

UV STABILITY OF THERMOCHROMIC INK ON PAPER CONTAINING CLINOPTILOLITE TUFF AS A FILLER

MIRELA ROŽIĆ,* RAHELA KULČAR,* SONJA JAMNICKI,* BRANKA LOZO* and
DIANA GREGOR-SVETEC**

**University of Zagreb, Faculty of Graphic Arts, Getaldičeva 2, Zagreb, Croatia*

***University of Ljubljana, Faculty of Natural Sciences and Engineering, Ljubljana, Slovenia*

✉ *Corresponding author: Branka Lozo, blozo@grf.hr*

The aim of the study was to analyse the possibility of using natural zeolite clinoptilolite as partial substitute of paper filler in order to improve the UV stability of thermochromic ink. Natural zeolite tuff was added to calcium carbonate in mass proportions of 0%, 20% and 60% and laboratory handsheets were prepared with 20% filler addition to fibre paperstock. The printability tester IGT A2 was used in the preparation of thermochromic prints on laboratory handsheets, which were exposed to the process of UV radiation in a Solarbox 1500e aging chamber (CO.FO.ME.GRA) for various time intervals during 40 hours. The measurements of the CIELab values (L*, a*, b* and C*) have shown changes as a function of accelerated aging time, which are very significant already after 1 hour. The smallest changes were obtained in the case of paper samples with 12% clinoptilolite (20% zeolite tuff addition). It was concluded that small proportions up to 20% of zeolite tuff in the paper filler act favorably on the UV stability of printed thermochromic ink, while higher proportions reduce the stability as an effect of photocatalytic oxidation features due to the presence of Fe-oxides in the sample of natural zeolite tuff.

Keywords: zeolite, clinoptilolite filler, thermochromic ink, photocatalytic oxidation

INTRODUCTION

Nowadays, printing inks are used on a range of different products, from packaging, commercial printing, protected documents, ceramics to textiles. The role of color is very often the key factor in the choice of a certain product. Chromogeneous printing inks are interesting from this point of view, as due to an external stimulus they change the color and thus give the product a new and added value. Of all the chromogeneous materials, the most broadly used are the thermochromic and photochromic materials. Thermochromic materials change color under the influence of temperature.¹

Reversible thermochromic organic materials usually consist of at least three components – the colorant, the color developer and the solvent. In order to achieve the desired effect the components are mixed in precisely determined proportions and usually encapsulated in a polymer envelope in order to protect the system for later applications. The reversible change of color appears through two competitive reactions, between the colorant and the developer and between the solvent and the developer. The first of these two interactions predominates at lower temperatures, when the

solvent and the colorant produce a colored complex. At lower temperatures, an organic solvent is in a solid state, and with the increase of temperature it becomes liquid. The solvent in liquid form causes the breakdown of the colorant – developer complex. When the thermochromic complex cools again, the solvent becomes solid, and the developer and the colorant blend again and the color returns to its original state.¹

The range of possible applications of such thermochromic materials has increased dramatically with the development of the process of microcapsulation, which protects the system from unwanted reaction with the environment. Every microcapsule contains the entire system necessary for the creation of coloring. Thermochromic printing inks are a mixture of thermochromic microcapsules and binders. The functionality of thermochromic inks can be adversely influenced by the UV radiation, temperatures above 200-230 °C and aggressive solvents. Their poor stability when exposed to UV radiation limits the time of exposure of products to external conditions.¹ The issues surrounding the application of thermochromic inks are largely

related to light resistance. This is the reason why today they are mainly used only for applications that are not directly exposed to sunlight. The increase in the stability of thermochromic inks to UV radiation is the subject matter of an increasing number of studies. The polymer envelope is much more stable than the mere polymer binder of the thermochromic ink.¹

