Optimization of the application of smart thermochromic dyes in textile printing

Assoc. prof. **Ana Sutlović**, Ph. D.
Assoc. prof. **Sandra Flinčec Grgac**, Ph. D.
Jagoda Mijač, mag. ing. techn. text.
Iva Brlek, mag. ing. techn. text.
University of Zagreb Faculty of Textile Technology
Prilaz baruna Filipovića 28a, Zagreb, Croatia
Correspondance: ana.sutlovic@ttf.unizg.hr
Recieved: September 30, 2020

UDC 677.016.4
Original scientific paper

With the development of microcapsulation technology, smart thermochromic dyes are increasingly being used in smart packaging as indicators of product freshness and temperature, in the field of document security, etc. In the field of textile printing, intelligent thermochromic dyes are increasingly being used as indicators of product freshness and temperature. They are used to realise products with added value in the field of aesthetic and functional design, but also in the field of smart textiles, which are widely used in medicine. In this papere, the optimisation of the use of a commercially available thermochromic orange dye in textile printing on cotton fabric was carried out using spectroscopic analysis methods. The investigation of the temperature range of the colour change shows visible changes in the real range of 28 to 45 °C, which are satisfactorily reproducible at temperatures of 30, 35 and 40 °C. The applied dye shows good laundry fastness after fixation at a temperature of 140 °C. Changes in the structure of the printed microcapsulated thermochromic dye were confirmed by FTIR GG-ATR analysis. The obtained results open the possibility to use the tested dye as a temperature change detector in the tested temperature interval.

Key words: *smart dyes, chromism, thermochromism, screen printing, spectrophotometry, FTIR GG-ATR*

1. Introduction

Modern textile materials are increasingly expected to change their properties in response to changes in the environment and are referred to as intelligent or smart materials [1-3]. Smart dyes that change colour under the influence of temperature, UV radiation, tension and various other stimuli and offer many other properties in addition to aesthetic ones are known as chromogenic dyes [2-4]. The process by which a reversible or irreversible change in the colour of a compound occurs is called chromism. In most cases, chromism is based on a change of electronic state in a molecule and refers to phenomena in which the colour is the result of a wide spectrum of light-material interactions, which can be classified into the following categories: reversible colour change, absorption and reflection of light, energy absorption, absorption light and energy transfer, and light manipulation [2-4]. The colour change can be:

- reversible, i.e. repeated and recurring, the material changes its colour under the influence of an external stimulus, and after the stimulus is removed, the colour returns to its original state in a short time;
- irreversible, i.e. unique and permanent. If the material is exposed to an external stimulus, it changes colour or the

original colour becomes more intense, but the system does not return to its original state [2-4].

Chromogenic compounds change their visual optical properties in response to external stimuli. Depending on the stimulus that causes the colour change, they are classified as: thermochromic (effect of a change in temperature), photochromic (effect of a change in light), electrochromic (response to a change in electric field), hygrochromic (change due to humidity), ionochromic (stimulus is a change in ionic species), biochrome (influence of a biochemical reaction), chemochrome (colour change due to certain chemical substances), solvatochrome (influence of the polarity of the solvent), mechanochrome (change due to deformation), piezochrome (influence of pressure), tribochrome (effect of friction), etc. [2-5]. Chromogenic materials are characterised by the following quality parameters: Colour change, intensity of colour change, transition conditions, rate of change, interval of change, ease of use, reversibility, number of cycles, behaviour during decomposition process, fading time, resistance to heat, light, humidity, allergic reactions, etc. [2-5].

Of all the chromogenic dyes on the market, photochromic [2, 4-7] and thermochromic dyes [8-11] are the most widely used and researched. Thermochromism is an easily observable reversible colour change caused by a change in the boiling or melting temperature of a thermochromic system. In thermochromic dyes, the activation temperature plays an important role, i.e. the threshold temperature at which a colour change or discolouration occurs and which is higher than the initial chromatic temperature and lower than the final achromatic temperature. Thermochromic dyes with a higher activation temperature provide a more stable and intense colour. The colour change can be reversible, i.e. it occurs repeatedly and reversibly, or irreversible, i.e. it is unique and permanent [12-17]. Thermochromic dyes are divided into two basic types, dyes based on liquid crystals and leuco dyes [4, 7]. Various printing techniques are used for its application, of which screen printing is preferred because it offers the greatest layer thickness, can be applied to all textile materials and offers a wide range of formats, which is why the range of applications is very wide [11, 13, 14, 18].

