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Colour Shift Photochromic Pigments in Colour Space CIE $L^*a^*b^*$

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One of possibilities for protection of human body against acute and cumulative exposure to ultraviolet is the wearing of special protective clothes. Nevertheless on the other side the protective clothes have not the same barrier features against the UV light.

The aim of present research work in LCAM on the Technical University of Liberec is research and development of original method of measurement by flexible textile based sensors reacting on the UVA part of electromagnetic radiation. In this article is publicized information about testing above mentioned sensors with weave structure and non-woven textiles. Results show that produced sensors shows sensitivity as to time of exposition so also to intensity of irradiation and their response characteristics is same as for classical luxmeters.

Keywords: colour hysteresion area; colour space; intensity of illumination; photochromism; sensor

INTRODUCTION

In present time become worse living conditions and increase harmful pollutants in environment, which can non-reversible damage our health and jeopardize full quality our life. Big attention is given in research area respectively in development and perfection of protective clothes specially their barrier features. Protective barriers we understand how the clothes or textiles protects wearer against

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above mentioned dangerous conditions and if the protection is only partial or the protection is time limited by ambient conditions. Most of protective clothes are not developed for long time wearing. During development of these barrier structures we have to keep in our mind full comfort of acting persons without limitation. Some of protective clothes are equipped by electronics, respectively other sensors or devices, which monitoring and quantify dangerous substances in environment. In present time is big attention given to miniaturization of electronics and also flexibility their connection with computing units [1].

Above mentioned describe concept of protective clothes we call as intelligent structure. Disadvantage of this intelligent structure is no adequate response on the external stimulus, there is only monitoring of external dangerous conditions. This structure we call as passive intelligent textile structure.

Sensors and textile structures, which react adequate response and they are able modulate protective degree in accordance on the external stimulus (change of intensity UV, temperature, press, electrical field etc.) is called as SMART textile. As example of passive intelligent textiles are optical fibres, which leading the not only signal, but they are also sensitive on the deformation, concentration of substances, press, electric power etc. As example of active intelligent textiles could be textiles which react by change own colour in dependence on external stimulus (light, temperature) and called as a chameleonic textiles or heat containing textiles, which are able to store or slack energy according external temperature. Moreover textile based sensors and active protective textiles has advantages that textile structure is easy customizable by sewing, thermal bonding or gluing. Also there are advantages of easy maintaining (washing, chemical drying) and low specific weight with good strength, tensibility and elasticity. Good features are also workability without change of technology of production and extremely large specific surface. Big advantages are possible integration these types of sensors into system of protective clothes and also their price availability. From these reason is this article directed to research of textile-based sensors with photo chromic behaviour, respectively to study of dynamic behaviour and modulation of sensitivity photo chromic sensors.

In this work is described new definition of colour reversible hysteresis, which is described by hysteresis of colour change curve. This colour hysteresis curve is described by kinetic model, which defines the speed of colour change initiated by external stimulus – UV light. Kinetic model verification is done for textile sensors with photo chromic pigment applied by textile printing, fibre mass dyeing.

MATERIALS AND USED METHODS

Our experiment was divided to 3 parts and every part is directed to special form of application of photochromic pigments and study of photochromic behaviour from point of kinetics and dynamics in different mediums:

a) Application of photochromic pigments by textile printing - **PTP**
b) Application of photochromic pigments by mass dyeing - **NWT**
c) Study of photochromic pigments behaviour in solution - **PPS**

In our research we follow the develop simple textile based sensor sensitive to UV light and kinetic study of behaviour and main attention was given to possibility use the technology of textile printing by stencil printing. This experiment was completed the study of influence of UV absorbers and ability of properties modulation of sensors. Also was studied dependence of Colour change intensity on concentration of photochromic pigment. Above mentioned studies was necessary complete by study of fatigue resistance in dependence on Intensity of source and time of exposition including also classic tests of light fastness on Xenon test and dry staining fastness, which are the same as for normal classic pigment use in textile finishing and these tests are also limitation of application offered sensors.