Experimental research in this study involved the testing of colorimetric characteristics of commercially available thermochromic ink printed on laboratory handsheets. The aim of the study was to determine the influence of natural zeolite clinoptilolite as paper filler on the UV stability of thermochromic print. In the most recent works, it has been shown that natural zeolite clinoptilolite disperses UV radiation, whereby the efficacy of protection by cotton materials is increased.² The porous structure of zeolite attracts and removes the molecules of free radicals, which makes zeolite an effective photostabilizer and antioxidant.³ Zeolites are widely used in the separation, purification, drying and environment treatment processes.⁴ Klass and Joyce patented a purified natural zeolite pigment for papermaking and paper coating, which can be used as a filler to eliminate the print-through in uncoated papers or in speciality papers, such as anti-tarnish, gas filtration, filter and absorbent papers.⁵ Special papers and boards with zeolite are used for the protection of archival material from pollutants.⁶

As zeolite has a unique absorptive ability and is already available as a desiccant,⁷ it can be applied in active packaging application. Together with the thermochromic ink, its application in smart packaging could be even wider. In accordance with the above, this study is an attempt to modify the surface of the paper by zeolite particles for the purpose of achieving a better UV protection of ink prints.

EXPERIMENTAL

Clinoptilolite tuff

A natural clinoptilolite tuff originates from a sedimentary deposit in Donje Jesenje, Croatia. Clinoptilolite mass fraction in the tuff is approximately 60%. Other important constituents, present in fractions of 10-15% of each, were feldspars and α -quartz, while illite was present in a fraction of 5%, and celadonite was present in traces (<5%).⁴

The clinoptilolite tuff sample was ground in a planetary ball mill (Fritsch Pulverisette 6 Planetary Mono Mill). The particle size distribution of the clinoptilolite tuff sample is broad, the mean particle

diameter being around 5.7 μm . The particle size distribution of the calcium carbonate sample is rather narrow and the mean particle diameter is 1.77 μm . The largest particles of the calcium carbonate sample are below 10 μm , whereas in the clinoptilolite sample more than 40% of the particles are larger than 10 μm .

Preparation of paper samples (printing substrates)

For the preparation of paper samples, an open system laboratory sheet former was used. Handsheets with a grammage of 70 g/m^2 were prepared according to ISO 5269-1. The pulp was provided by a "Vevece" paper mill, Ljubljana, Slovenia. A mixture of bleached sulphate pulps, (softwood:hardwood = 50:50) was used as fibrous material for handsheet preparation. Each pulp was beaten separately in the laboratory PFI mill, at 30 °SR; 20% (w/w) filler based on fibrous material was added to the pulp suspension. Calcium carbonate and clinoptilolite tuff were used as fillers in different ratios, as shown in Table 1.

The clinoptilolite tuff proportion of the overall filler mass was 20% and 60%. Considering that zeolite tuff contains approximately 60% of clinoptilolite, the proportions of clinoptilolite in the overall filler mass are 12% and 36%. Cationic starch (0.5%), retention aid (0.01%) and sizing agent AKD (2%) were used in stock preparation for handsheets as well. Laboratory handsheets were marked as follows: 0Cl, 12Cl and 36Cl, in accordance with the proportion of clinoptilolite in the overall filler mass.

Thermochromic ink and the printing method

A commercially available offset ink with $T_A = 27$ °C of blue color was applied. For the production of prints, an IGT A2 printability tester was used. Firstly, the printing ink was distributed on the tester. The quantity of 3 cm^3 of ink was applied on the distribution rollers. The thickness of the print was of about 24 μm . The pressure during printing was 550 N/cm^2 . The thermochromic ink was 30% pigmented, and the particle size of the pigment was 6 μm .

Measurement of colorimetric value of the print

The colorimetric properties of the thermochromic samples were described in the CIELAB color space. CIELAB color space is a color-opponent space with dimension L^* for lightness and a^* and b^* for the color-opponent dimensions, based on nonlinearly compressed coordinates. The lightness L^* represents the darkest black at $L^*=0$, and the brightest white at $L^*=100$. The red/green opponent colors are represented along the a^* axis and the yellow/blue opponent colors are represented along the b^* axis. C^* represents chroma or saturation. This ranges from 0 at the centre of the circle, which is completely unsaturated to 100 or more at the edge of the circle for very high chroma. Temperature-dependent colorimetric properties were measured using the Ocean Optics USB2000+ spectrophotometer and Ocean Optics SpectraSuite