Thermochromic dyes, which are based on liquid crystals, are based on the property that the layers can move and change their inclination depending on the ambient conditions. Gradual heating and temperature increase lead to a violation of the geometric order, a change in the reflected wavelength and a colour change that can cover almost the entire colour spectrum. At the end of heating and cooling, the liquid crystal molecules return to their original position, so that the dye itself returns to its original colour [2, 4]. Thermochromic dyes, which are based on leuco dyes, consist of large organic molecules whose structures can absorb light of a specific wavelength. These thermochromic organic compounds consist of dyes, developers (usually organic acids) and solvents, and the components are mixed in precisely defined ratios (Fig.1). The colour change occurs through two reactions: between the dye and the developer and the solvent and the developer, which is much more important for achieving the thermochromic effect. The reaction between the dye and the developer takes place at lower temperatures when the solvent is in a solid state. As you increase the temperature, the state of the solvent changes from a solid to a liquid state, causing the dye and developer complex to break down, the solvent and developer to predominate and the whole system to become colourless (Fig.1). When the whole system cools down, the solvent changes to a solid state, and the developer and dye are reunited and the original colour of the system is restored [2, 4, 6-9].

Microcapsulation of the active thermochromic material is one of the basic requirements for the successful application of thermochromic dyes [4]. Some of the main advantages of microencapsulation of liquid crystals and leuco dyes are easier work with the inner phase, as it is protected by a

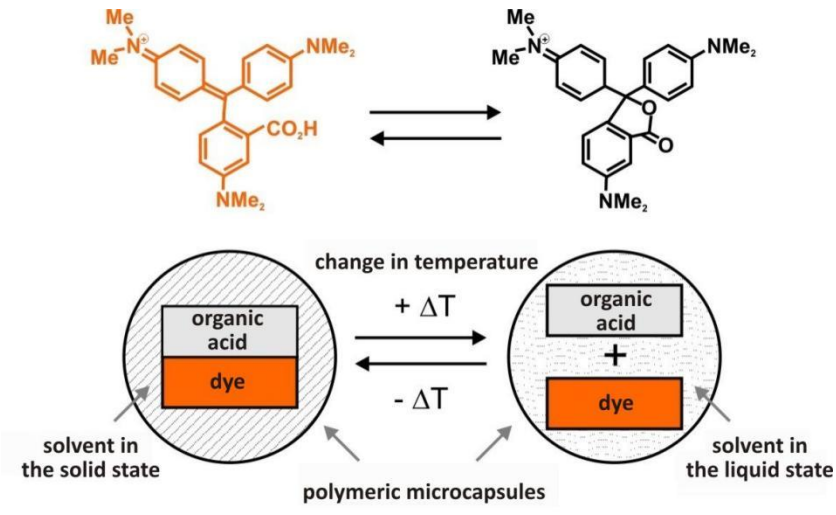


Fig.1 Schematic representation of changes in the molecular structure of thermochromic microcapsulated dyes upon heating / cooling [18]

water-soluble material; the inner phase with thermochromic properties is protected, which reduces the possibility of degradation; each individual liquid crystal droplet is completely capsulated, which prevents crystallisation of the mixture and mutual mixing of microcapsules of liquid crystals with different activation temperatures to achieve the effect of transition into multiple colours (Fig.1) [4].

Research into the application of thermochromic dyes in textile printing is aimed at solving problems in the area of achieving satisfactory colour fastness and uniformity, as mainly pastel shades are obtained due to the fact that they are microcapsulated dyes used in combination with an acrylic base [7, 23, 24]. Another major problem is the poor fastness, especially against laundering and rubbing [7, 13]. This problem can be exacerbated if the printed material is treated at high temperatures for a long time (e.g. during fixing), which can damage the microcapsules [13]. The optimisation of the objective spectrophotometric evaluation of the basic properties of thermochromic dyes, i.e. the determination of the functional dependence of the colour change and the temperature change, is based on the investigation of the temperature range of the colour change and the determination of the reversibility of the process [14-16]. The problem of reversibility, i.e. the occurrence of hysteresis, the difference in the colouring of textiles when heated to a certain temperature and cooled to the same temperature, is based on the structure of microcapsulated dyes (Fig.1) [9, 11]. The team of authors [9, 11, 13] carried out tests of the colour and thermal properties in correlation with changes in the structure of the dyes, and phase transitions, i.e. crystallisation of the system in two temperature ranges, cold (<15 °C) and hot (>50 °C) were detected, which leads to the hysteresis.

The contribution of the research in this work manifests itself in the analysis of the printing paste used and the optimisation of the fixing conditions with the aim of achieving satisfactory stability. The screen-printing of the thermochromic dye was carried out using standard acrylic paste, taking into account that microcapsules are used as conventional pigments as they have no affinity with fibres [7]. In addition, an investigation of the temperature range of the visible colour change was carried out in the realistic range of 28 to 45 °C, which proved to be satisfactorily reproducible at temperatures of 30, 35 and 40 °C. The structural changes of the microcapsulated orange thermochromic dye were confirmed by FTIR GG-ATR analysis. The tested thermochromic dye, which has a high sensitivity for a small temperature range, could be a simple and rapid method for monitoring body temperature, but such an application requires additional research towards its toxicological and dermatological effect on human health.

2. Experimenatal part

2.1. Textile material

It was used 100 % chemically bleached cotton fabric in plane weave from producer, Čateks d.o.o., Croatia. Textile has the following structural characteristics: weight 191.45 g/m^2, density in warp direction 26 cm^{-1}, density in weft direction 25 cm^{-1}.

