Dependence of Binder and Photocatalyst in Photocatalytically Active Printing Ink

Andreja Pondelak[1], A. Sever Škapin[1], M. Klanjšek Gunde[2], O. Panák[3], M. Kaplanová[3]

[1]Slovenian National Building and Civil Engineering Institute, Dimičeva 12, Ljubljana, Slovenia
[2]National Institute of Chemistry, Ljubljana, Hajdrihova 19, Slovenia
[3]University of Pardubice, Faculty of Chemical Technology, Department of Graphic Arts and Photophysics, Studentská 95, Pardubice, Czech Republic

Abstract: *Photocatalytically active printing ink changes its colour when exposed to UV light. The ink is based on photocatalyst which decomposes organic dye in presence of UV light causing the changes in colour. Such process can be used as a simple UV dosimeter as its colour change depends on duration to UV light exposure.*

We have prepared such an ink based on redox dye 2,6-dichloroindophenol (DCIP), photocatalyst titanium dioxide (nanodimensional anatase), reducing agent (glycerol) and two different water based binders – hydroxyethylcellulose (HEC) and polyvinyl alcohol (PVA). Prepared ink was applied onto a substrate, exposed to UV light and analysed by UV/Visible spectra. When the ink was exposed to UV light, the colour of the redox dye DCIP was changing from blue to colourless that belongs to the dihydro DCIP form. The colour change depends on several factors: on the amount of TiO_2 *and UV exposure, as well as on the type of binder. In this work the influence of two selected binders and the amount of photocatalyst on the properties of ink was observed. The results show that the ink based on polyvinyl alcohol has a greater initial absorption and absorbs at higher wavelength. Colour changes were faster when higher amount of photocatalyst and HEC as a binder were used. Nevertheless, it has been confirmed that both binders are appropriate for preparation of UV active functional printing inks.*

Keywords: *UV indicator dye, 2,6-dichloroindophenol, photocatalyst, hydroxyethylcellulose, polyvinyl alcohol*

1. Introduction

Quantitative measurement of UV radiation is an area of significant importance. There are many electronic UV dosimeters available but they are rather bulky and relatively expensive, therefore an inexpensive and easy to use UV dosimeter is needed.

One way of preparing such a dosimeter is by using photocatalytically active materials. Such an ink can, with a help of UV light and photocatalyst, decompose organic dye, which can be seen as a change of colour.

Some experiments with photocatalytic inks based on indicator dye already exist [1–5] but they are mostly used for rapid determination of photocatalycal activity on self-cleaning glasses. Based on these researches a number of UV indicators have been reported [6, 7], using glass as a substrate. Except in two [8, 9], in all other works hydroxyethylcellulose was used as a binder.

In order to check the possibility of preparation of UV dosimeters on other substrates, we prepared a dosimeter based on redox dye 2,6-dichloroindoohenol which is based on two different binders – hydroxyethylcellulose and polyvinyl alcohol. A polyester foil was used as substrate as a substitute of glass.

The activity and colour of this active ink depend on many factors, but mostly on the concentration of photocatalyst TiO_2, binder and other components. These factors are critical to create the ink which then discolours in suitable steps upon UV irradiation and can be therefore used as a UV dosimeter.

2. Materials and methods

A typical DCIP ink was prepared as follows: 3 g of a 1.5 wt% hydroxyethylcellulose, HEC, (SIGMA-ALDRICH, ZDA) or 3 g of a 10 wt% polyvinyl alcohol, PVA, (laboratory prepared, Uni. Pardubice), 0.3 g of glycerol (Lach-Ner s.r.o. Czech Republic, 99%), 5 mg of 2,6-dichloroindophenol, DCIP, (SIGMA-ALDRICH, USA) and 0.3 wt% of 11.8% TiO_2 – Sachetleben Hombikat XXS 700 in nanodimensional anatase crystal form (SACHTLEBEN, Germany). The ink was stirred for about 5 minutes to assure a homogenous mixture. When analysing the dependence of TiO_2 on colour change different levels of photocatalyst were used: 0.1 wt%, 0.3 wt% and 0.5 wt%, other compounds remained the same.

The substrate used in this work was a polyester foil Melinex® ST504. Full details about this foil can be found elsewhere [10]. Prepared ink was applied onto the adhesive site of substrate with automatic film applicator Elcometer® 4340. Used speed was 90 mm/s and the thickness of spiral bar was 20μm. Other details of Elcometer® can be found elsewhere [11]. Prints were prepared using 4 layers of ink, where each layer was coated on a dry layer of previously applied ink.

