Measurement 127 (2018) 554–564

Contents lists available at ScienceDirect

Measurement

journal homepage: www.elsevier.com/locate/measurement

Colorimetric analysis of thermochromic samples in different forms employing a digital camera

Ondrej Panák*, Markéta Držková, Natálie Kailová, Tomáš Syrový

Department of Graphic Arts and Photophysics, Faculty of Chemical Technology, University of Pardubice, Studentská 95, 532 10 Pardubice, Czech Republic

ARTICLE INFO

Keywords:
Reversible thermochromism
Thermochromic coating
Dynamic color change
Cumulative color difference
Calibrated camera

ABSTRACT

The calibrated and characterised digital camera was used for the recording of a dynamic colour change of thermally treated three-component leuco dye based thermochromic samples in various forms – bulk system, dry pigment, water- and solvent-based ink formulations, and their dry layers coated on different paper substrates. The study has proved that the proposed approach enables to examine the thermochromic behaviour through the individual stages of the thermochromic coating preparation process. The measured path in CIELAB colour space and derived characteristics of the dynamic colour change were obtained with higher time-temperature resolution than with previously employed methods, enabling to observe even the less distinct features. The most significant differences were related to the length and complexity of the colour path. Dry layers of the water-based thermochromic ink coated on papers had higher values of the total length of the path and the total colour contrast than the layers of the solvent-based ink. The colour of water-based coatings had higher chroma and also it was less influenced by paper substrate. When compared to the bulk thermochromic system, the dry pigment and dry ink layers on paper substrates exhibited a larger width of a hysteresis loop at the decolouration limit, mainly due to the decrease of the temperature at which the colouration starts on cooling.

1. Introduction

Leuco dye based thermochromic (TC) systems showing a reversible dynamic colour change in reaction to temperature changes are a popular choice in applications that require simple indication whether the matter was heated or cooled over or below a certain activation temperature. The dynamic colour change of these systems is based on a formation and destruction of a colour former and developer complex in an environment formed by a co-solvent [1–4]. The temperature interval, within which the colour change appears, is predominantly determined by the phase change characteristics of the co-solvent [5–9]. Other parameters, such as the difference between fully coloured and fully decoloured state and the hysteresis behaviour, depend on the interaction and ratio of selected substances [6,7,10–15]. The incorporation of the above-described materials into a binder of a printing ink or a coating requires their microencapsulation into a stable polymeric shell [4,16,17]. The in situ microencapsulation involving polycondensation of melamine-formaldehyde prepolymer [18–20] can be utilised.

The proper characterisation of a dynamic colour change is one of the key premises in the complex development process, going from the preparation of TC system through its conversion to a form enabling its incorporation into an ink formulation up to the application of TC ink on a substrate. There is a variety of techniques described in the literature allowing to obtain parameters carrying the information about the colour change. Such parameters are evaluated in dependence on the temperature. This dependence serves to determine characteristics of a dynamic colour change such as the colour contrast, the temperatures belonging to the start and end of colouration/decolouration, the colouration/decolouration rate and the width of a colour hysteresis loop.

The evaluation of colour density is often used in the literature, however without closer specification according to which standard was the colour density measured [5,6,16,17,21]. Reflectance spectroscopy is another widely used method. The spectra are evaluated according to predominant wavelength characterising the absorption maximum of the dye in its coloured form [1,3,10,11,22]. This approach is, however, limited [14]. More precise evaluation of a dynamic colour change is by computation of colorimetric parameters in CIELAB space from reflectance spectra [7,13–15,23–26]. The evaluation of a dynamic colour change is then based on the temperature dependence of colour coordinates or colour attributes in this colour space.

The observation of a dynamic colour change of leuco dye based TC materials by a digital camera has been used only rarely up to now;

---

*Abbreviations:*TC, thermochromic

* Corresponding author.

E-mail addresses: ondrej.panak@upce.cz (O. Panák), marketa.drzkova@upce.cz (M. Držková), natalie.kailova@student.upce.cz (N. Kailová), tomas.syrovy@upce.cz (T. Syrový).

https://doi.org/10.1016/j.measurement.2018.06.025
Received 1 March 2018; Received in revised form 18 May 2018; Accepted 13 June 2018

moreover, the setup and process of data collection and evaluation are not described [27], or the description raises doubts about the proper colour characterisation [12]. Employing of a digital camera is rather common in liquid crystal thermometry, where the colour response of TC liquid crystals is calibrated against temperature to investigate temperature or convective heat transfer distribution. Hue–temperature calibrations are the most common and widely used colour–temperature representations [28], utilising various techniques to calculate hue from the RGB components of the digitised images [29], mostly based on HSI or HSV colour space. Farina et al. [30] proposed a colour correction of measured RGB values using a scaled-down version of a standard colour chart (ColorChecker, MacBeth), but to the authors' knowledge, the proper camera colour characterisation step is usually omitted in practical investigations. The emphasis is put on optimising the colour-–temperature calibration, regardless the correct colorimetric representation of measured RGB values (see e.g. [28, 31, 32]).

Acquisition of colour information by a digital camera requires very good control over the image capture and processing. The first important factor is the proper and uniform illumination, which must be accompanied by the appropriate camera calibration and characterisation [33,34]. Camera characterisation provides a transformation of RGB data to CIEXYZ colorimetric coordinates, mostly by polynomial models that provide reasonable colour prediction [35–37]. Camera calibration and characterisation require set of colour patches with known colour characterisation, e.g. X-Rite ColorChecker [38]. The number of colour patches recorded influences the quality of camera characterisation [39]. More complicated methods apply the procedures where the spectral sensitivity of a camera is obtained in order to characterise the reflectivity of captured object [40–42].