2.2. Screen-printing with thermochromic dye

The application of the commercial microencapsulated thermochromic dye of orange tone Thermoseri Orange 21068 (Petrel, France) was investigated, in a concentration of 20% with an acrylic transparent base for pigment printing Printperfekt 226 EC (CHT Bezema, Germany).

The printing process was conducted by manual screen-printing, using the following tools: a manual lab-type flat screen-printing table, a wooden-handled polyurethane blade squeegee of 60 durometer hardness, and an aluminium 40 × 50 cm screen with a mesh of 62 threads/cm^2, the squeegee angle was kept between 7-10°. After screen-printing, the samples were dried in the air and the fixation was optimised.

2.3. Fixing of printed samples

The printed samples were fixed on the Fixotest 7501 device (Original Hanau, Hanau, Germany) by contact heat for 1, 2 and 4 minutes at temperatures of 100, 120 and 140 °C.

2.4. Analysis of printed samples

The following analyzes were performed on the samples printed with microncapsulated orange thermochromic dye Thermoseri Orange 21068:

– Microscopic analysis

To evaluate the uniformity of the impression and surface coverage, the analysis was performed using a Dino-Lite AM7013 USB microscope (New Taipei, Taiwan) at 50.7x and 216.7x magnification. Microscopic analysis of the thermochromic dye was carried out by taking a photo at room temperature of 23±2 °C and as a change in color loss during heating by recording a video.

– Spectrophotometric analysis

The investigation of the temperature range of colour change from 28 to 45 °C and the influence of reversible cycles of colour change during heating to temperatures of 30, 35 and 40 °C and cooling in five consecutive

cycles was carried out by determining remission curves and spectral characteristics on a Datacolor 850 spectrophotometer (Datacolor , Basel, Switzerland) with an integrated sample heating/cooling system [3].

– Analysis with FTIR spectrometer with ATR unit heated up to 300 °C

The samples were analysed using a Fourier transform infrared spectrophotometer (FTIR, Spectrum 100, Perkin Elmer, Shelton, CT, USA). The spectral curves of the samples were recorded using the attenuated total reflectance (ATR) technique with the possibility of heating to 300 °C (Golden Gate ATR) and the spectral curves obtained were processed using the Spectrum 100 programme. Four scans with a resolution of 4 cm^{-1} between 4000 and 380 cm^{-1} were recorded for each sample.

The analysis of the cotton fabric, the colour powder and the printed sample was carried out without heating and after heating to 40 °C immediately after reaching the temperature and after 2 and 5 minutes.

– Colour fastness to laundering

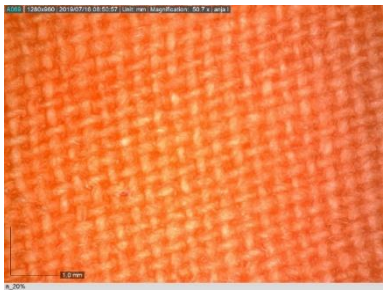
Testing the effect of fixing conditions on colour fastness to laundering was performed in laboratory apparatus for wet processes (Polycolor, Mathis) according to ISO 105-C06:2010 (A2S) *Textiles—Tests for colour fastness—Part C06: Colour fastness to domestic and commercial laundering*. Laundering was carried out with 0.5 g/l Kemopon 30 detergent (Kemo, Croatia) at a bath ratio of 1:30 at 30 ± 2 °C for 30 minutes. The samples were air dried. The analysis of colour fastness to laundering was evaluated as the value of the total colour difference (dE_{CIE76}), which was determined by comparing the samples before and after laundering (1st, 2nd and 3rd cycle). The colour difference values were calculated using equation (1):

$$dE_{CIE76}=((dL^*)^2+(dC^*)^2+(dh)^2)^{1/2}$$

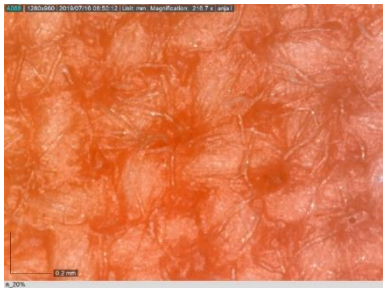
where: dL* difference in lightness value, dC* difference in chromaticity value and dh difference in tone value of samples before and after laundering.

3. Results and discussion

Considering that in the application of thermochromic microencapsulated dyes, the non-uniformity of deposition, surface coverage and satisfactory chromaticity [7, 23, 24] are considered to be the key problems, in the first phase of research, a microscopic analysis of the thermochromic dye at a room temperature of 23±2 °C (Fig.2) and the dynamic change in colour loss upon heating (Fig.3) was performed. The samples shown in Figs.2 and 3, i.e. the microscopic images and the video recording, confirm that uniform colouration with good chromaticity was obtained, which fade uniformly upon heating and complete decolourisation occurs.



a.



b.