In second part of our experiment was studied change of photochromic behaviour tested pigments in non-woven textiles produced by technology Melt Blown (mass dyeing) and in third part was checked the photochromic behaviour used pigments in solution via measurement of transmission characteristics as completive study how is changed the photochromic response via kind application. For experiment was used commercial photochromic pigments PPG-Photosol 33672 (P1),

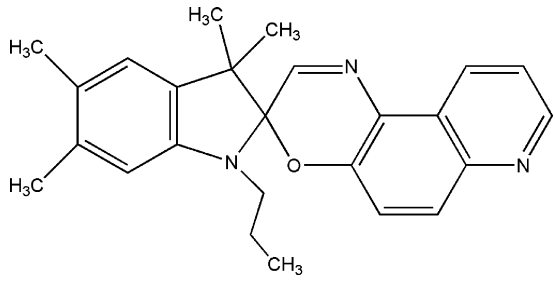

FIGURE 1 P1 structure.

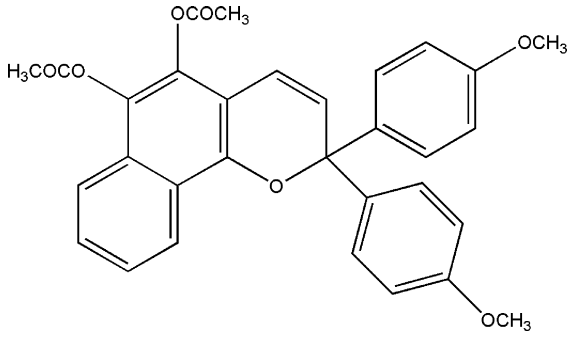

FIGURE 2 P3 structure.

PPG-Photosol 7106 (P2), PPG-Photosol 749 (P3), PPG-Photosol 0265 (P4) and PPG-Photosol 5-3 (P5). Chemical structure illustration is shown on Figure 1 and Figure 2 [2].

As was mentioned in our experiments were prepared two kinds of solid media – textile substrate with photochromic pigments. Illustrations of fixation of photochromic pigments on the textile substrates are shown on Figures 3–6:

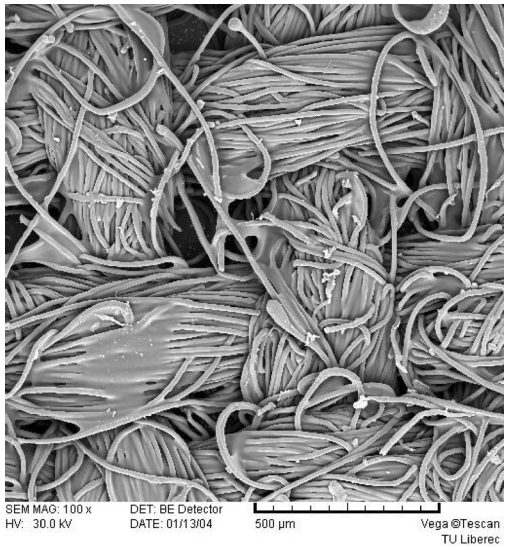

FIGURE 3 P1 print on PET.

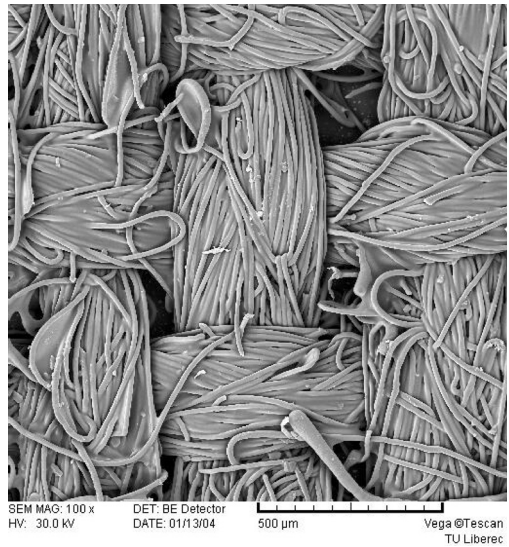

FIGURE 4 P3 print on PET.

