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Enhancing Colour Development of Photo chromic Prints on Textile

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***Abstract*- Textile UV-radiation sensors has lately been introduced to the field of smart textiles. Inkjet printing has been used as means of application due to the effective and resource efficient process. UV-LED radiation curing has been used in combination with inkjet printing in favour of low energy requirements, solvent free solution and reduced risk of clogging in the print heads. The problems arising when exposing photo chromic prints to UV-radiations are that oxygen inhibition during the curing and photo-oxidation in the print reduces the prints ability to develop colour. It is the oxygen in the air in combination with UV-radiation that gives the photo-oxi dating behavior. The aim of the study is to with the aid of physical protection reduce the effect of oxygen inhibition and photo-oxidation in the prints. Three types of physical treatments were used, wax coating, protein based impregnation and starch based impregnation. Treatments were applied before curing as well as after curing and the colour development after activation during 1 min of UV-radiation was measured with a spectrophotometer. Multiple activations were also tested to see how the treatments affected the fatigue behaviour of the prints over time. The aim was to have as high colour development as possible reflecting reduced oxygen inhibition and photo-oxidation. Results showed significantly higher colour development for samples treated with wax and whey powder before curing, but reduced colour development for amylase impregnation. Over time whey powder before curing showed highest colour development due to highest initial colour development. Lowest fatigue was seen for washed samples containing the chemical stabilizer HALS, showing an increased colour development. In reference to earlier studies the protective properties of wax and whey powder is due to their oxygen barrier properties protecting the print. The tested treatments have shown that it is possible to reduce the effect of photo-oxidation during curing leading to prints giving higher colour development. This gives a great stand point when improving existing and future application of photo chromic prints on textiles.**

***Key words*- Photo chromism, photo chromic, textile, inkjet, UV-radiation, curing, physical stabilization, wax, whey powder, and amylase, photo-oxidation, and oxygen inhibition**

I. INTRODUCTION

UV-radiation is a key element to life on earth and is essential for human existence. UV-radiation, most often from the sun, not only helps to create life but can also be harmful if the exposure is too high. It is the long term exposure to UV-radiation caused by sunlight in combination with the individual's pigment type and genetic preconditions that are the main factors responsible for development of skin cancer. There are many ways to protects the skin from UV-radiation for example by spending less time in the sun, using sunscreen or protecting the body with textiles.

(Tarbuk, Grancarić et al. 2016) There are many factors to take into consideration when it comes to exposure to UV radiation and it is difficult to estimate the radiation dose without measurement equipment. One apparent feature visible to the naked eye is the skin turning red, but at this stage it is already too late and the skin can already be damaged. Long term exposure can be shown using UV-radiation sensors and can be produced in several ways. One quite recent development is to use photo chromic materials that reacts with the UV-radiation and shows a change in colour. One field in which photo chromic substances has been used in great extent for decades is the ophthalmic industry, producing lenses that change colour depending on the exposure of light from the sun.

Photo chromic dyes and prints have great potential when it comes to many different smart textiles and technical applications as well as in design features. (Little and Christie 2010, Gulrajani 2013) The advantage of using textile sensors compared to traditional sensors is the possibility to integrate the sensors in the structure of garments. The flexibility of a textile sensors permits movement of the textile in which it is incorporated. By using resource efficient methods like inkjet printing and UV-LED radiation curing, UV sensors can be printed on textiles with low energy and material consumption as well as producing low material wastes (Magdassi 2009). The field of research when it comes to inkjet printing on textiles is quite new and a lot of research has been done the last decade. One problem emerging in the usage of photo chromic dyes is photo oxidation. Photo-oxidation causes reduction in photo chromic effect of the dye due to chemical reaction with oxygen during exposure to UV-radiation. Overcoming this problem would make it possible to produce good quality photo chromic textile UV-sensors. (Dietz and El'tsov 1990)

1. Objective

The aim of this study is to improve the print quality of photo chromic dyes on textiles by reducing oxygen inhibition and photo-oxidation and thereby improving the colour development. Shielding the print from oxygen using physical protection while still letting the print be activated by UV-light is the main focus. Inspiration for the protective treatments has been found in the food pocketing industry looking at materials often used to protect fresh food from the environment, in this case wax , proteins and starches. The study will evaluate if the barrier properties of these materials can be used in a textile context protecting the photo chromic prints and enhancing their colour development.

II. PHOTOCHROMISM

Photo chromism is defined as a reversible transformation of a chemical compound between two states responsible for different absorption spectra of electromagnetic radiation. The original state referred to as A, and the transformed state referred to as B are both excited simultaneously, but the amount of each state will depend on the electromagnetic radiation present (Crano and Guglielmetti 1999, Bouas-Laurent and Dürr 2001). In most photo chromic compounds the B form absorbs longer wavelengths, in the visible spectra for the human eye (400-700 nm), while A absorbs in the UV-radiation spectra, see figure 1.