Fig.2 Microscopic image of cotton fabric printed with 20% thermochromic dye Thermoseri Orange 21068, at magnification a. 50.7x, b. 216.7x

The objective spectrophotometric evaluation of the colouration obtained was carried out in the temperature range from 28 to 45 °C, i.e. in the temperature range of the possible realistic application of the printed samples as a heating indicator. The results obtained are presented as remission curves in the visible range of the spectrum

Tab.1 Colour parameters of cotton fabric printed with 20% thermochromic dye Thermoseri Orange 21068 in the temperature range from 28 to 45 °C

Sample	L*	a*	b*	C*	h°
N_20_28	62.58	51.74	36.28	63.19	35.03
N_20_29	62.99	51.15	35.34	62.17	34.64
N_20_30	63.69	50.15	33.88	60.52	34.04
N_20_31	64.85	48.45	31.55	57.82	33.08
N_20_32	67.14	44.83	27.05	52.36	31.10
N_20_33	69.32	41.10	22.96	47.08	29.19
N_20_34	70.58	38.92	20.83	44.14	28.16
N_20_35	71.50	37.33	19.35	42.04	27.40
N_20_36	73.32	34.12	16.70	37.99	26.08
N_20_37	75.56	30.14	13.78	33.14	24.58
N_20_38	78.48	24.69	10.54	26.85	23.12
N_20_39	81.60	18.48	7.85	20.07	23.03
N_20_40	84.69	11.91	5.57	13.15	25.07
N_20_41	86.17	8.50	4.73	9.73	29.08
N_20_42	87.20	6.10	4.25	7.43	34.89
N_20_43	87.90	4.38	3.95	5.89	42.04
N_20_44	88.13	3.81	3.86	5.42	45.33
N_20_45	88.24	3.54	3.80	5.19	47.03

Fig.3 Dynamic change in color loss of thermochromic dyes upon heating; https://youtu.be/HawcwXMoF-w [25]

from 400 to 700 nm (Fig.4), colour parameters of lightness (L*), colour coordinates (a* and b*), chromaticity (C*) and hue (h°) (Table 1) and the ratio of coordinates a*/b* (Fig.5). Fig.4 shows that the samples retain the orange base colour with the highest remission value (λ_{max}) at 440 nm when heated over the entire temperature range. The density of the curves is higher at temperatures from 28 to 30 °C and from 43 to 45 °C, which is consistent with the literature [9, 11], i.e. the fact that microcapsulated thermochromic dyes crystallise at phase transitions (Fig.1) in two temperature ranges. The same is evident from Fig.5 and Tab.1, i.e. the change in colour hue (h°) occurs in the interval from 35.03 (at 28 °C) to 47.03 (at 45 °C), with the difference between the measurements being smaller, i.e. the beginning and end of the temperature interval. The print at 28 °C has a high chromaticity value (C*) of 63.19, which confirms a good choice of dye concentration and print paste composition in general. When heated to 45 °C, the chromaticity value increase to 5.19, which, together with the lightness (L*) of a high 88.24, results in a satisfactory colour loss, i.e. a "colourless" sample, which is also evident from the remission curve with a value at 440 nm of over 70%.

Due to the phase change (Fig.1) in the structure of microencapsulated thermochromic dyes, hysteresis occurs, i.e. different colouration at