For measurement of colour response of tested photochromic media were used following spectrophotometers:

- Spectraflash SF 300 X – viewing geometry D/8, aperture 20 mm, SCI

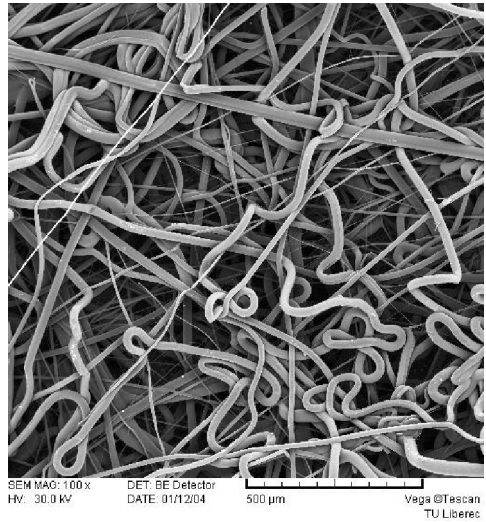

FIGURE 5 NWT without pigment.

FIGURE 6 NWT with P3.

- Modified Chroma Sensor CS-5 – viewing geometry T/8, aperture 30 mm in modus SCI (Fig. 7)
- AVANTES S2000 – optical fibre spectrometer arranged on 0/45 viewing geometry (Fig. 8)

Besides measurements of prints and NWT via classical spectrophotometer Spectraflash 300UV was used arrangement of AVANTES

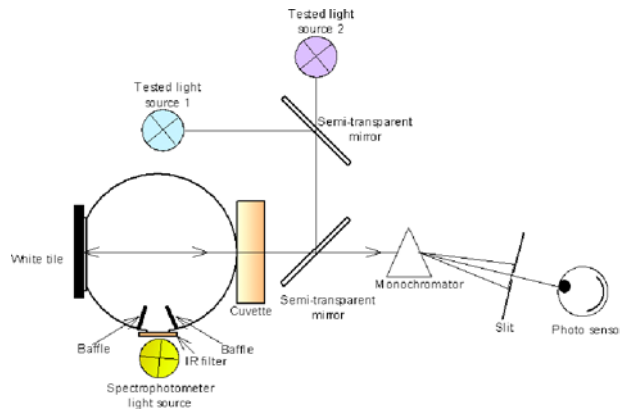

FIGURE 7 CS-5 spectrophotometer modification.

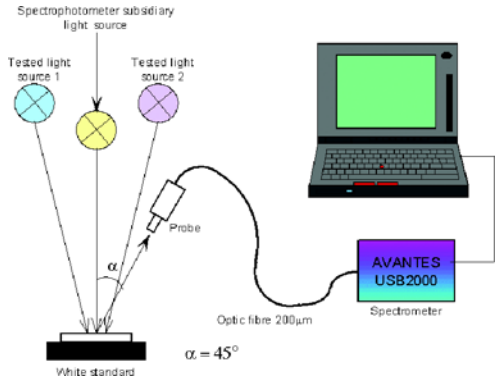

FIGURE 8 S2000 spectrometer arrangement.

S2000 spectrometer due to short time, continuous measurement respectively. S2000 arrangement make possible using different light sources for tested samples illumination, as is shown on the Figure 8. Same possibility was obtained via modification of CS-5 spectrophotometer for measurement of photochromic solutions. Spectral power distribution curves of used light sources are shown on Figures 9–10.