software for the calculation of the CIELab values L^* , a^* , b^* and C^* from measured reflectance in the entire spectral range (380-730 nm in 1 nm steps). The D50 illuminant and 2° standard observer were applied in these calculations. Color differences were calculated using the *CIEDE2000* total color difference formula.⁸ Each sample was heated by the Full Cover water block (EK Water Blocks, EKWB, Slovenia). The temperature of the copper plate surface was varied by circulation of thermostatically controlled water in channels inside the water block, which was assured to be up to 1 °C accurate in the applied temperature region. All the samples were heated and measured at three different temperatures: 20, 27 and 30 °C.

UV radiation of the prints by xenon light

For accelerated aging of the prints under xenon light, a Solarbox 1500e device (CO.FO.ME.GRA) was used. This device enables the simulation of environmental conditions in an open or closed space, and ensures the control of temperature and radiation. All the samples were exposed to filtered xenon light for a period from 1 to 40 hours at a temperature of 60 °C; a type of UV filter was used to change the xenon spectral curve into the ultraviolet range. The indoor filter – (soda lime glass filter extra long life) – was used for the simulation of conditions of internal exposure (equivalent to sunrays filtered through a window pane).

Table 1
Designation of paper samples according to clinoptilolite content of added filler

Paper sample	Filler		
	CaCO ₃ , %	Zeolite, %	Clinoptilolite, %
0Cl	100	0	0
12Cl	80	20	12
36Cl	40	60	36

RESULTS AND DISCUSSION

Chromatic values before UV radiation

Table 2 shows the colorimetric values of laboratory printed samples before the accelerated aging process at temperatures of 20, 27 and 30 °C. It is evident from the data that when sample is heated, L^* becomes higher and the samples become brighter – this is the reaction of thermochromic prints to temperature changes.

Figure 1 presents the reflection curves of prints on non-aged laboratory paper samples and on papers to which the treatment with UV radiation was applied. The reflection curves were measured at the temperature of 20 °C. In the case of UV radiation, the reflection curves of the samples shift towards greater wavelengths, and the reflection maxima increase.

Table 2
Colorimetric values of laboratory handsheets before UV radiation

T, °C	20	27	30
Sample		L^*	
0 Cl	51.8	78.1	72.3
12 Cl	52.0	79.0	82.5
36 Cl	49.0	77.6	81.4
		a^*	
0 Cl	3.0	-1.0	-0.4
12 Cl	3.4	-0.8	-0.3
36 Cl	3.6	-1.2	-0.7
		b^*	
0 Cl	-35.2	-8.3	-2.9
12 Cl	-36.3	-8.2	-3.8
36 Cl	-36.4	-7.4	-2.8
		C^*	
0 Cl	35.3	8.4	3.0
12 Cl	36.4	8.1	3.9
36 Cl	36.6	7.4	2.8

