Paar MCR 101. For shear rates of 0–100 s^{-1} the fluids viscosities were shown to be independent of the shear rate. All measurement values are the result of averaging three individual measurements.

All samples rested for at least 72 hours before measurement, as experience has shown that this time contributes to higher stability during measurement. The cuvette, binders and diluents do not have their own thermochromism. However, temperature-specific baseline corrections related to a cuvette only filled with the diluent are made since a slightly decreasing absorbance with increasing temperature can be observed.

Table 3: Viscosities of a 1:1 solution of RK 7495 binder and ethanol for temperatures of 20–50 °C

Temperature (°C)	Viscosity (mPa·s)
20	99
30	65
40	41
50	27

Applying Equation [1], all spectral absorbances measured with the UV-Vis spectrometer are converted to spectral transmittances and can then be further processed to colourimetric numbers.

$$T = (10^{-A}) \cdot 100 \tag{1}$$

3. Results and discussion

3.1 Characteristic and reversibility

Figure 1 shows transmittance spectra for three samples in 20 °C resp. 50 °C ($\Delta T_{30°C}$) each. For most areas the transmittance increases with increasing temperature. But, deviations from this behaviour can be observed especially in areas with changing gradients. The peak of P.B. 15:1 (1.48 ΔE_{00} for 20 °C to 50 °C) is slightly shifted from 512 nm towards 514 nm while the regions of low transmittance on both sides of the peak show increasements. P.V. 19(β) (1.23 ΔE_{00}) shows increased transmittances and small peak shifts at around 550 nm. The distinct slopes of P.Y. 129 (1.71 ΔE_{00}) become somewhat blurred in areas of changing

gradients between 400 nm and 500 nm while one also sees a decrease at those blurred areas, in contrast to areas with higher transmittances.
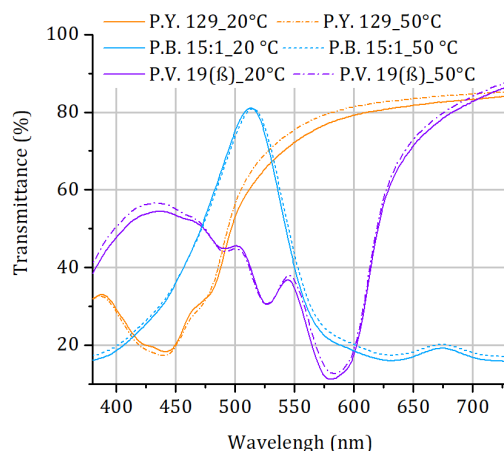

Figure 1: Transmittance spectra for three pigmented suspensions at two temperatures of 20 °C resp. 50 °C

The presence of a spectral red shift for blue and violet correspond to the findings of other researchers. Thermochromism does not seem to be limited to areas with changing gradients, a finding that differs from the ones in existing literature.

Except from Song, et al. (2014) and Yarborough, Haskin and Lambdin (1954) none of the mentioned authors have measured liquid suspensions but solid samples. It must be kept in mind that the temperature-dependent properties of a liquid phase have a potential influence on the measurements.

When a typical sample returns to 20 °C, the characteristic of its thermochromism is preserved in the spectrum, as Figure 2 shows. The 20 °C measurements already shown in Figure 1 are depicted with the spectra that are measured after the return to 20 °C. In this work, measurements of the second heating cycle are denoted with '_2'. In cases where the transmittance intensity increased due to heating, it remains and does not necessarily decrease during cooling. The peak shift of P.B. 15:1 recedes, but the areas off the peak only decrease slightly and remain on a level about two percentage points higher. P.Y. 129 at 400–500 nm loses even more transmittance intensity from 50 °C back to 20 °C and is clearly altered when it returns to 20 °C. Beside P.Y. 129, only P.V. 19(β) and 19(α) show a similar effect to some extent at 500 nm. Apart from such effects, the samples of this work are to be characterised as not fully reversible during their first heating and differ in this from the samples of other studies. Even after a rest period of three hours, the samples do not return to pre-first heating state.
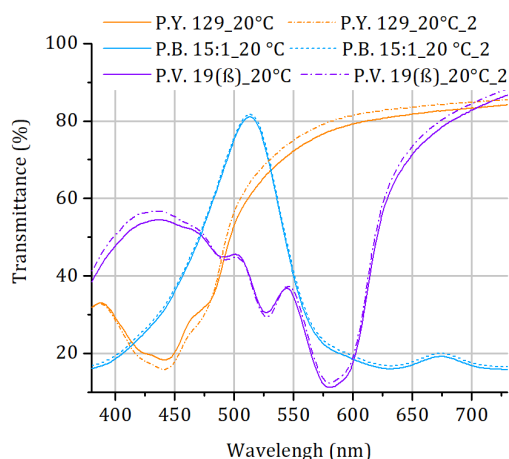

Figure 2: Transmittance spectra for three pigmented suspensions at 20 °C, before and after the first heating cycle