Transformation of a photo chromic compound from uncolored in state A to coloured in state B when exposed to light it is called positive photo chromism. In opposite when state A is coloured and state B is uncolored the transformation is called negative photo chromism or inverse photo chromism (Pardo, Zayat et al. 2011). It is the absorption of light that triggers the colour change from invisible to visible, or from one colour to another. When light is absorbed it will rearrange the bondings within the molecule where the new structure causes the compound to exhibit colour (or colour change) (Nigel Corns, Partington et al. 2009). Photochromic compound do not only experience colour change caused by light, butalso show different colour development due to theromo chromism and solva chromism, e.i. they can react both photo chromic and thermo chromic. Even when working with a compound in the purpose of using its photo chromic properties the effects of thermo chromism and solva chromism has to be taken into account (Bam field 2001). Thermo chromism is the chromism that will give a reversible change in colour depending on temperature and is called an intrinsic thermo chromic system.

There are also indirect systems, these are not thermo chromic but can show colour changes due to changes in the environment that is caused by temperature (Ortica 2012). Photo chromic compounds also experience solva chromism and are greatly affected by the medium or material they are integrated in, affecting the kinetics of the photo chromic reaction. This colour change is due to changes in absorption spectra or emission spectra. The nature of the colour change is depending on the salvation energies in ground and excited states. (Crano and Guglielmetti 1999, Bam field 2001).

III. PHOTOCHROMISM TYPE T AND TYPE P

When state A is transformed into state B by irradiation it can transform back to state A in two different ways. In the T-type photo chromism the compound is reversed thermally. Compounds of P-type revert photo chemically by irradiation of another range of wavelengths than the irradiation that induces the activation. (Bouas- Laurent and Dürr 2001, Nigel Corns, Partington et al. 2009) In the uncolored state the photo chromic compound showing photo chromism type T has a ring formed structure. When the compound is transformed ring-opening occurs giving a new structure that exhibit colour. The structure of compounds that show photo chromism type P have a ring-opened structure in its uncoloured form. In the coloured form this structure is closed and the compound undergoes a cyclisation. (Gulrajani 2013)

IV. PHOTOCHROMIC DYES

There are both organic and inorganic compounds that show photo chromic effect. The inorganic substances are often metals and minerals not suited for dyeing of textiles. There are several groups of organic photo chromic compounds the most important being spiropyrans, spirooxazines, naphthopyrans, fulgides, fungicides and diary lethylenes. (Rijavec and Bračko 2007) The first group of organic photo chromic compounds that was investigated and therefore the most studied is the spirogyra group. Spirogyras show however some limitation in colour spectra and has a tendency to be sensitive to fatigue and has therefore nowadays often been substituted for other photo chromic compounds. Spirooxazines have also been investigated for a long time due to their photo chromic effect, but especially because the resistance to fatigue is much better than for spirogyra's. It is the fatigue resistance, or resistance to light-induced degradation that has made the compounds commonly used in eyewear. Another group that has been used more frequently lately is the naphthopyran group, similar to spirooxazines also show better resistance to fatigue than spiropyrans.

The broad spectra of colours that naphthopyrans exhibit has also been a great factor in the increased interest in these compounds. Fulgides are mainly reversed to their original state by photochemical reaction and are therefore used when this property is desired. Increasing the thermal stability of this group has been of great interest to be able to use fulgides in for example security printing. (Crano and Guglielmetti 1999)

Fig.1 Photo chromic T-Shirt.

V.PHOTOCHROMIC NAPHTHOPYRANS

Naphtopyrans are some of the most used photo chromic compounds. The advantage of Naphthopyrans, also called chormenes, compared to the commonly used spirooxazines is the reduced sensitivity towards temperature changes (Nigel Corns, Partington et al. 2009). Like most of the photo chromic compounds, naphthopyrans have a ring structure in its uncolored state A. It is the C-O bond in the pyran ring that is broken when the dye is exposed to UV-radiation, which gives the dye its open form B exhibiting colour, see figure 2 (Bam field 2001). Naphthopyrans can be produced in many different colours such as yellow, orange, red, violet and blue making them desirable for many different applications. This photo chromic group has been especially interesting for the ophthalmic industry since it can produce compounds with desire colours such as brown and grey used in glasses. (Gulrajani 2013).

VI. CONCLUSIONS

It has been shown that it is possible to enhance the colour development of photo chromic prints cured with UV-LED radiation curing using physical stabilizers, through impregnating the fabric with whey powder or coating it with wax. For both unwashed and washed samples all treated samples showed higher colour development than samples containing the chemical stabilizer HALS. Over time washed samples containing HALS were the only samples showing increased colour development. Higher colorations was achieved if samples where coated or impregnated before the curing process.

This was experienced for both unwashed and washed samples where unwashed samples showed highest colour development. The physical stabilization using impregnation and coating gives protection agains oxygen 56 inhibition through forming a barrier protecting print. Whey powder impregnation gave the highest colour development after a single activation. After multiple activations of unwashed samples all tested samples showed fatigue. Washed samples showed a lower fatigue than unwashed samples but had a lower initial colour development. After multiple activations wax and whey powder treated prints showed reduced fatigue compared to the reference, but only the chemical stabilizer HALS gave a sufficient protection against photo-oxidation giving increased colour development over time. These results could also be supported statistically using t-test and ANOVA.

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