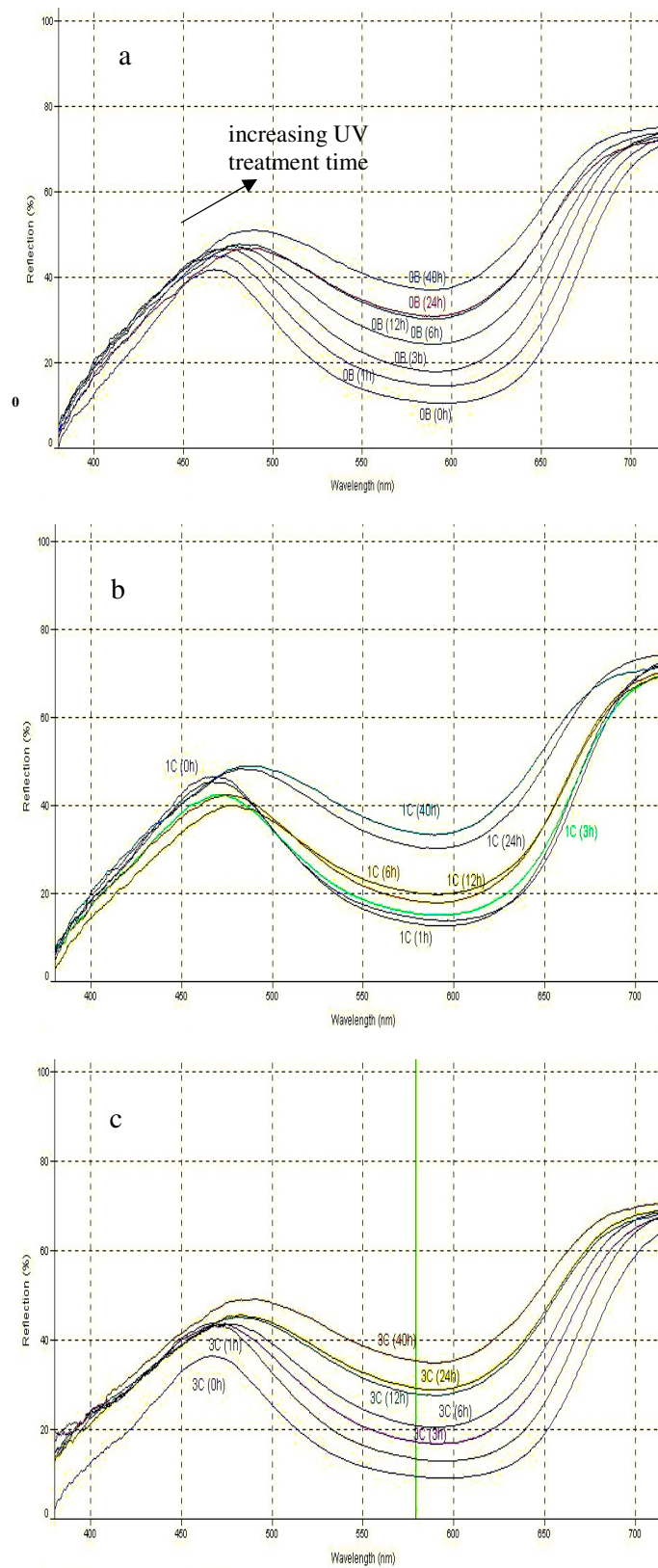


Figure 1: Reflection curves (at 20 °C) of prints on handsheets with 0% (a), 12% (b) and 36% (c) clinoptilolite (CI)

Chromatic values after UV radiation

Figures 2-6 present the colorimetric values (L^* , a^* , b^* , C^*) and colour differences $CIEDE2000$ for laboratory samples aged under UV radiation. Colorimetric values were measured at the temperature of 20 °C. A fast initial change of colorimetric values is followed by a slower one. In fact, the change of colorimetric values occurs in approx. 12 hours, and then the slower change of the measured parameters follows at a constant speed. The curves belong to type II of fading rate curves, which means that the colorants are present in the aggregates.⁹

During the same period of exposure to UV radiation, the smallest colour difference $CIEDE2000$ values (differences in coloring) are obtained for the sample with 12% clinoptilolite. The samples with 0% and 36% clinoptilolite present similar values of $CIEDE2000$, noting that

they are somewhat greater in the sample with 36% clinoptilolite. After 24 hours, the $CIEDE2000$ differences between individual samples become smaller (Figure 2).

The smallest Δb^* values were also obtained for the sample with 12% clinoptilolite. In this sample, the change in color shows the smallest migration from the blue area into the yellow area. In the samples with 36% clinoptilolite, greater Δb^* values were obtained compared to the sample with 0% Cl . After 24 hours, Δb^* differences among individual samples were also growing progressively, but to a lesser extent (Figure 3).

In the first 24 hours of exposure, the greatest ΔL^* values were obtained for the sample with 36% clinoptilolite, and the smallest for that with 12% Cl . The prints became brighter (Figure 4).