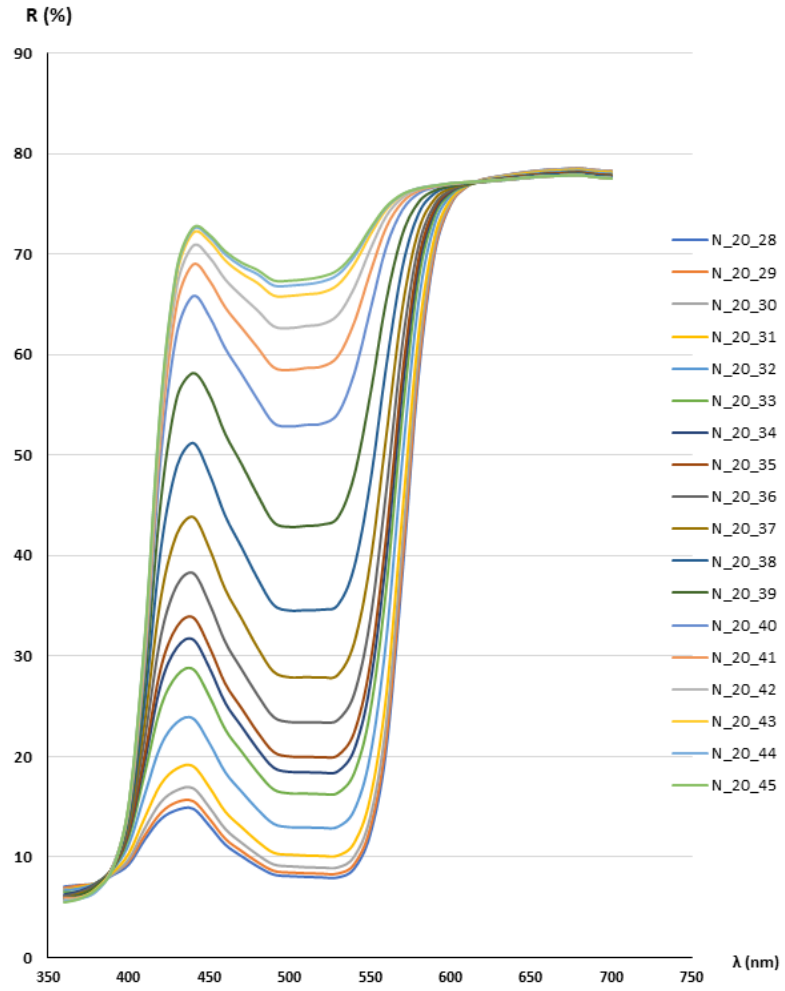


Fig.4 Remission curves of cotton fabric printed with 20% thermochromic dye Thermoseri Orange 21068 in the temperature range from 28 to 45 °C

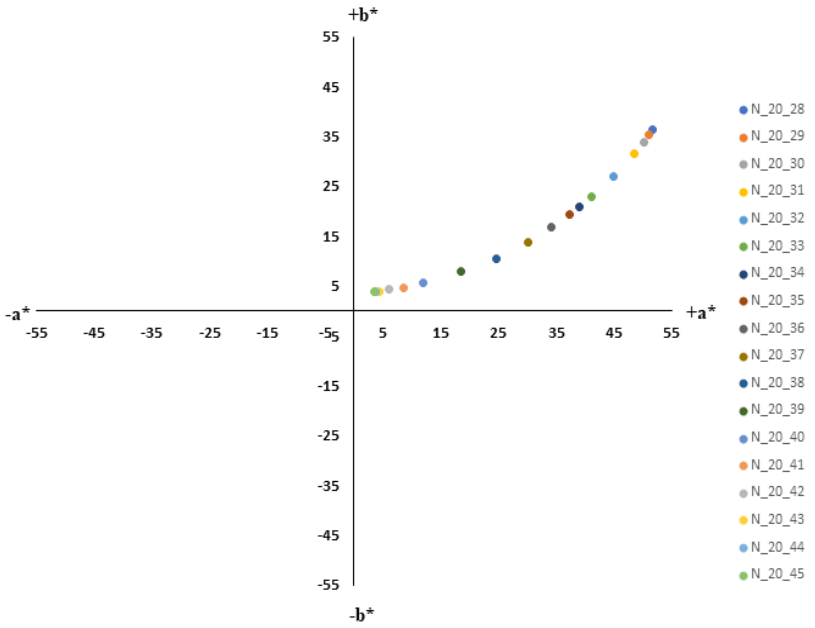


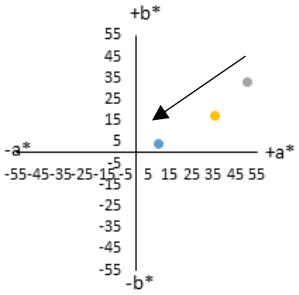
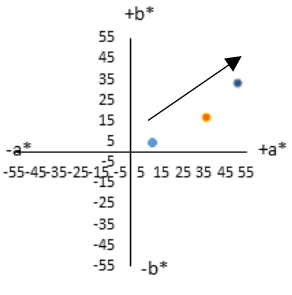
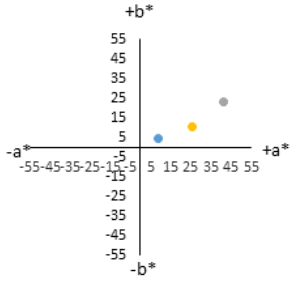
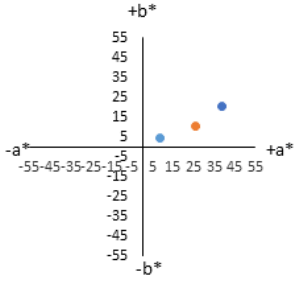
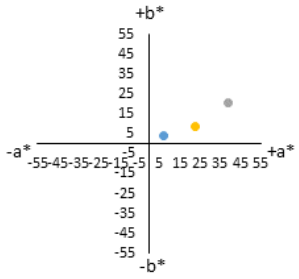
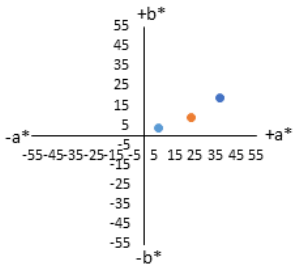
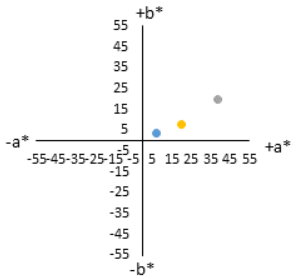
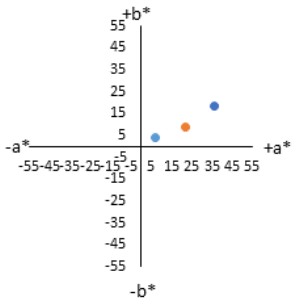
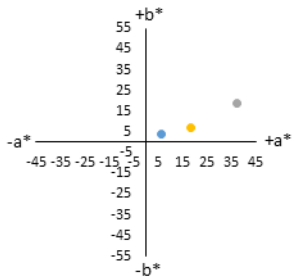
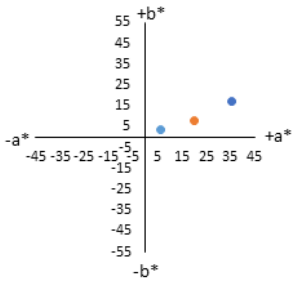
Fig.5. a*/b* graph of cotton fabric printed with 20% thermochromic dye Thermoseri Orange 21068 in the temperature range from 28 to 45 °C