Because is relationships between remission and concentration of colorant agent non-linear, in colour measurement is obviously used relation between Kubelka-Munk function ($\boldsymbol{K}/\boldsymbol{S}$) and concentration, colour change intensity $\boldsymbol{I}$ respectively. Colour change intensity, $\boldsymbol{I}$ that we used, is defined as following equations:

$$\frac{K}{S} = \frac{(1-\beta_\infty)^2}{2\beta_\infty} = f(\beta_\infty) \tag{1}$$

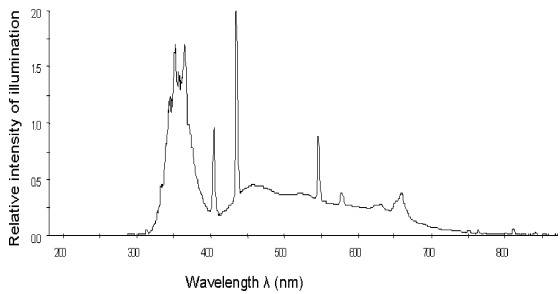

FIGURE 9 Relative spectral power distribution of D65 simulator + UV tube (JUDGE II).

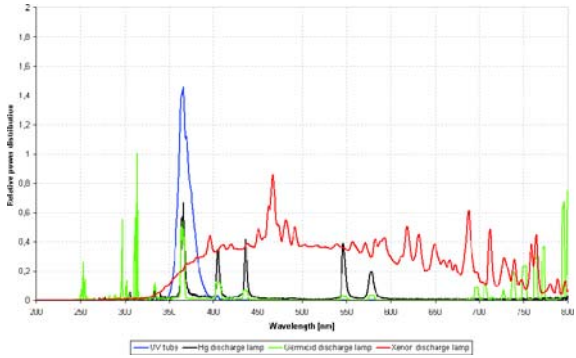

FIGURE 10 Relative spectral power distribution of tested light sources.

$$I = \int_{400}^{700} K/S_\lambda \, d\lambda \tag{2}$$

For description of kinetic behaviour of our UV sensors we used first class kinetic model as is shown in following equations [3]:

$$\text{Exposition: } I = I_\infty + (I_0 - I_\infty) \cdot \mathrm{e}^{(-kt)} \tag{3}$$

$$\text{Relaxation: } I = I_0 + (I_\infty - I_0) \cdot \mathrm{e}^{(-kt)} \tag{4}$$

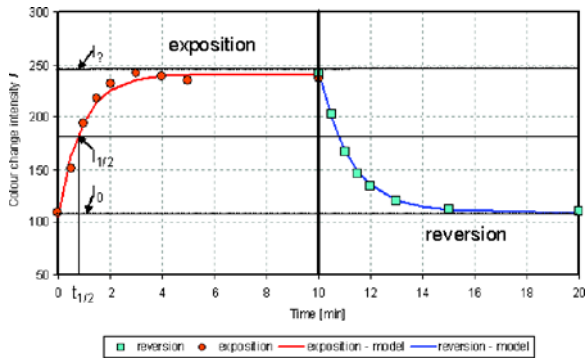

FIGURE 11 Typical growth and decay processes of colour change intensity for sample illumination of 714,6 $\mu W \cdot cm^{-2}$ power (979,3 lx).

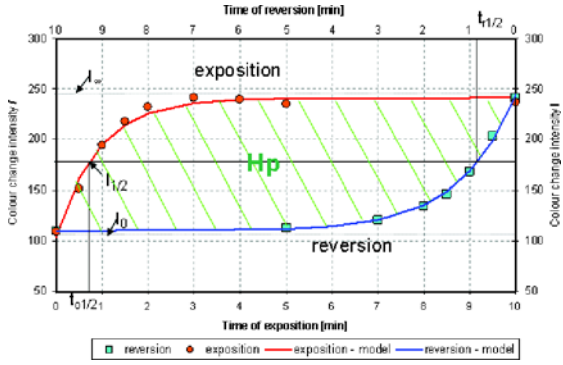

FIGURE 12 Colour hysteresis area ***Hp*** construction for sample at same condition as Figure 11.

