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Influence of Different Colourants on Properties of Cotton Fabric, Printed with Microcapsules of Photochromic Dye

Vpliv različnih kolorantov na lastnosti bombažne tkanine, potiskane z mikrokapsulami fotokromnega barvila

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Abstract
In this study, the influence of the addition of classical pigment, phosphorescent pigment and microcapsules of thermochromic dye on the photocolouration as well as on physical-mechanical properties of cotton fabric printed with microcapsules of photochromic dye was studied. Seven printing pastes of different compositions were prepared. Printing pastes were applied onto 100% cotton fabric using a flat screen printing technique. The thickness, mass per unit area, stiffness, tear strength and elongation, and air permeability of printed samples were measured, whilst colour and colour fastness to rubbing, washing and light were spectrophotometrically evaluated. The thickness, mass per unit area, stiffness and tear strength and elongation of printed fabric increased, whilst air permeability decreased by at least a third in comparison with unprinted fabric. The addition of classical pigment, phosphorescent pigment or microcapsules of thermochromic dye into printing paste that already includes microcapsules of photochromic dye decreases the photocolouration of printed fabric, among which classical pigment has the smallest and microcapsules of thermochromic dye has the largest impact. Photocolouration of fabric decreases with increasing numbers of rubbing cycles; the addition of classical pigment has the smallest and the addition of microcapsules of thermochromic dye has the largest influence. The colour fastness to washing of printed fabric was decreased by increases in the number of washing cycles. The addition of any pigment into printing paste that already contains microcapsules of photochromic dye impairs its colour fastness to washing. By lengthening the time of exposure of printed fabric to the Xenotest apparatus, a reduction of colour fastness to light of printed fabric is produced. The addition of classical pigment, phosphorescent pigment or microcapsules of thermochromic dye into printing paste that already contains microcapsules of photochromic dye slightly slows down the reduction of colour fastness to light exposure of fabric printed with microcapsules of photochromic dye.
Keywords: photocolouration, microencapsulated photochromic dye, cotton, flat screen print

Izvleček
V raziskavi je proučevan vpliv dodatka klasičnega pigmenta, fosforescenčnega pigmenta in mikrokapsuliranega termokromnega barvila na fotoobarvanje in fizikalno-mehanske lastnosti bombažne tkanine, potiskane z mikrokapsulami fotokromnega barvila. Pripravljenih je bilo sedem tiskarskih past različnih sestav. Tiskarske paste so bile nanesene na 100-odstotno bombažno tkanino s tehniko ploskega filmskega tiska. Potiskanim vzorcem so bili izmerjeni debelina, ploščinska masa, togost, pretržna sila in raztezek, zračna prepustnost, barva in barvne obstojnosti pri drgnjenju, pranju in na svetlobi. Slednji sta bili spektrofotometrično ovrednoteni. Potiskanim tkaninam so se povečali debelina, ploščinska masa, togost, pretržna sila in pretržni raztezek, medtem ko se je zračna prepustnost v primerjavi z nepotiskano tkanino za več kot tretjino zmanjšala. Dodatek klasičnega pigmenta, fosforescenčnega

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pigmenta ali mikrokapsuliranega termokromnega barvila v tiskarsko pasto, ki je že vsebovala mikrokapsule fotokromnega barvila, je zmanjšal fotoobarvanje tkanine, med katerimi je imel klasični pigment najmanjši vpliv, mikrokapsule termokromnega barvila pa največjega. Fotoobarvanje tkanine se je zmanjšalo z naraščajočim številom ciklov drgnjenja. Na to je najmanj vplival dodatek klasičnega pigmenta, najbolj pa dodatek mikrokapsuliranega termokromnega barvila. Barvna obstojnost potiskanih tkanin pri pranju se je zmanjšala z naraščajočim številom ciklov pranj. Dodatek kateregakoli pigmenta v tiskarsko pasto, ki je že vsebovala mikrokapsule fotokromnega barvila, je poslabšal barvno obstojnost tkanin pri pranju, potiskanih z mikrokapsulami fotokromnega barvila. S podaljševanjem časa osvetljevanja vzorcev v aparatu Xenotest se je zmanjševala barvna obstojnost vzorcev na svetlobi. Dodatek klasičnega pigmenta, fosforescenčnega pigmenta ali mikrokapsuliranega termokromnega barvila v tiskarsko pasto nekoliko upočasni poslabšanje barvne obstojnosti bombažne tkanine na svetlobi, potiskane z mikrokapsulami fotokromnega barvila.

Ključne besede: fotoobarvanje, mikrokapsulirano fotokromno barvilo, bombaž, ploski filmski tisk

1 Introduction

Interest in colour-active textiles has significantly increased. The specific structure of some dyes allows them to be responsive to changes in electromagnetic waves (visible light, UV and IR radiation), electric current, temperature, pressure, pH value and other environmental factors. The change in dye structure can be visually perceived by the formation of or change in colour. Therefore, several types of chromism exist according to the external factors that activate the dye, namely, photochromism (UV radiation), thermochromism (heat), solvatochromism (solvent), halochromism (pH change), piezochromism (pressure), ionochromism (ions), metallochromism (coordination of metal ions with ligands), and electrochromism (electric current or electric potential) [1]. To date, photochromic dyes, which are responsive to UV radiation, have been rarely used in textile products for commercial purposes, due to their low light fastness properties, but they are more often used for technical purposes. Photochromic dyes are already used for prints to increase security and to protect brands, as well as in textile sensors [2, 3]. Photochromic dyes are capable of changing their chemical structures and, thus, their colour due to UV radiation. Under UV light, molecules of photochromic dye pass from the ground state (colourless form) to the excited state (coloured form). The change in the absorption spectrum of the dye is the result of a chemical change in the dye. When the dye passes from the ground to the excited state, the bathochromic shift of the absorption spectrum is noticed, i.e., a shift to longer wavelengths.