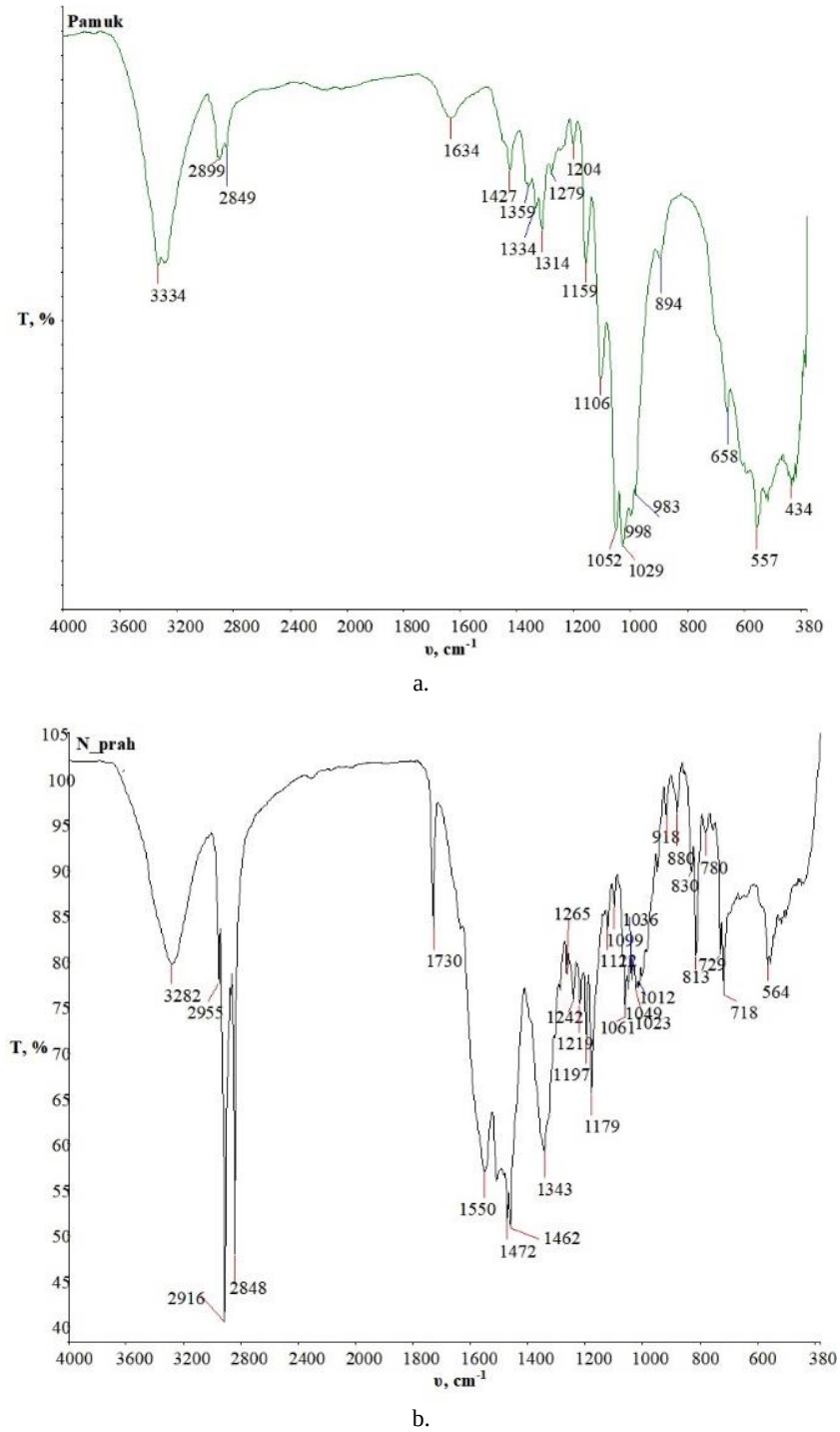
the same temperature, depending on whether it was caused by heating or cooling [9, 11]. Due to this property, the influence of reversible cycles of colour change when heating to temperatures of 30, 35 and 40 °C and when cooling in five consecutive cycles was investigated. The results obtained, (Tab.2), show satisfactory reproducibility within one cycle. When repeating the heating and cooling process, deviations occur at 35 °C, while the samples at 30 and 40 °C are satisfactorily reproducible. This study confirmed the stability of the printed sample with repeated use.