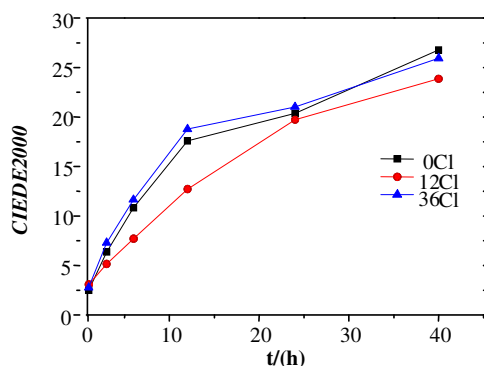


Figure 2: Changes of $CIEDE2000$ value as a function of UV radiation time (at 20 °C)

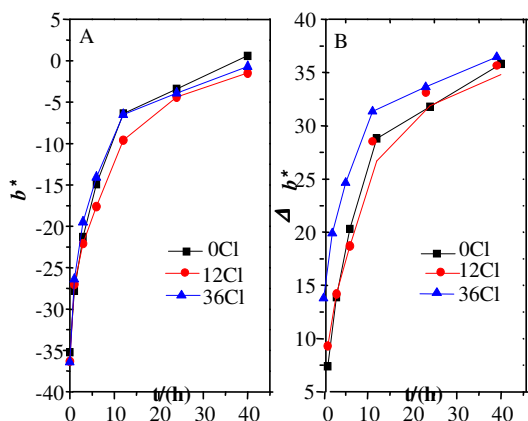


Figure 3: Changes of parameters b^* (A) and Δb^* (B) at 20 °C

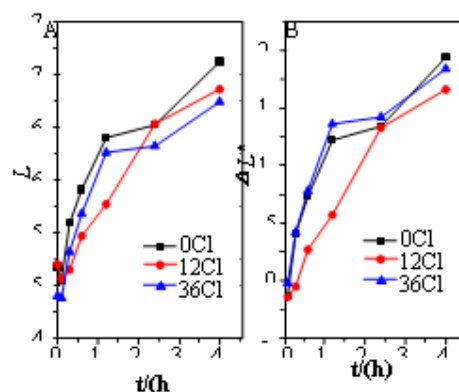


Figure 4: Changes of parameters L^* (A) and ΔL^* (B) at 20 °C

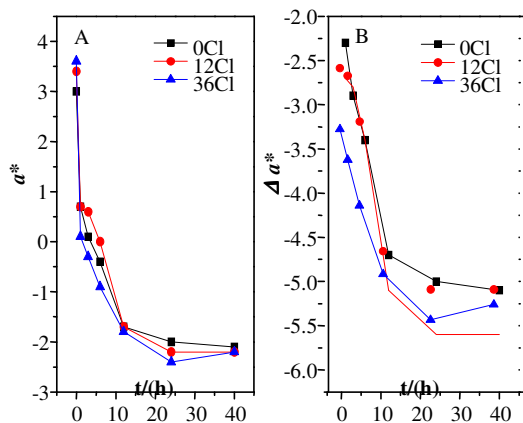


Figure 5: Changes of parameters a^* (A) and Δa^* (B) at 20 °C

The greatest Δa^* values were obtained in the case of the sample with 36% clinoptilolite. In this sample, the color migrated mostly to the area of green. The smallest color change towards the area of green were obtained for the sample with 0% Cl (Figure 5).

The chromaticity is reduced in time. The smallest reduction of ΔC^* value was obtained for the sample with 12% clinoptilolite. In the sample with 36% clinoptilolite, the greatest changes in C^* , chromaticity, were observed (Figure 6).

Efficiency of clinoptilolite tuff as photo-stabilizer

Two principal types of photo-degradation can take place when solar radiation falls on a dyed polymer: (i) change in shade and/or depth of shade of the colorant and/or (ii) chemical degradation of the substrate. Many factors influence the light fastness of the dyes on polymers, and these include mainly the chemical structure, and the physical state of the dye, the chemical structure of the substrate, the additives within the substrate, atmospheric composition (oxygen, water and/or contaminants), ambient temperature and the spectral distribution of the incident light. Significant progress has been made in understanding the photochemistry of the dyes and polymers and the mechanisms of their photo-degradation. There is much evidence to show that the vast majority of the photo-degradation pathways are oxidative in nature. Therefore, it is not surprising that free radical species play an important role in the initiation and propagation of the complex reactions involved. For example, one radical can extract hydrogen from the polymer