In previous studies, different factors that affect the intensity of the photocolouration of textiles that were dyed or printed with photochromic dyes, were explored. The following factors were investigated: the type of textile substrate (different degree of fibre crystallinity), photochromic dye structure, dye concentration, type of solvent, type of fixation and after-treatments and the influence of UV-absorbers and different stabilizers [1–16]. Since the photocolouration also depend on irradiated light and irradiation time, researchers also studied the influence of those factors [5, 6]. In the literature, no studies were found that evaluate how the addition of classical pigment, microcapsules of thermochromic dye or phosphorescent pigment affects the photocolouration of cotton fabric printed with microcapsules of photochromic dye using the flat screen printing technique. It was assumed that different pigments (classical or phosphorescent) or microencapsulated thermochromic dye would reduce the photoresponsiveness of printed fabric and offer some additional effect. After printing, physical-mechanical changes of the printed fabric are also expected.

2 Experimental

2.1 Materials

2.1.1 Fabric

Chemically pre-treated 100% cotton fabric with mass of 124 g/m^2, warp density of 50 threads/cm and weft density of 30 threads/cm, in plain weave, produced by Tekstina, Ajdovščina was used.

2.1.2 Dyes, pigments and auxiliaries

Cotton fabric was printed with microcapsules of photochromic dye (MFC) Itofinish UV BLUE (Lj Specialities, UK), classical pigment (KP) Minerprint RED RTL HC (Achitex Minerva, Italy), ready-to-use printing paste with phosphorescent pigment (FS) Itoglow in Dark Neutral (Lj Specialities, UK) and microcapsules of thermochromic dye (TK) Itothermochromic Lime (Lj Specialities, UK).

For the preparation of printing pastes, the following auxiliaries were used: a synthetic thickening agent for pigments with good stability to electrolytes (Clear CP), a self-crosslinking binding agent (Legante SE Conc.), a highly stable silicone softening agent for improvement of both printing handling and dry rubbing (Finish S), and a non-formaldehyde self-crosslinking agent (Fixator NFO). The producer of above listed auxiliaries is Achitex Minerva, Italy.

2.1.3 Preparation of printing paste and printing

Stock thickening agent (MZ) was prepared in accordance with the producer's instructions using the following recipe: 740 g cold distilled H_2O, 40 g Clear CP, 200 g Legante SE conc., 10 g Finish S and 10 g Fixator NFO.

Seven printing pastes (TP) with different concentrations of dyes, pigments or their mixtures were prepared. Their compositions are presented in Table 1.

Samples of cotton fabric were printed with printing pastes of different compositions, using a laboratory magnetic printing machine Mini MFD R 390 (J. Zimmer, Austria). Prints were made by two passages of a squeegee with a diameter of 6 mm, velocity of 80%, and a degree of magnetic force of 3. An unpatterned screen stencil with mesh of 42 threads/cm, was used. After printing, the samples were dried for 2 min at 100 °C and then cured for 4 min at 150 °C in a laboratory dryer (Mathis, Switzerland).

2.2 Methods

Thickness

Measurements of the thicknesses (*d*) of the printed samples were performed with a Metrimpex TYP 6-12-1/B micrometer apparatus (Mitutoyo Corp., Japan) using the EN ISO 5084:1996 standard [17]. Measurements were taken with a pressure of 25 cm² and a 20 cN/cm² load.

Mass per unit area

Mass per unit area of unprinted and printed samples was determined using the EN 12127:1997 standard [18]. Mass per unit area (*T*), expressed in g/m², was determined from the average value of all measurements.

Stiffness of fabric

The stiffness of unprinted and printed samples was determined according to the ASTM D 1388-64 standard [19].

Air permeability

The EN ISO 9237:1995 standard [20] was used for the determination of the air permeability of the fabric using an Air Tronic 3240B apparatus (Mesdan, Italy). Measurements of airflow were performed with a measuring area of 100 cm² and an air pressure of 150 Pa. It should be emphasized that the face of the printed sample was turned to the air aperture during the measurements.

Table 1: Sample labels and compositions of printing pastes

Sample	Printing paste	MZ[a)] [g/kg]	MFC[b)] [g/kg]	KP[c)] [g/kg]	FS[d)] [g/kg]	TK[e)] [g/kg]
VZ0	/	/	/	/	/	/
VZ1	TP1	800	200	/	/	/
VZ2	TP2	995	/	5	/	/
VZ3	TP3	995	/	/	5	/
VZ4	TP4	995	/	/	/	5
VZ5	TP5	795	200	5	/	/
VZ6	TP6	795	200	/	5	/
VZ7	TP7	795	200	/	/	5

[a)] Stock thickening agent, [b)] Microcapsules of photochromic dye, [c)] Classical pigment, [d)] Ready-to-use printing paste with phosphorescent pigment, [e)] Microcapsules of thermochromic dye

Breaking force and elongation

Measurements of breaking force and elongation were performed on an Instron 5567 apparatus (Instron, UK) according to the EN ISO 13934-1:1999 standard [21]. The method was modified with the measurements performed at a fasten length of 50 mm, velocity load of 100 mm/min and sample size of 15 cm × 2.5 cm. From each printed sample, five test pieces in the warp direction and five test pieces in the weft direction were cut out.