Dry samples were cut into smaller pieces to fit into the UV-vis and exposed to intensive ultra-violet (UV) light. GREEN Spot UV curing system was used for that purpose which uses a super-pressure mercury 100 W lamp, with a maximum in UV range at about 365 nm and the size of illuminated aperture of 5 mm. UV irradiation of samples was conducted using a stencil with a size of aperture at approximately 15 mm diameter to ensure the exposed surfaces were big enough to be appropriately measured with spectrophotometer. The stencil was used to protect unexposed parts of samples from UV light. In this way a quick visual comparison of colour change can be seen. Samples were illuminated on distance between the sample and illumination source of 2 cm every 0.1 s. In this measuring geometry energy was approximately 50 mJ cm^{-2}, measured by UV-Integrator SR (UV-technik, Germany). The colour of samples was measured in dependence on exposure of irradiated time. All UV-visible absorption spectra were recorded using SPECORD® 210 UV/Visible spectrophotometer (Analytic Jena AG, Germany) in the range of 450–750 nm. For calculating the change in colour, ΔE^*, CIELAB values before and after irradiation were measured accomplished with spectrophotometer Eye-One (Gretag-Macbeth). This equipment uses 45°/0° measuring geometry, and the size of the measurement aperture 4.5 mm. Instrument measured wavelengths in the range 380–730 nm in 10 nm steps.

3. Results and discussion

Firstly, two typical DCIP inks were prepared, one based on HEC and the other on PVA as a binder. Both inks were blue in colour when dried on the substrate. Expectedly, with exposure to UV light the samples gradually discoloured. However, the discolouration rate seemed to depend significantly on binder used (Fig. 1a).

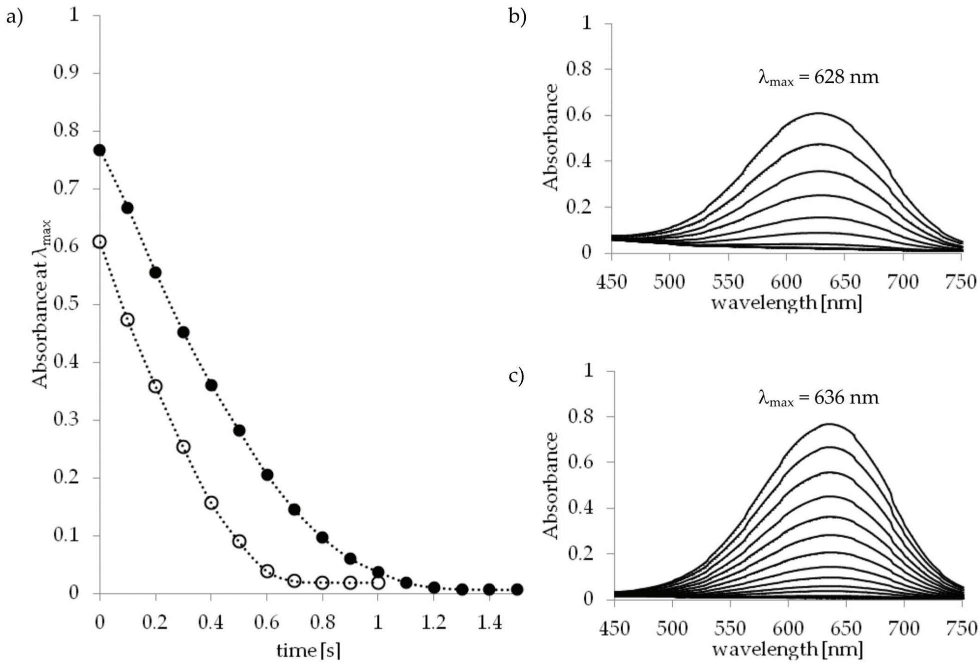

Figure 1: a) Change in absorbance at λ_{max} of DCIP ink with HEC (o) and PVA (●) as binder, Δabs, as a function of time. Δabs are based on the data presented in the plots b) and c). Generated respective constants are: – 0.86 for HEC and – 0.75 for PVA as binder. b) UV-Vis absorption of DCIP film with (b) HEC and (c) PVA binder as a function of irradiation time (one spectrum every 0.1 s).

Initial maximum absorbance

Firstly the initial maximum absorbance was measured. The UV/Visible absorption spectrum was used for that purpose. Absorption spectrum of DCIP film as a function of UV exposure time was measured as illustrated in a) and b) plots in Fig. 1 from which it is clear that unexposed samples with different binders absorb at different maximum wavelengths, λ_{max}. From plots b) and c) in Fig. 1 can be seen that λ_{max} for samples with HEC as binder is at 628 nm and λ_{max} for samples with PVA as binder at 636 nm. Maximum absorption for aqueous solution, a dilute (i.e. 6.9 x 10^{-5} M) solution of DCIP has also been measured, from where we have measured a λ_{max} at 602 nm at pH >7. Red shift is observed.