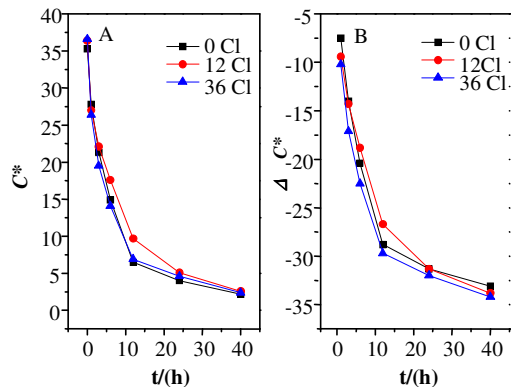


Figure 6: Changes of parameters C^* (A) and ΔC^* (B) at 20 °C

molecule to generate a new radical, which by reaction with oxygen will form peroxide radical. This itself may abstract hydrogen to produce the polymer hydroperoxide and yet another radical. Hydroperoxides are susceptible to the thermal and photochemical homolytic cleavage giving two radicals, $\text{HO}\cdot$ and $\text{polymer-O}\cdot$, and thus they play a major role in accelerating and propagating subsequent degradation processes. Consequently, it is clear that any species that scavenges free radicals or reacts with hydroperoxides in such a way that it neutralizes their propagating effect will be a useful photo-stabiliser.¹⁰

The porous structure of zeolite attracts and removes the molecules of free radicals, which makes zeolite an efficient photo-stabilizer and antioxidant. Traditional antioxidants reduce the energy of free radicals and break the chain reactions of oxidation, while zeolite attracts them into its complex structure and deactivates them.³

The encapsulation of thermochromic dyes on silica nanoparticles prior to their incorporation into textiles, enhances the color durability and washing fastness of the textiles.¹¹

In this study, the addition of 20% natural zeolite tuff (12% clinoptilolite) in the overall filler mass resulted in a small improvement in the photo-stabilization of the printed thermochromic ink. However, after 1 hour of accelerated degradation, colour differences *CIEDE2000* were already greater than 2 *CIELAB* units in all samples, which means the difference in colour is visible to the eye. The increase in the proportion of natural zeolite in the overall filler mass has a negative influence on the photo-stability of thermochromic inks. This can be explained by the

fact that in zeolite tuff there are also adhered Fe (hydro)oxides, which can act as photo-catalyst in the processes of oxidation of the thermochromic ink.¹² In the photo-catalytic oxidation, the energy of light causes a stirring of electrons in the particles of semiconductors (FeO, TiO₂, CuO). Unbound electrons and cavities appear as a result. Photo-generated cavities react with the adsorbed molecules of water and OH• radicals appear. Photo-generated electrons react with the adsorbed molecules of oxygen in the process of which the OOH• radicals appear. OH• and OOH• radicals react with organic species and then are disintegrated.¹³ Such photo-catalysts with transition metal oxides (FeO, ZnO, CuO, TiO₂) are often quoted as the catalysts of oxidation of volatile organic pollutants (e.g. toluene).¹⁴ Thus, Fe-zeolite Y is a promising catalyst for the oxidation of the solution of the colorant Acid red.¹⁵ The efficiency of photo-degradation of 2,4-dichlorophenol with the use of Fe-O deposited on nanoparticles of zeolite P very much depends on the experimental conditions, such as pH, concentration of substrate, loading with the active component FeO.¹⁶ Natural clinoptilolite incorporated in CuO is used as photo-catalyst for the degradation of *p*-aminophenoles in water solution.¹⁷ The photo-catalytic activity of CuS incorporated into clinoptilolite is examined for the decolorization of the mixture Methyl Orange and Bromocresol Green under sunlight.¹⁸

As the efficiency of the photo-catalyst depends on its concentration on the surface of zeolite, we can presume that in the samples with 20% zeolite tuff, the concentration of Fe (hydro)oxides adhered onto clinoptilolite is relatively low to cause a photo-catalytic oxidative effect on the thermochromic ink. With an increase in the proportion of clinoptilolite in the samples of laboratory handsheets, the proportion of photo-catalyst also grows, so the effect of photo-catalytic oxidation predominates over that of photo-stabilization. Better results could be achieved probably if pure zeolite without Fe-(hydro)oxide had been used.