Resistance to rubbing

The printed samples were exposed to rubbing on a Martindale M235 apparatus (SDL International LTD, UK). Rubbing was performed only on samples printed with MFC, namely, VZ1, VZ5, VZ6 and VZ7. The test pieces were rubbed for 100, 300, 500 and 1,000 cycles at a load of 9 kPa. The number of rubbing cycles was selected according to the study Ocepek et al. [22]. Resistance to rubbing was spectrophotometrically evaluated by the determination of the colour difference of the rubbed test pieces before and after irradiation of the test peace with ultraviolet A (UV-A) light and compared to unrubbed pieces. Exposure of test peace to UV-A light last 1 min using two Philips TL-D 18 W actinic bulbs. The distance between the bulbs and the test peace was 11 cm.

Colour fastness to washing

The EN ISO 105-C06:2010 [23] standard was used to determine the colour fastness of the printed samples to domestic and commercial laundering. Washing was performed in a Gyrowash apparatus (James Heal, UK). Three test pieces with dimensions of 10 cm × 4 cm were cut out of samples VZ1, VZ5, VZ6 and VZ7. The first test piece was washed using the A1S method, whilst the other two were washed using the A1M method. The third test piece was subjected to the A1M washing method twice, which corresponds to ten domestic washing cycles.

Colour fastness to artificial light

Printed samples were subjected to the EN ISO 105-B02:2014 [24] standard in a Xenotest Alpha apparatus (Atlas, USA). One test piece of each sample was illuminated for 1, 6, 12 and 24 h.

Colour measurements

The colour of the printed samples was analysed using a Datacolor Spectraflash 600 PLUS-CT spectrophotometer. Measurements were performed in the range of 400–700 nm, with a d/8° measuring geometry, under D_{65} illumination, 10° standard observer, with specular reflectance included and the UV component excluded (0% UV, filter FL40 on), with a 9-mm aperture. Four layers of sample were used for the measurements. An average of five measurements was taken for each sample. CIE $L^*a^*b^*$ colour values were measured before and after irradiation of the samples with UV-A light for 1 min.

The total colour difference (ΔE^*) between the samples, tested to rubbing, washing and light, before and after irradiation with UV-A light, were calculated in accordance with the Equation 1 [25] and compared to untested samples:

$$\Delta E^*_{ab} = \sqrt{(L^*_v - L^*_{st})^2 + (a^*_v - a^*_{st})^2 + (a^*_v - a^*_{st})^2} \qquad (1),$$

where L^* is lightness, a^* is the red/green coordinate and b^* is the yellow/blue coordinate. Index *st* presents the sample before irradiation and index *v* after irradiation with UV-A light.

Scanning electron microscopy (SEM)

Test pieces of samples VZ1, VZ6 and VZ7 subjected to different numbers of rubbing cycles in the Martindale apparatus were also investigated using a JSM-7600F scanning electron microscope (JEOL, Japan) at 1500x magnification.

3 Results and discussion

In Table 2, measurements of thickness, mass per unit area, stiffness and air permeability of the studied samples are collected. From the values of thickness, it can be seen that the application of printing paste slightly increases the fabric thickness (samples VZ1-VZ7) since all printing paste ingredients stay on fabric surface after printing. Among the studied samples, no crucial difference between values of thickness is noticed. They are in the range of an experimental error.

From Table 2, it can also be seen that there is an increase of mass per unit area in all printed samples, irrespective of the printing paste composition. When MFC or pigment was added into the printing paste (samples VZ1, VZ2, VZ3 and VZ4), the addition of MFC (sample VZ1) has a greater influence on the increase of mass per unit area than the addition of

Table 2: Thickness, mass per unit area, stiffness in the warp and weft directions, overall flexural rigidity and air permeability of the studied samples

Sample	Thickness [mm]	Mass per unit area [g/m²]	Stiffness in the warp direction [mg·cm]	Stiffness in the weft direction [mg·cm]	Overall flexural rigidity [mg·cm]	Air permeability [mm/s]
VZ0	0.230	124	307.32	110.16	184.00	307.30
VZ1	0.237	143	525.32	144.12	275.15	19.47
VZ2	0.236	136	490.46	138.83	260.94	84.77
VZ3	0.236	137	506.62	139.78	266.11	99.50
VZ4	0.236	137	490.80	137.35	259.64	76.94
VZ5	0.237	146	608.07	150.52	302.53	23.15
VZ6	0.242	144	669.90	145.85	312.58	18.55
VZ7	0.242	143	575.75	144.09	288.03	26.30