The analysis of the cotton fabric, the thermochromic microencapsulated dye and the cotton fabric printed using the mentioned dye was carried out by FTIR spectrometry using a heated unit of ATR (GG-ATR). The results are shown in Figs.6 and 7.

Fig.6 shows the spectra of cotton fabric (Cotton) and orange coloured, thermochromic microencapsulated dye powder (N_powder). The spectrogram of the cotton material in Fig.6a shows the appearance of a spectral band characteristic of cellulose material. In the range from 3650 to 3590 cm^{-1} vibrations occur within the non-bonded O-H groups. The peak at the wavenumber 1425 cm^{-1} indicates the symmetrical bending of the CH_2 bond at the C-6 atom. To better understand of the changes that occur after printing the cotton material, the properties of the cellulose peaks from 1157 to 660 cm^{-1} are given. The vibrations occurring in the cellulose are as follows: 1157 cm^{-1} asymmetric C–C bonds; 1104 cm^{-1} C–O–C bridges of the glycosidic bonds, with the antisymmetric stretching of the bonds occurring in the plane of the rings; 1054 cm^{-1} C–OH secondary alcohols and the stretching of the C-O bond, 1027 cm^{-1} C–OH primary alcohols; 1001 and 983 cm^{-1} –CH bonds and 897 cm^{-1}

Tab.2 a*/b* graphs of cotton fabric printed with 20% thermochromic dye Thermoseri Orange 21068 heated to 30, 35 and 40 °C and cooled in 5 consecutive cycles

Cycles	Heating	Cooling
1.		
2.		
3		
4.		
5.		
Legend:	N_20_z_30 N_20_z_35 N_20_z_40	N_20_h_40 N_20_h_35 N_20_h_30



a.

b.

Fig.6. Spectral curves of cotton fabric (a.) and thermochromic dye powder (b.)

C(1)–O–C(4) symmetric bond [26].

The spectral band of the thermochromic microencapsulated dye powder (Fig.6b) shows a series of peaks as follows: 3282 cm^{-1} caused by NH stretching, peaks ranging from 2955 to 2848 cm^{-1} caused by symmetric and asymmetric CH_2 stretching, peak at 1730 cm^{-1} indicates C=O stretching, 1343 cm^{-1} stretching in the C–N group and the peak at 1462 cm^{-1} caused by bending within the methylene groups. From this it can be concluded that polyurethane is present in the dye itself, i.e. in the microcapsules, which probably forms the shell of the thermochromic dye micro-capsules [27].

From the spectral curves shown in Fig.7, it can be seen that all spectral curves have characteristic peaks, including the thermochromic dye powder shown in Fig.6b. When thermochromic microencapsulated dyes are heated, the dye/organic acid components separate and the dye transforms into an insoluble form. In the insoluble form, the carbonyl group C=O is present in the dye molecule, while the dye dissolves when the heat is removed, i.e. the alcoholic C-OH group is present (Fig.7). The peaks in the spectra that appear upon heating indicate changes in the microencapsulated dye molecule and are the result of the decomposition of the dye-developer complex that causes the discolouration. The visible changes in the samples mentioned consist of a reduction in the intensity of the characteristic peaks when the dye comes into contact with heat. The peaks at 2915, 2917 and 2849 cm^{-1} indicate the stretching of the CH, CH_2 and CH_3 groups in the aliphatic chains of the fatty acids, and the peak at 1728 cm^{-1} indicates the presence of ester groups. The peak at 1550 cm^{-1} indicates the vibrations of the carboxylate and is significantly reduced when the sample comes into contact with the ATR crystal heated at 40 °C, while the peaks at 1239 and 1100 cm^{-1} also indicate the presence of an ester group. At peak 1177 cm^{-1} characteristic of O-C-O stretching is observed, while at 813 cm^{-1} a peak characteristic of the vinyl group CH_2=CH- is seen [16,17].

In all samples of cotton fabrics treated with thermochromic dyes, there are clearly visible differences in the intensity of the individual peaks, indicating a change in physical and chemical properties due to the effect of heat.