It could be shown that by heating up the samples initially, processes are initiated that affect the spectral characteristics. A subsequent second heating cycle leads to significantly different thermochromism, as Figure 3 illustrates. The visible spectral alterations are weakened. Unlike the first heating cycle, P.Y. 129 now shows an increased transmittance in areas of changing gradients. Again, one can observe a peak shift for the blue pigment, whereas violet no longer shows a shift at 550 nm. The spectra seem to follow the systematics of increased transmittance intensities and possibly slightly shifted peaks. Despite all the changes one can observe, the spectra at 50 °C are almost identical, regardless of whether they are measured during the first or second heating. P.V. 19(β) is among the samples heated up three times. Compared to the second cycle, both the 20 °C and 50 °C spectra of the third cycle are nearly identical to their temperature equivalent and do not indicate any other changes comparable to those determined for heating cycle one.
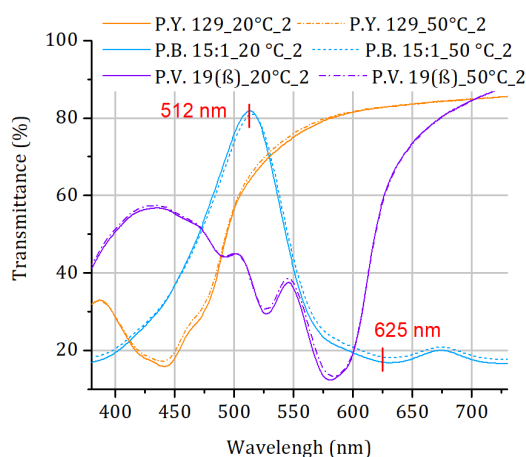

Figure 3: Transmittance spectra for three pigmented suspensions at 20 °C, second heating cycle

From this point on, the spectra reach a steady state and the thermochromism also appears to be completely reversible – as far it can be said for three measurement cycles. This reversibility is in accordance with results of other studies.

One conceivable explanation for the different results regarding reversibility in the heating cycles can be changes in absorption due to particle interactions. Agglomerations triggered by the first heating, for example, could change the particle size during the first phase. The viscosity changes due to heating can potentially facilitate these processes. However, particle interactions do not explain the opposed spectral effects for P.Y. 129 in the first cycle with decreasing (~ 430 nm) and increasing (~ 550 nm) wavelength areas. Considering that this behaviour is not observed in second heating phase, one can assume that structural changes occur in the pigment molecule during the initial heating.

3.2 Linearity

Other researchers described the linearity of thermochromism. The question whether the relationship between thermochromism intensities of the pigmented suspensions and temperature increases is linear or not can be answered by Figure 4. It shows the monochromatic transmittances for two wavelength intervals of P.B. 15:1 for seven temperatures from 20 °C to 50 °C. Depicted are the monochromaticities 512 nm and 625 nm in order to show a distinct peak as well as an area of high absorbance. The temperature-dependent rise reps. fall of the transmittance intensities shows a clear linear behaviour. Spectra from the second heating (cf. Figure 3) are used to check the linearity so that potential transformations during the first heating phase cannot falsify the outcome.
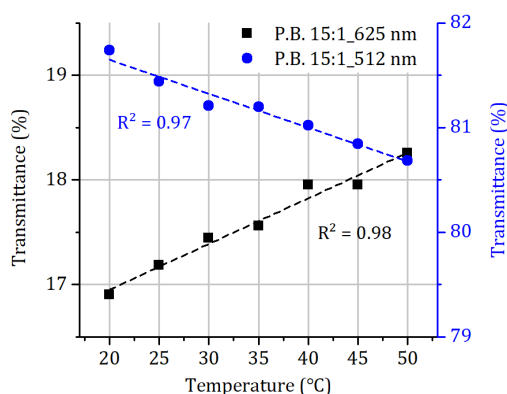
Figure 4: Transmittance intensities for PB 15:1 in wavelength intervals 512nm and 625 nm
for seven temperatures, second heating cycle

3.3 Colourimetric

To give an impression of changes in colour characteristics, Figure 5 shows a polar chroma-hue plot of all 43 samples, again for 20 °C and 50 °C measurements (depicted as coloured resp. black bordered circles). The data pairs corresponding to the spectra depicted in Figures 1 to 3 are marked.

For the majority of samples, chromaticities decrease, recognisable by the fact that the circles tend towards the centre. Remarkable here as well are the shifts in hue, especially for blue and green shades. The hues become smaller, hence the shades move towards the yellow areas. The spectral anomalies characterised in Figure 1 are also reflected in the colourimetric coordinates, as one can see aberrations in the data set. This refers to data points that do not show decreasing but increasing chromaticity values due to temperature rise, for example data point 1 for P.Y. 129.
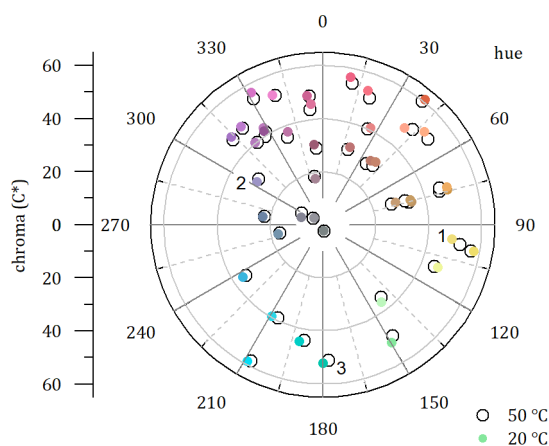