pigment. The reason could lie in larger concentration of MFC than concentration of KP, FS or TK. For printing pastes that include mixtures of MFC and pigment, printing paste TP5 contributed the most to the increase of mass per unit area, but it only increased 2 g/m^2 compared to printing pastes TP6 and TP7. Due to the very small amount of classical pigment, phosphorescent pigment or microcapsules of the thermochromic dye added to MFC, the differences in mass per unit area are almost negligible among the VZ5, VZ6, VZ7 samples and the VZ1 sample. Concentration of microcapsules in printing paste influences mass per unit area of printed fabric, published by Golja et al. [26]. They proved that the mass per unit area of printed fabric increases with the increase number of microcapsules in the printing paste [26]. The stiffness of the printed samples significantly differs in the warp and weft directions; it is higher in the warp direction due to the higher number of treads in warp than in weft direction. The same is observed for the unprinted sample, which is in accordance with fabric density. The highest stiffness in the warp direction was observed for the VZ5, VZ6 and VZ7 samples, whilst the lowest was observed for the VZ2 and VZ4 samples. The stiffness of the printed samples in the weft direction is in some cases more than half the stiffness in the warp direction. VZ5, VZ6 and VZ7 samples in the weft direction are the stiffest, followed by the VZ1 sample. The results of the overall flexural rigidity of the samples printed with MFC or pigment show that the VZ1 sample is the stiffest, followed by the VZ3 and VZ2 samples, whilst the VZ4 sample is least stiff. The reason lies in both the printing paste composition and the concentration of dye or pigment (Table 1). The TP1 printing paste includes the highest concentration of MFC comparing to the TP2, TP3 and TP4 printing pastes, which contain lower concentrations of KP, FS or TK. The results of the overall flexural rigidity also indicate that the combination of MFC and pigment affects the fabric stiffness to a greater extent than the application of MFC or pigment itself. Unlike the results of the measurements of stiffness in the warp and weft directions, the VZ6 sample has the highest overall flexural rigidity. The lowest impact on the overall flexural rigidity was for the sample printed with TK (VZ4 sample). The same observation was noticed by Golja et al. [26], when different concentration of microcapsules with essential oils were applied onto cotton fabric by screen printing. The researchers established stepwise increase of stiffness of printing fabric with increase number of microcapsules in the printing paste [26].

From the air permeability results, it can be seen that the unprinted fabric (VZ0 sample) is the most air permeable. The application of any printed paste decreased the air permeability of cotton fabric by more than a third. The lowest impact of printing paste on air permeability of fabric is noted in the VZ2, VZ3 and VZ4 samples, which were printed with only one pigment or dye. An exception is the VZ1 sample. This is due to the low concentration of TK, FS or KP (5 g/kg) in comparison with the VZ1 sample, where the concentration of MFC is 200 g/kg. The comparison of the air permeability measurements of the samples that were printed with one microencapsulated dye or pigment with the samples that were printed with a mixture of microencapsulated dye and pigment shows that the combination of microencapsulated dye and pigment in the printing paste significantly reduces the air permeability of the fabric. Among samples VZ5, VZ6 and VZ7, sample VZ6 has the lowest air permeability. The printing paste of the VZ6 sample contains a combination of MFC and phosphorescent pigment as a ready-to-use printing paste. Although the concentration of the phosphorescent pigment is low, we conclude that the ingredients in the ready-to-use printing paste contribute to the reduction of fabric air permeability. The content of both thickener and binder, beside pigment and additives in the ready-to-use printing paste cause the formation of binder layer during curing process and thus close the pores between the fibres and consequently hinders the air flow through the fabric.

In Table 3, the values of breaking force and elongation of the studied samples are presented.

In accordance with the construction parameters of the fabric, differences in the breaking force and in the elongation of the fabric in the warp and weft directions are noticed. From Table 3, it can be seen that the breaking force in the warp direction is much higher than that in the weft direction. The application of the printing paste caused an increase in the breaking force in both directions, which was attributed to the formation of a binder layer on the fabric surface. The application of the printing paste onto the cotton fabric does not significantly affect breaking elongation in both directions, but slightly improve it at all samples, with the exception of VZ4. For this sample, significant fluctuation in the values of breaking elongation in the weft direction is observed (19.40% ± 1.96%). To claim with certainty that the binder significantly increases breaking elongation of printed fabric more measurements should be done on each sample. In our case only ten measurements (five in warp and five in weft direction) were done, therefore the obtained results should be taken only as a rough estimate.

The testing of fastness to rubbing showed that the total colour difference (ΔE^*) between samples before and after exposure to UV-A irradiation decreases irrespective of the printing paste type, which can be seen in Figure 1.

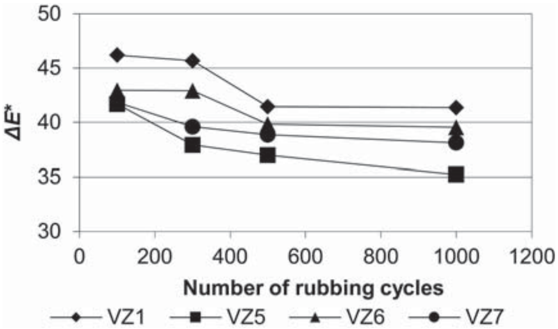

Figure 1: Colour difference (ΔE^*) vs. the number of rubbing cycles of printed samples

For the VZ1 sample, no essential difference in fastness to rubbing is noticed at 100 and 500 rubbing cycles compared to the VZ5, VZ6 and VZ7 samples, for which printing pastes include a combination of MFC and pigment. Among them, the classical pigment (VZ5 sample) has the highest impact on the reduction of values of ΔE^* at a low number of rubbing cycles. Between 300 and 500 cycles, the greatest reduction of

Table 3: Breaking force and elongation of samples in the warp and weft directions