Fixing of the printed samples was carried out by exposing them to contact heat for 1, 2 and 4 minutes

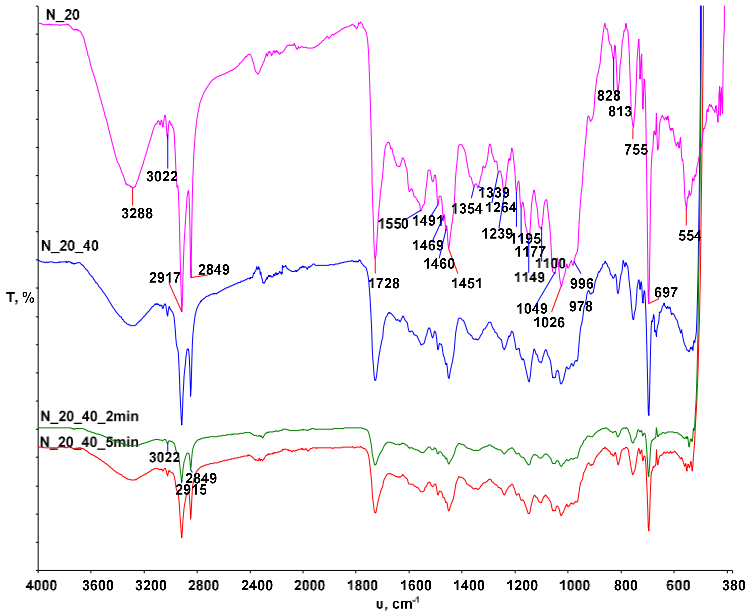


Fig.7 FTIR spectra of cotton fabric printed with thermochromic paste (dye concentration 20%) at room temperature (N_20), immediately after contact with the heated ATR crystal at 40 °C (N_20_40) and after 2 (N_20_40_2min) and 5 minutes (N_20_40_2min) i 5 minuta (N_20_40_5min)

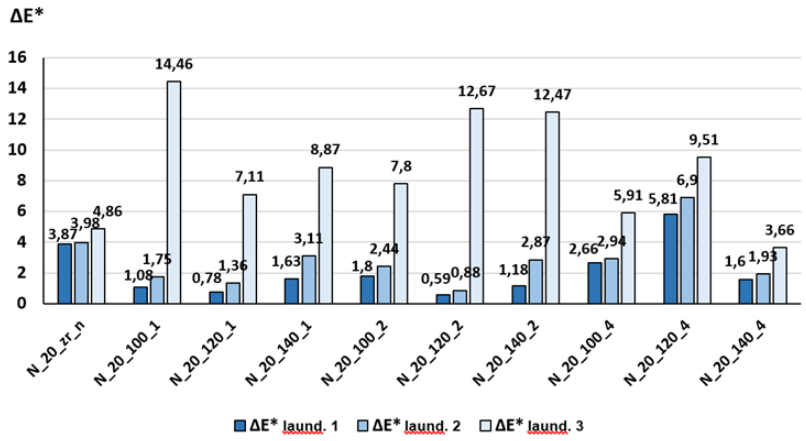


Fig.8 Colour fastness to laundering

at temperatures of 100, 120 and 140 °C, and the influence of the fixing conditions on the colour fastness to laundering was tested. The analysis of colour fastness to laundering was evaluated by calculating the total colour difference (dE_{CIE76}), comparing the samples before and after laundering (1st, 2nd and 3rd cycle). The results obtained are shown in Fig.8. Since microcapsules are used as conventional pigments because they have no affinity for fibres, the screen-printing of the thermochromic dye was carried out using standard acrylic paste as the base, the main disadvantage of which is its relatively poor durability [7, 11-18, 23]. In addition, the evaluation of the fixation conditions in combination with the repeated washing process indicates the stability of the microcapsules used. The results obtained (Fig.8) show that unfixed samples have an overall colour difference (dE) of 3.87 (1st laundering cycle) to 4.96 (3rd cycle) before and after laundering. When fixed under all conditions after the 1st laundering cycle, dE increase below 3 and reaches an satisfactory value of 0.59 after fixation at 120 °C, 2 minutes. After the 3rd cycle, however, the fastness is worse, i.e. dE increases to a value of over 5. The fixation conditions of 140 °C, 4 minutes, can be set as optimal. The fastness achieved after exposing the printed sample to a high temperature for a relatively long period of time indicates the stability of the printing paste, the microcapsules and the dye itself.

4. Conclusion

Thermochromic dyes occupy an important place in the development of modern materials, as they contribute to the development of smart materials and have not yet been fully researched in the field of application on textile substrates. Scientific research focuses on the definition of analysis methods for microcapsulated thermochromic dyes with the aim of extending their application, improving their properties (e.g. laundry and light fastness) and simplifying application procedures.

Based on the research results in this paper, it can be concluded that the applied microscopic and spectroscopic methods confirmed the possibility to define the temperature range of visible colour change and to test the reversibility, i.e. the occurrence of hysteresis, the difference in the coloration of textiles when heated to a certain temperature and cooled down to the same temperature.

For the commercially available microencapsulated thermochromic dye Thermoseri Orange 21068, it was confirmed that a uniform colour of extremely good saturation (C*=63.19) was obtained, which disappears evenly when heated and complete decolourisation occurs. The proposed printing paste shows satisfactory colour reproducibility after five heating and cooling cycles and excellent stability under the con-

ditions of fixation at 140 °C for 4 minutes. Phase transitions rela-ted to the chemical composition of the dyes were confirmed by FTIR GG-ATR analysis.

Acknowledgement

This work was co-financed by the Croatian Science Foundation with the project UIP-2017-05-8780 *Hospital protective textiles*.

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