From these equations is possible to calculate halftime of colour change $\mathbf{t}_{1/2}$ [4] and colour hysteresis area ***Hp***:

$$t_{1/2} = \frac{\ln 2}{k} \cdot 60 \tag{5}$$

$$H_P = \int I_\infty + (I_0 - I_\infty)\mathrm{e}^{-kt}dt - \int I_0 + (I_\infty - I_0)\mathrm{e}^{-kt}dt \tag{6}$$

As is from equation (6) evident that colour hysteresis area ***Hp*** arise by time reverse of reversion data as is shown on the Figure 12.

RESULTS

Data on both Figures 11 and 12 were obtained for lowest intensity of illumination ***E*** (979,3 lx). On the Figure 12, we can see, that already for this ***E*** in the colour change speed is higher during of exposition than reversion phase.

In our study we prepare new view on the relationship between intensity and time of exposition, time of relaxation respectively. Name of this new kind of graphs is colour hysteresis area ***Hp***. When we will test relationship between halftime of colour change $\mathbf{t}_{1/2}$ and intensity of illumination ***E***, we obtain decreasing linear relation – Figure 13. That means time of colour change is shorter during intensity of illumination increasing.

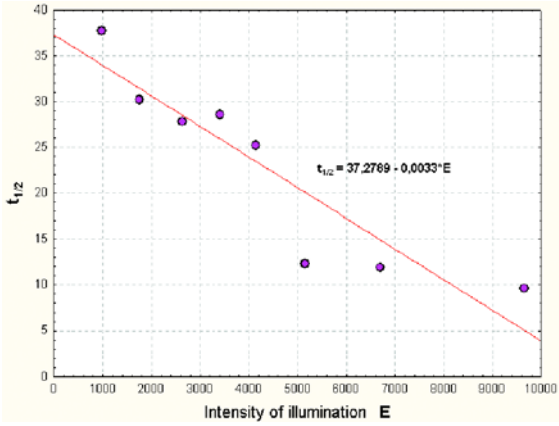

FIGURE 13 Halftime of colour change $t_{1/2}$ relation on intensity of illumination.

Linear relation we obtain also via dependency of hysteresis area on intensity of illumination ***E***. On the Figure 14, is shown dependences hysteresis area relation to UV absorber dose also. It is evident, that increasing of UV absorber dose gives decreasing of ***Hp***.

As was mentioned before used measuring units were prepared for measuring colour change of tested samples under different light sources. On Figure 15 and Figure 16 are shown results for photochromic pigments solutions **PPS** and prints **PTP**.

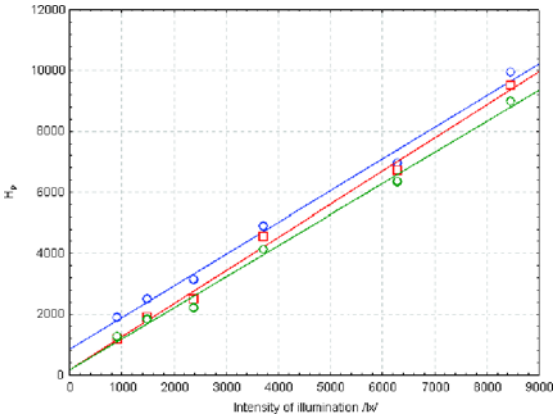

FIGURE 14 Colour hysteresis area ***Hp*** relation on intensity of illumination.

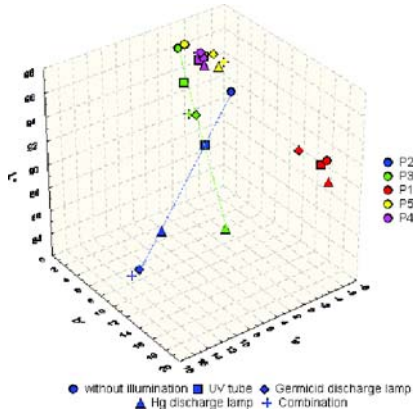

FIGURE 15 Change of **PPS** colour position dependent on different light source.