Sample	Breaking force [N]		Breaking elongation [%]	
	Warp	Weft	Warp	Weft
VZ0	316.10	195.24	16	20.47
VZ1	353.40	229.16	22.2	23.07
VZ2	370.22	200.21	19.13	20.17
VZ3	334.96	203.00	20.53	21.97
VZ4	348.88	219.34	22.63	19.40
VZ5	360.17	198.90	22.03	23.37
VZ6	389.68	207.78	23.70	23.80
VZ7	406.46	210.18	23.53	21.17

*ΔE** is noticed in the VZ1 sample. Further comparison of values of *ΔE** after 500 and 1,000 rubbing cycles showed a very small, almost imperceptible colour difference for all samples with the exception of the VZ5 sample, where a slight decrease in the values of *ΔE** is observed between 500 and 1,000 rubbing cycles. The latter was attributed to the very low fastness of classical pigment to rubbing. The addition of TK or FS into the printing paste, which already includes MFC, has no significant influence on colour change at a higher number of rubbing cycles. The low fastness of MFC to rubbing was confirmed by SEM micrographs of samples VZ1, VZ6 and VZ7 before and after 300 and 1,000 rubbing cycles (Figures 2–4). It can be seen from those figures that the microcapsules of photochromic dye are damaged or removed. Before rubbing, the shells of the microcapsules are undamaged, but after 300 rubbing cycles, they show signs of injury. After 1,000 rubbing cycles, no untouched microcapsules can be found, since they burst and flatten. The same phenomenon was noticed by Ocepek et al. [22] but at much lower number of rubbing cycles and without additional load

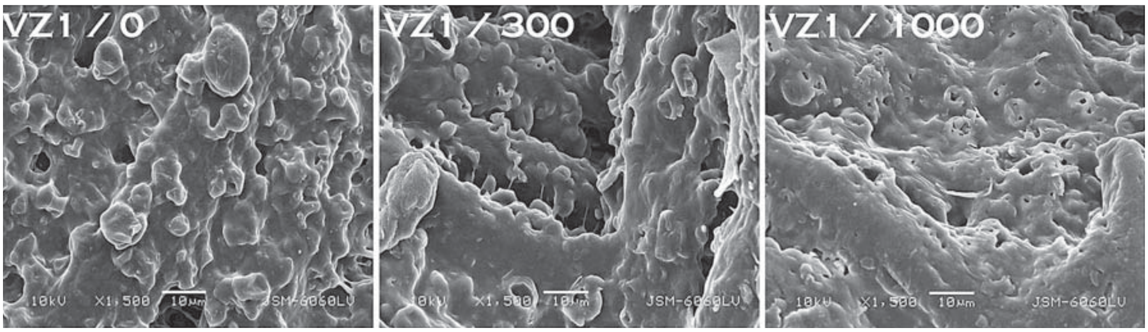

Figure 2: SEM micrographs of the VZ1 sample before and after 300 and 1,000 rubbing cycles at 1500x magnification

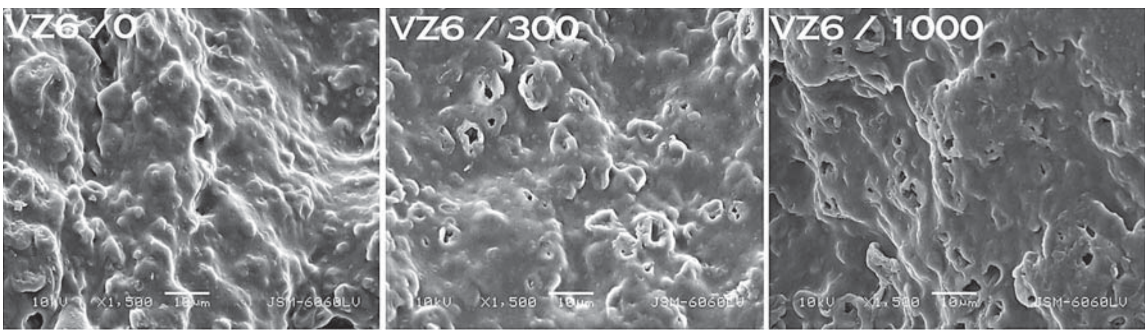

Figure 3: SEM micrographs of the VZ6 sample before rubbing and after 300 and 1,000 rubbing cycles at 1500x magnification

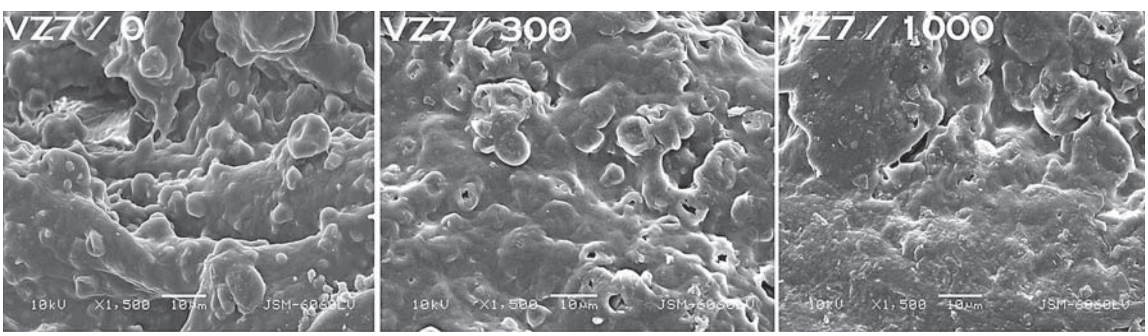

Figure 4: SEM micrographs of the VZ7 sample before rubbing and after 300 and 1,000 rubbing cycles at 1500x magnification

at Martindale apparatus. Since no data is available for the material, used for preparation of microcapsule shell of the commercial product Itofinish UV blue, the obtained results clearly show that the shell of microcapsules is less resistant to mechanical action. However, higher resistance to rubbing was expected, since commercial product was used in the research.