CONCLUSION

In the present paper, natural zeolite with 60% clinoptilolite content was investigated as partial filler substitute to improve the UV stability of thermochromic ink prints. After 1 hour of accelerated degradation, colour differences CIEDE2000 were greater than 2 CIELAB units in

all samples, which means the difference in colour is visible to the eye. A small addition of zeolite tuff can improve the color stability of thermochromic ink prints. The smallest $\Delta(E_{00}, a^*, b^*, c^*, L^*)$ changes in thermochromic prints were obtained in the sample with 12% clinoptilolite, and the greatest in the sample with 36% clinoptilolite in the overall filler mass.

The results could be explained by the presence of Fe (hydro)oxides on the surface of zeolite tuff, which can act as photo-catalysts in the processes of thermochromic ink oxidation. With the increase in the proportion of clinoptilolite in the samples, the proportion of photo-catalysts also grows, and the effect of photo-catalytic oxidation of Fe (hydro)oxides predominates over the effect of photo-stabilization of zeolites.

REFERENCES

- ¹ R. Kulčar, M. Friškovec, N. Hauptman, A. Vesel and M. Klanjšek Gunde, *Dyes Pigments*, **86**, 271 (2010).
- ² A. M. Grancarić, A. Tarbuk and D. McCall, *Polimeri*, **28**, 219 (2007).
- ³ M. Montinaro, D. Uberti, G. Maccarinelli, S. A. Bonini, G. Ferrari-Toninelli *et al.*, *Life Sci.*, **92**, 903 (2013).
- ⁴ D. Gregor-Svetec, M. Rožić, T. Muck and B. Lozo, *Nord. Pulp Pap. Res.*, **27**, 721 (2012).
- ⁵ C. P. Klass and M. K. Joyce, US Patent No. 6679973 (Jan. 20, 2004).
- ⁶ S. Rempel, *WAAC Newsletter*, **18**, 13 (1996).
- ⁷ H. Ichiura, T. Kitaoka, H. Tanaka, *Chemosphere*, **50**, 79 (2003).
- ⁸ CIE Central Bureau, *Colorimetry*, 3rd ed., Vienna, CIE Central Bureau, 2004.
- ⁹ D. Cristea and G. Vilarem, *Dyes Pigments*, **70**, 238 (2006).
- ¹⁰ J. C. V. P. Moura, A. M. F. Oliveira-Campos and J. Griffiths, *Dyes Pigments*, **33**, 173 (1997).
- ¹¹ L. S. Ribeiro, T. Pinto, A. Monteiro, O. S. G. P. Soares, C. Pereira *et al.*, *J. Mater. Sci.*, **48**, 5085 (2013).
- ¹² M. Rožić, Đ. Ivanec Šipušić, L. Sekovanić, S. Miljanić, L. Čurković *et al.*, *J. Colloid. Interf. Sci.*, **331**, 295 (2009).
- ¹³ Y. Suzuki, H. Arakawa, A. Maezawa and S. Uchida, *Int. J. Photoenerg.*, **1**, 1 (1999).
- ¹⁴ W. J. Ma, Q. Huang, Y. Xu, Y. W. Chen, S. M. Zhu *et al.*, *Ceram. Int.*, **39**, 277 (2013).
- ¹⁵ H. Hassan and B. H. Hameed, *Desalination*, **276**, 45 (2011).
- ¹⁶ A. Nezamzadeh-Ejhieh and Z. Ghanbari-Mobarakeh, *J. Ind. Eng. Chem.*, **21**, 668 (2015).
- ¹⁷ A. Nezamzadeh-Ejhieh and M. Amiri, *Powder Technol.*, **235**, 279 (2013).
- ¹⁸ A. Nezamzadeh-Ejhieh and N. Moazzeni, *J. Ind. Eng. Chem.*, **19**, 1433 (2013).