On Figure 17 and Figure 18 are shown results for colour shift of photochromic pigments solutions **PPS** and prints **PTP** in chromatic-plane of CIELAB colour space. From these results is evident, that used media has control influence on colour shift in colour space and hysteresis trajectory is little bit complicated. At the same time we can see, that relaxation after same time and intensity illumination for samples with comparable concentration is distinctively slower for photochromic solution than for photochromic prints.

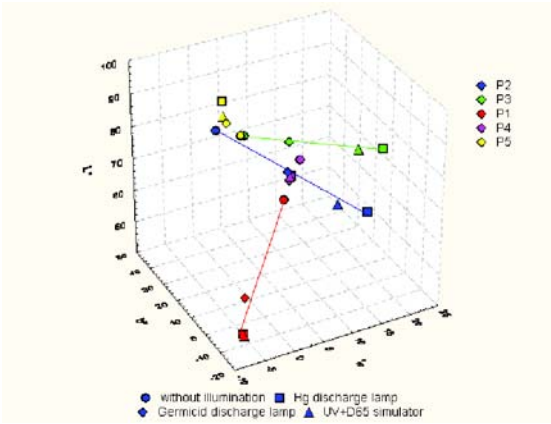

FIGURE 16 Change of **PTP** colour position dependent on different light source.

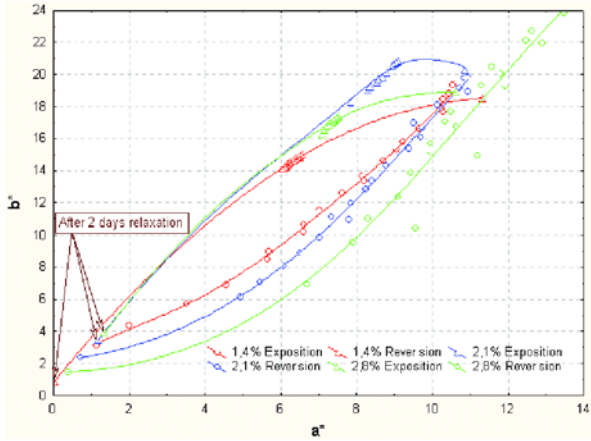

FIGURE 17 Colour shift of **PPS** in chromatic plane of CIELAB colour space.

CONCLUSION

This paper is introducing study of dynamic properties of photo chromic textile sensors. In our study we prepare new view on the relationship between intensity and time of exposition, time of relaxation respectively. That means colour hysteresis area ***Hp*** is linear related to the intensity of illumination ***E***. Via this relation we demonstrate

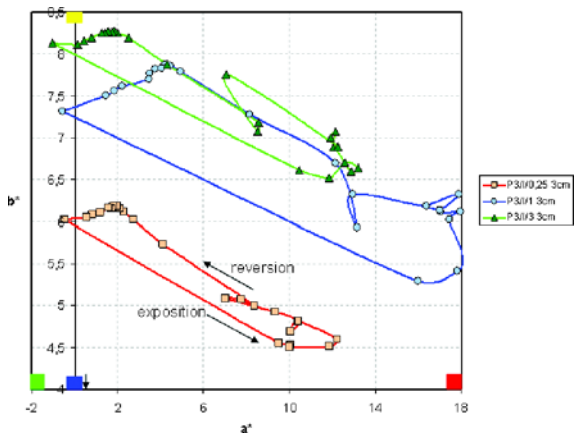

FIGURE 18 Colour shift of **PTP** in chromatic plane of CIELAB colour space.

the possibility of flexible textile-based sensors construction in area identification of radiation intensity. Beside of this one, we demonstrate differences between photochromic pigments behaviour in solution and prints on textiles: differences in hysteresis trajectory, differences between spectral power distribution of light source sensitivity of this one's. Bi-exponential functions, which are used in ***Hp*** calculation, well described the kinetics of colour change intensity of photochromic pigments. They give good fits to the growth curves as well as to the relaxation one's.

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