There are several approaches in the literature, how to determine characteristics of a dynamic colour change from CIELAB coordinates or colour densities. The colour contrast can be determined as the difference between the values of the selected colour parameter at the upper and lower temperature limits [14] or it can be determined as the total colour difference between CIELAB colour coordinates at these two limits [13,23,26]. Characteristic temperatures can be evaluated from the colour density [5,16,17,43,44] or in the CIELAB space – from the lightness or chroma parameter [7,13,23–25] or from the cumulative colour difference [9,14].

In the literature, different combinations of characteristic temperatures chosen for the evaluation can be found, with various names and designations (even within publications from the same research group) [5,15–17,24,26,43,44]. The evaluated characteristic temperatures most commonly include the temperatures at which the colour change starts and ends, both on heating and cooling, respectively. The first of these four temperatures is called e.g. onset achromic [5], initial achromic [24], decolouration initiation [16,44], quenching starting [43], and decolouring starting [17] temperature. Moreover, the exact procedure of their determination from experimental data is not specified in most of the cases, which complicates or even disables reliable comparison of individual systems and methods.

The hysteresis can be characterised by a variety of parameters. The width of a hysteresis loop is often evaluated in a two-step process; first, the middle value of the respective colour parameter between colouration and decolouration limit is determined and then the width of a hysteresis loop is calculated as the difference between the temperatures at which the middle value was achieved on heating and cooling [13,14,16,17,44]. The degree of hysteresis can be also evaluated on the basis of the colour difference between CIELAB coordinates taken at the same temperature for the heating and cooling sequence [23–25]. Another approach implements the computation of the area which is enclosed by the two trajectories in CIELAB space characterising the heating and cooling sequence [24,26]. In our recently published work, we have introduced the cumulative colour difference as the parameter from which we can determine all characteristics of a dynamic colour change [8,9,14]. The cumulative colour difference incorporates changes in all colour attributes into one parameter that can be used as a basis for evaluation of characteristic temperatures and calculation of derived characteristics. The colour contrast determined as the difference between its values at upper and lower temperature limits, i.e. as the total length of the respective colour path, reflects the extent of a dynamic colour change. In addition, it ensures better resolution than the methods mentioned above when comparing samples undergoing similar colour changes. However, it depends on the course of the path in CIELAB space and thus it might diverge from the total colour contrast evaluated as the colour difference between upper and lower temperature limits as introduced in [23].

In respect to the experimental setup, obtaining colorimetric parameters by a spectrophotometer is limited by the size of the aperture and only one sample can be measured at a time. Sample dimensions and its accessibility by the measuring probe must be considered as well. Another limitation is the heating and cooling power of temperature controlled tables, on which the sample is placed, and the temperature resolution of the measurement, which was not smaller than 1 °C according to the literature dealing with leuco dye based TC systems.

This paper aims to evaluate the approach which applies the calibrated and characterised digital camera as a tool for recording the images of sample thermally treated by a programmable unit. The intention is to detect colour parameters with higher time-temperature resolution and evaluate the characteristics of a dynamic colour change by this approach for different kinds of samples. The set of samples studied by this setup comprises the selected leuco dye based TC system in a bulk form, the TC pigment formed by microcapsules containing this system as a functional core, the TC ink formulations with this pigment, and finally, the TC ink layers coated on paper substrates.

2. Materials and methods

2.1. Sample preparation

The functional core of microencapsulated TC pigments comprised the blue three-component TC system containing crystal violet lactone (6-(dimethylamino)-3,3-bis[p-(dimethylamino) phenyl] phthalide, > 95%) as the colour former, bisphenol A (2,2-bis(4-hydroxyphenyl) propane, > 99%) as the developer and 1-tetradecanol (> 98%) as the co-solvent in the molar ratio of 1:4:100, respectively. All compounds were obtained from Tokyo Chemical Industry and used without further purification. The TC system preparation is described in [14].

The formation of polymeric shell employed in situ polycondensation of melamine-formaldehyde prepolymer Melapret NF 70 (Melamine) in a water environment. First, 20 g of melted TC core were emulsified in 170 ml of deionised water by IKA Ultra Turax T18 homogenizer at 7000 rpm. Poly(ethylene-*alt*-maleic anhydride) with M_w = 100,000–500,000 (Sigma Aldrich), partly hydrolysed by sodium hydroxide, was used as the emulsifier; the content was 2 g. Amount of 9.5 g of the prepolymer was dissolved in 20 ml of water and the solution was slowly added to the reactor with the emulsion. The pH was adjusted to the value of 4.8 and the temperature during the microencapsulation process was kept in the interval of 69–72 °C. After 180 min, the pH in the reactor was adjusted to 7 and the suspension of microcapsules was cooled down. Dry particles were obtained by Mini Spray Dryer B-290 (Büchi); the temperature of the jet was set to 120 °C. The size distribution of microcapsules was obtained by Mastersizer 2000/MU (Malvern Instruments), a laser scattering analyser, applying Fraunhofer diffraction theory. The majority of particles (78.74% by volume) lied in the interval of 3.8–26.3 μm. No particles were found above 34.7 μm. The maximum of the particle size distribution lied in the interval of 10.0–11.4 μm.

Pigment powder was mixed into water-based and solvent-based binders in a mass ratio of 1:4. A 3% solution of carboxymethyl cellulose (M_w 250,000, Sigma Aldrich) was used as the water-based binder and a commercially available screen-printing varnish Polyplast PY383 with a