CIE $L^*a^*b^*$ colour values (Table 4) indicate that the application of MFC (VZ1 sample) changes the background colour of the fabric. The fabric becomes darker, greener and bluer compared to the VZ0 sample. The addition of a very small concentration (5 g/kg) of KP or FS pigment or TC microcapsules into printing paste affects the CIE $L^*a^*b^*$ values of the samples printed with MFC. After the addition of KP, the sample becomes darker, redder and yellower, whilst upon the addition of FS or TK, it becomes darker, greener and yellower in comparison with the VZ1 sample. After the samples are irradiated with UV-A light, the CIE $L^*a^*b^*$ values of the VZ1, VZ5, VZ6 and VZ7 samples change significantly. The VZ5 sample becomes redder, less blue, and the VZ6 and VZ7 samples become greener and less blue compared to the VZ1 sample. The greatest colour change between UV-A unexposed and exposed samples is obtained for sample VZ1, as seen in Table 5. This is attributed to the TP1 printing paste, which contains only MFC without any addition of pigments that could influence the intensity of the fabric photocolouration and colour change. Sample VZ5 has the second most pronounced colour change after UV-A irradiation. Because the classical pigment is not photoresponsive, a different colour effect is obtained on the printed sample. The photo-induced colour of the VZ5 sample is darker, due to the addition of classical pigment, whilst the colour difference is smaller than in the case of the VZ1 sample. This proves that classical pigment decreases the photoresponsiveness of photochromic dye, but to a lesser extent than phosphorescent pigment (VZ6 sample) and microcapsules of thermochromic dye (VZ7 sample). For samples VZ5, VZ6 and VZ7, the addition of microcapsules of thermochromic dye has the

*Table 4: CIE L*a*b* colour values, chroma (C*) and hue (h) of samples before UV-A irradiation*

Sample	L^*	a^*	b^*	C^*	h [°]
VZ0	94.21	–0.33	3.17	3.19	95.96
VZ1	90.00	–9.39	13.54	16.48	124.73
VZ2	54.98	54.62	19.58	58.03	19.72
VZ3	93.49	–0.45	6.08	6.10	94.19
VZ4	93.11	–1.78	7.38	7.60	103.46
VZ5	54.09	53.25	22.61	57.86	23.01
VZ6	90.30	–9.20	13.62	16.43	124.06
VZ7	89.69	–10.06	13.89	17.15	125.90

*Table 5: CIE L*a*b* colour values, chroma (C*), hue (h) and colour difference (ΔE*) of samples after UV-A irradiation*

Sample	L^*	a^*	b^*	C^*	h [°]	ΔE^*
VZ1	56.90	–18.16	–22.64	29.05	231.25	49.82
VZ2	55.27	53.98	19.05	57.24	19.43	/
VZ3	93.46	–0.41	5.74	5.76	94.10	/
VZ4	93.36	–0.87	6.70	6.75	97.36	/
VZ5	36.54	20.58	–4.85	21.17	346.67	46.15
VZ6	62.48	–19.83	–18.85	27.37	223.52	44.06
VZ7	63.06	–19.76	–18.10	26.82	222.46	42.74

greatest impact on the reduction of photoresponsiveness of the photochromic dye on cotton fabric. The latter is understandable, since thermochromic dye can be discoloured due to heat emission of the UV-A lamp during a one-minute exposure of sample to UV-A irradiation, which consequently affects the CIE $L^*a^*b^*$ colour values and colour difference. The results of colour fastness to washing of the printed fabric, presented in Figure 5, show that the values of ΔE^* decrease with an increasing number of washing cycles, indicating that MFC is removed from cotton fabric during washing due to weak adhesion of both the thickener and binder into which the microcapsules are entrapped. Similar results were obtained with the washing of cotton, cotton/polyester and polyester fabric coated with MFC using the pad-dry-cure process [27]. The addition of KP, FS or TK into the printing paste, which already contains MFC, reduces the photoresponsiveness of the fabric and impairs colour fastness to washing since a greater slope of the line is observed between the first and tenth washing cycles for the VZ5, VZ6 and VZ7 samples than for the VZ1 sample. It can also be seen from Figure 5 that the slope of the line decreases in the following order VZ6>VZ7>VZ5>VZ1.