Figure 5: First heating cycle: Chroma (C*) and hue values of 43 organic pigments for temperatures of 20 °C resp. 50 °C,
P.Y. 129 (1), P.V. 19(β) (2) and P.B. 15:1 (3) are denoted

Figure 6 shows a chroma-hue plot for the second heating cycle. The shifts in chroma and hue are consistent with those of Figure 1, except for the fact that the initial spectral changes during the first heating no longer occur in the second cycle. This is well illustrated by data point 1 that shows decreased chromaticities and is in line with the majority of the data. The magnitude of chroma loss tends to be smaller for colours with rather low initial chroma values than the loss of colours of high chromaticities. Other researchers found that green and especially blue have low thermochromism compared to red and orange tones. This observation also applies to our examination, considering only ΔE_{00} values. But if one looks at the spectral characteristics and also the chroma and hue indicators, this rule does not hold. The magnitude of the percentage

spectral changes is quite similar for different wavelength intervals. But for pure reds, for example, these spectral changes add up to larger ΔE_{00} values due to their long edge and low absorptions in the red range and suggests a hue dependency.

In order to sum up the findings, colour distance ΔE_{00}, differences in lightness ΔL^*_{ab}, chromaticity ΔC^*_{ab} and hue Δh_{ab} values are provided in Table 4. For the pigmented suspensions, ΔE_{00} values >1 are observed.
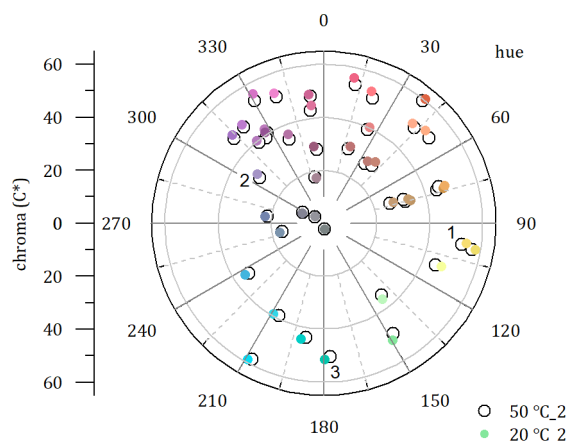

Figure 6: Second heating cycle: Chroma (C*) and hue values of 43 organic pigments
for temperatures of 20°C resp. 50 °C, P.Y. 129 (1), P.V. 19(β) (2) and P.B. 15:1 (3) are denoted

Table 4: Colourimetric results: ΔE_{00}, ΔL^*_{ab}, ΔC^*_{ab} Δh_{ab} are given as arithmetic mean $\bar{x}$ and 90th percentile,
related to measurements at 20°C and 50 °C ($\Delta T_{30°C}$) and two heating and measurement cycles

	First heating cycle ($\Delta T_{30°C}$)				Second heating cycle ($\Delta T_{30°C}$)			
	ΔE_{00}	ΔL^*_{ab}	ΔC^*_{ab}	Δh_{ab}	ΔE_{00}	ΔL^*_{ab}	ΔC^*_{ab}	Δh_{ab}
$\bar{x}$	1.05	0.72	1.35	1.36	0.95	0.64	1.37	1.00
p = 0.9	1.56	1.29	2.34	3.10	1.35	1.08	2.27	2.25

4. Conclusions

All pigment suspensions show temperature-dependent thermochromic effects whose linearity is in line with other researchers' findings. The spectral changes indicate alterations at the structural level between the first and subsequent heating cycles for three of the pigments. Apart from these phenomena, all samples aren´t reversible for the first measurement while there is reversibility for the subsequent measurements. This is either related to structural changes that affect all pigments or, more likely, to particle interactions triggered by the initial heating that lead to changes in absorbance strength. However, the study shows that even 'non-thermochromic' organic pigments show thermochromic behaviour, at least as liquid suspensions. Next steps in the thermochromism project are the use of further binders to put the absorption studies on a broader basis. In addition, the inks generated are to be applied and measured in order to investigate thermochromism in solid phase as well. In this work, thermochromism was measured at magnitudes well above 1 ΔE_{00}. If this is confirmed for printed samples, and the results of other studies suggest that it probably will be, thermochromism is a parameter that should be considered in temperature-variable production processes. Production tolerances of 2 ΔE_{00} are realistic for demanding print productions with inline colour measurement. A deviation from 1 ΔE_{00} merely due to temperature differences should not be ignored against this background.

Acknowledgements

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