From Fig. 1 it can also be seen that samples with DCIP ink and PVA as binder has greater initial absorption than samples with HEC binder, where first one reaches around 0.8 and the latter around 0.6. These phenomena can also be seen in Fig. 2 where samples with PVA binder (full shapes) always have greater initial absorbance than the samples with HEC as binder (empty shapes). The maximum initial absorbance decreases according to amount of added photocatalyst TiO_2, since greater amount lighten DCIP ink.

Kinetics of photobleaching DCIP film

Sensitivity of the UV dosimeter towards UV light can be readily varied by changing the amount of TiO_2 in the ink formulation. For this experiment, a set of ink formulations with different amounts of TiO_2 and two different binders was prepared. The concentrations of TiO_2 were 0.1 wt%, 0.3 wt% and 0.5 wt%. The change in the absorbance as a function of irradiation time for a series of different DCIP films as a function of the amount of TiO_2 used in the formulation is illustrated in Fig. 2. These results show that the higher the level of TiO_2 in ink formulation the greater its sensitivity towards UV light. Using the data in Fig. 2, the rate corresponding to each plot can be calculated; this rate is shown as insert plot in Fig. 2. The data indicate that the sensitivity of UV dosimeter films is proportional to the level of TiO_2 present in the ink formulation. The line of best fit for DCIP film with HEC as binder has a gradient of 2.48 abs s-1 %-1 and 1.31 abs s^{-1} $\%^{-1}$ for DCIP film with PVA as a binder. These data indicate that DCIP ink with HEC as binder discolours approx. two times faster than DCIP ink with PVA as binder.

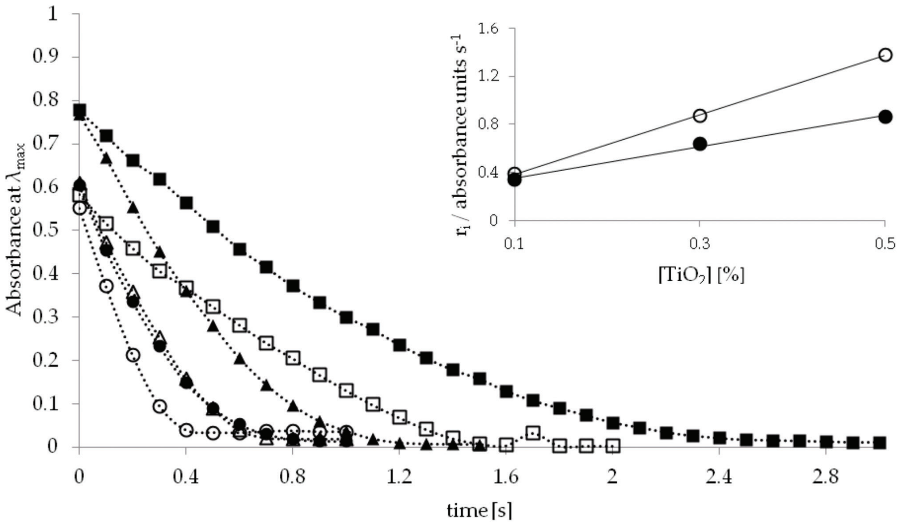

Figure 2: The change in the absorbance (at λ_{max}), Δabs, for DCIP film with different levels of TiO_2: (■) 0.1 wt%, (▲) 0.3 wt%, (●) 0. 5wt% with PVA and (□) 0.1 %, (Δ) 0.3 % TiO_2 and (o) 0.5 % TiO_2 with HEC, as a function of time. Insert diagram shows variation of initial rate ($\Delta A_{\lambda max(t=0)}$ /$t_{decolouration}$) with concentration [TiO_2] in % for HEC (o) and PVA (●) samples, calculated using data in the main diagram.

In continuation, the kinetics of samples from Fig. 1 were investigated. From absorbance of samples at λ_{max} and the UV irradiation time data, a first-order kinetics mechanism is obtained, as shown in Fig. 3. The calculated rate constants for the samples with HEC and PVA as binders were -4.42 and -2.98, respectively.

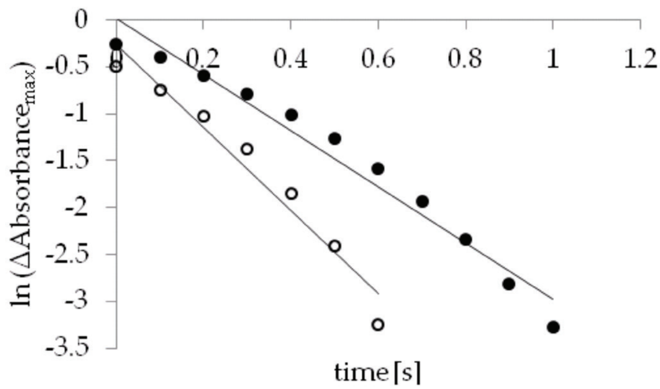

Figure 3: First-order plots for DCIP film with HEC (o) and PVA (●) as binder. Plots are based on the data presented in the Fig. 1.