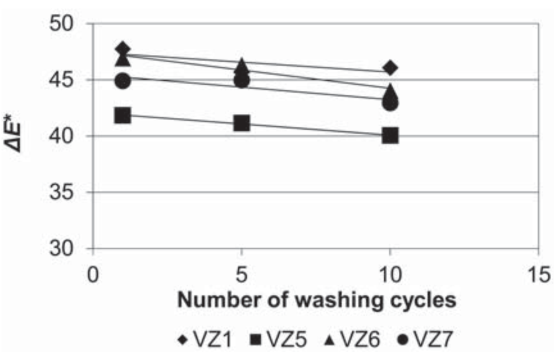

Figure 5: Colour difference (ΔE) vs. the number of washing cycles of printed samples*

The results of colour fastness of printed fabric exposed to light for different lengths of time in the Xenotest apparatus are presented in Figure 6. From Figure 6, it can be observed that values of ΔE^* decrease with increasing time of exposure in the Xenotest apparatus irrespective of the printing paste type. The addition of KP, FS or TK into printing paste that already includes MFC reduces the photoresponsiveness of the fabric and consequently affects the colour fastness of photochromic dye to light. In the case of TP5, TP6 and TP7 printing pastes, the colour fastness of MFC on printed fabric is dependent on both the contributions of colour fastness of the photochromic dye and on the colour fastness of the classical pigment, phosphorescent pigment and thermochromic dye. The results, presented in Figure 6, also show that the highest slope of the line is obtained for the VZ1 sample, whilst the slopes of the lines for the other samples decrease in the following order: VZ6>VZ7>VZ5. According to these results, it can be concluded that the addition of KP, FS or TK slightly slows the deterioration of the colour fastness properties of photochromic dye to light.

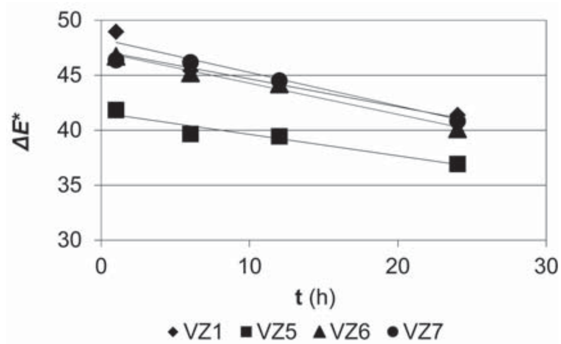

Figure 6: Colour difference (ΔE) vs. the time of exposure (t) of the studied printed samples to the Xenotest apparatus*

4 Conclusion

According to the obtained results, the following can be concluded:

- Cotton fabric was successfully printed with the prepared printing pastes.
- The application of printing pastes to cotton fabric caused changes in the mechanical-physical properties of the fabric, irrespectively of the printing paste type and composition. Thickness, mass per unit area, stiffness, breaking force and elongation were increased, whilst the air permeability of the printed fabric decreased by more than a third. Printing pastes that include a combination of MFC and KP, FS or TK have the highest impact on the alteration of physical-mechanical properties of the printed fabric.
- All added pigments (KP or FS) or microcapsules of thermochromic dye reduce the photocolouration of cotton fabric printed with microcapsules

of photochromic dye. Among them, the classical pigment has the least and the microcapsules of thermochromic dye have the most influence.

- With increasing numbers of rubbing cycles, the lightness of the samples increases, whilst the values of ΔE^* decrease. The smallest decrease in ΔE^* values was noticed with the addition of phosphorescent pigment in the form of ready-to-use printing paste, and the largest decrease was noticed with the addition of classical pigment. Microcapsules were damaged and removed to a greater extent after 500 rubbing cycles, whilst there was only a slight decrease in values of ΔE^* after 1,000 rubbing cycles.
- Values of ΔE^* for all printed samples decreased with increasing number of washing cycles. The addition of classical pigment, phosphorescent pigment or microcapsules of thermochromic dye reduces the photocolouration of printed cotton and simultaneously reduces the colour fastness of printed fabric to washing.
- The time of irradiation of samples in the Xenotest apparatus affects the colour fastness of printed fabric to light. By extending the irradiation time, the colour fastness of printed fabric to light is reduced. The addition of classical pigment, phosphorescent pigment or microcapsules of thermochromic dye moderates the photocolouration of cotton fabric printed with microcapsules of photochromic dye and slightly slows the impairment of colour fastness of printed fabric to light.

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References

1. RIJAVEC, Tatjana. Barvno aktivne tekstilije – kromizem ali reverzibilno spreminjanje barve. *Tekstilec*, 2005, **48**(1–3), 7–20.
2. ALDIB, Mohanad, CHRISTIE, Robert, M. Textile applications of photochromic dyes. Part 4: Application of commercial photochromic dyes as disperse dyes to polyester by exhaust dyeing. *Coloration Technology*, 2011, **127**(5), 282–287, doi: 10.1111/j.1478-4408.2011.00308.x.
3. FECZKO, Tivadar, SAMU, Krisztian, WENZEL, Klara, NERAL, Branko, VONČINA, Bojana. Textile screen-printed with photochromic ethyl cellulose-spirooxazine composite nanoparticles. *Coloration Technology*, 2012, **129**(1), 18–23, doi: 10.1111/j.1478-4408.2012.00404.x.
4. BAMFIELD, Peter. *Chromic phenomena: Technological applications of colour chemistry.* Cambridge : The Royal Society of Chemistry, 2001, pp. 7–33.
5. LITTLE, Anna, F., CHRISTIE, Robert, M. Textile application of photochromic dyes. Part 2: Factors affecting the photocoloration of textiles screen-printed with commercial photochromic dyes. *Coloration Technology*, 2010, **126**(3), 164–170, doi: 10.1111/j.1478-4408.2010.00242.x.
6. LITTLE, Anna, F., CHRISTIE, Robert, M. Textile applications of photochromic dyes. Part 3: Factors affecting the technical performance of textiles screen-printed with commercial photochromic dyes. *Coloration Technology*, 2011, **127**(5), 275–281, doi: 10.1111/j.1478-4408.2011.00307.x.
7. LEE, Soo-Jong., SON, Young-A, SUH, Hee-Jung, LEE, Dong-Nyung, KIM, Sung-Hoon. Preliminary exhaustion studies of spiroxazine dyes on polyamide fibers and their photochromic properties. *Dyes and Pigments*, 2006, **69**(1–2), 18–21, doi:10.1016/j.dyepig.2005.02.019.
8. GULRAJANI, M. L. Chromic materials for technical textile application In *Advances in the dyeing and finishing of technical textiles*. Oxford, Cambridge : Woodhead Publishing, 2013, pp. 3–36, doi: 10.1533/9780857097613.1.3.
9. BOH PODGORNIK, Bojana, STAREŠINIČ, Marica. Microencapsulation technology and applications in added-value functional textiles. *Physical Sciences Reviews*, 2016, **1**(1), 1–27, doi: 10. 1515/psr-2015-0003.
10. KULČAR, Rahela, KLANJŠEK GUNDE, Marta, KNEŠAUREK, Nina. Dynamic colour possibilities and functional properties of thermochromic printing inks. *Acta Graphica,* 2012, **23**(1–2), 25–36.
11. PANDA, Himadri. *Modern technology of textile dyes & pigments. 2nd revised edition.* Delhi : Niir Project Consultancy Sevices, 2016, pp. 247–255.
12. SON, Young-A., PARK, Young-Min, PARK, So-Yeon, SHIN, Chang-Ju, KIM, Sung-Hoon. Exhaustion studies of spiroxazine dye having reactive anchor on polyamide fibers and its photochromic properties. *Dyes and Pigments*, 2007, **73**(1), 76–80, doi:10.1016/j.dyepig.2005.10.012.

13. ALDIB, Mohanad. Photochromic ink formulation for digital inkjet printing and colour measurement of printed polyester fabrics. *Coloration Technology*, 2015, **131**(2), 172–182, doi: 10.1111/cote.12136.
14. ALDIB, Mohanad, CHRISTIE, Robert M. Textile applications of photochromic dyes. Part 5: Application of commercial photochromic dyes to polyester fabric by a solvent-based dyeing method. *Coloration Technology*, 2012, **129**(2), 131–143, doi: 10.1111/cote.12008.
15. HOU, L., SCHMIDT, H., HOFFMANN, B., MENNIG, M. Enhancement of the photochromic performance of spirooxazine in sol-gel derived organic-inorganic hybrid matrices by additives. *Journal of Sol-Gel Science and Technology*, 1997, **8**(1–3), 927–929.
16. BILLAH, Shah, M., CHRISTIE, Robert, M., MORGAN, Keith, M. A molecular modeling approach applied to a study of the photochromic behaviour of screen printed protein and polyamide substrates. *Fibers and Polymers*, 2011, **12**(6), 701–705, doi: 10.1007/s12221-011-0701-4.
17. EN ISO 5084 *Textiles – Determination of thickness of textiles and textile products (ISO 5084:1996)*, 1996, 5 p.
18. EN 12127 *Textiles – Fabrics – Determination of mass per unit area using small samples*, 1997, 7 p.
19. ASTM D 1388–64 *Standard test method for stiffness of fabric*, 1964, 3 p.
20. EN ISO 9237 *Textiles – Determination of permeability of fabrics to air (ISO 9237:1995)*, 1995, 5 p.
21. EN ISO 13934–1 *Textiles – Tensile properties of fabrics – Part 1: Determination of maximum force and elongation at maximum force using the strip method (ISO 13934-1:1999)*, 1999, 16 p.
22. OCEPEK, Barbara, FORTE TAVČER Petra, Behaviour of printed melamine-formaldehyde microcapsules exposed to different mechanical and physical impacts. In *Magic world of textiles : Book of proceedings*. Edited by Z. Dragčević. Zagreb: Faculty of Textile Technology, University of Zagreb, 2010, pp. 360–364.
23. EN ISO 105-C06 *Textiles – Tests for colour fastness – Part C06: Colour fastness to domestic and commercial laundering (ISO 105-C06:2010)*, 2010, 9 p.
24. EN ISO 105-B02 *Textiles – Tests for colour fastness – Part B02: Colour fastness to artificial light: Xenon arc fading lamp test (ISO 105-B02:2014)*, 2014, 21 p.
25. LITTLE, Anna, F., CHRISTIE Robert, M. Textile applications of photochromic dyes. Part 1: establishment of a methodology for evaluation of photochromic textiles using traditional colour measurement instrumentation. *Coloration Technology*, 2010, **126**(3), 157–163, doi: 10.1111/j.1478-4408.2010.00241.x.
26. GOLJA, Barbara, ŠUMIGA Boštjan, TAVČER FORTE, Petra. Fragrant finishing of cotton with microcapsules: comparison between printing and impregnation. Coloration Technology, 2013, **129**(5), 338–346, doi: 10.1111/cote.12044.
27. KERT, Mateja, GORJANC, Marija. The study of colour fastness of commercial microencapsulated photoresponsive dye applied on cotton, cotton/polyester and polyester fabric using a pad-dry-cure process. *Coloration Technology*, 2017, **133**(6), 491–497, doi: 10.1111/cote.12297.