Correlation between absorbance and colour change

In another experiment, colour changes, ΔE*, of samples presented in Fig. 1 have been measured. CIELAB values before and after each UV irradiation have been calculated with an EyeOne spectrophotometer. The results are presented in Fig. 4.

The total reduction time for DCIP film with HEC as a binder is 0.5 s. For the samples with PVA as a binder this time equals 0.8 s, which is significantly longer. The same factor was obtained when the absorbance at λ_{max} of samples with the same formulation were measured (see Fig. 1). Furthermore, the rate constants obtained from the colour change in Fig. 3 and the absorbance in Fig. 1 were also similar. A correlation between these two measurement methods was demonstrated.

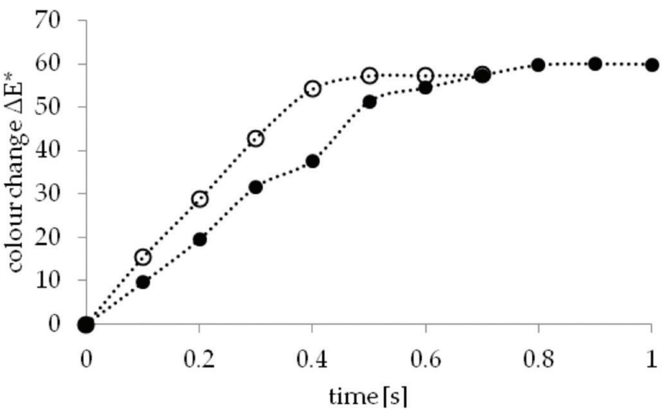

Figure 4: The colour changes, ΔE, of DCIP ink with HEC (o) and PVA (●) binder as a function of time. Generated respective constants are: 135.90 for HEC and 100.78 for PVA as binder.*

4. Conclusions

A compression study of an indicator ink based on 2,6-dichloroindophenol for UV indicators has been conducted. The initial maximal absorbance of DCIP ink depends on the binder used in the ink formulation and is higher in case of DCIP film with PVA as binder. According to that, DCIP film with PVA as a binder absorbs at greater maximum wavelengths than the DCIP film with HEC as a binder. The rate of photoreduction of the dye in the ink formulation is proportional to the level of added photocatalyst TiO_2 and is approximately two times faster on samples with HEC as a binder. The kinetics are first-order. The response of the dosimeter films to UV irradiation is proportional to the level of photocatalyst and can be varied with the type of binder in ink formulation as well. By varying selected components in ink formulation it is possible to prepare a UV dosimeter that is sensible to different UV energies.

5. References

1. Mills, A.; McGrady, M., A study of new photocatalyst indicator inks. *Journal of Photochemistry and Photobiology a-Chemistry* **2008**, *193* (2–3), 228–236.
2. Mills, A.; McGrady, M.; Wang, J.; Hepburn, J., A rapid method of assessing the photocatalytic activity of thin TiO(2) films using an ink based on the redox dye 2,6-dichloroindophenol. I*nternational Journal of Photoenergy* **2008**.
3. Mills, A.; Wang, J. S.; McGrady, M., Method of rapid assessment of photocatalytic activities of self-cleaning films. *Journal of Physical Chemistry B* **2006**, *110* (37), 18324–18331.
4. Mills, A.; McFarlane, M., Current and possible future methods of assessing the activities of photocatalyst films. *Catalysis Today* **2007**, *129* (1–2), 22–28.
5. Mills, A.; Cusick, A.; Hepburn, J., The Kinetics of Semiconductor Photocatalysis in Activity-Indicator Films. *Journal of Advanced Oxidation Technologies* **2009**, 12 (2), 152–157.
6. Mills, A.; Grosshans, P., UV dosimeter based on dichloroindophenol and tin(IV) oxide. Analyst 2009, *134* (5), 845-850.
7. Mills, A.; Lee, S. K.; Sheridan, M., Development of a novel UV indicator and dosimeter film. *Analyst* **2005**, *130* (7), 1046–1051.
8. Mills, A.; Grosshans, P.; McFarlane, M., UV dosimeters based on neotetrazolium chloride. *Journal of Photochemistry and Photobiology a-Chemistry* **2009**, *201* (2–3), 136–141.
9. Brezova, V.; Ceppan, M.; Vesely, M.; Lapcik, L., PHOTOCATALYTIC OXIDATION OF 2,6-DICHLOROINDOPHENOL IN THE TITANIUM-DIOXIDE AQUEOUS SUSPENSION. *Chemical Papers* **1991**, *45* (2), 233–246.
9. Melinex® ST Polyester Films web site, http://www.tekra.com/, accessed March 2013.
10. Elcometer 4340 Motorised web site, http://www.elcometer.com/, accessed March 2013.