

Title of the dissertation: Properties of Photochromic Textiles

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## Opponent's review

The present dissertation deals with the incorporation of commercial photochromic dyes/pigments into polypropylene by a process of mass coloration and the application of one dye/pigment by sol-gel process to the surface of PET fibers. The work is very useful for the textile industry because it basically solves the technology of preparing fabrics with photochromic dyes/pigments so that the correct optical effects are achieved.

Formally, the work is written very well by very good English and a reasonable range.

As far as the content is concerned, I will start with the introduction and the literary research part and the philosophy of the whole work. The author of the paper describes nicely the chemistry and photo-physical properties of the photo-chromic dyes and pigments, but the great weakness is that it does not distinguish whether it is a dye or a pigment. The situation is at present such that they are essentially disperse dyes, which are additionally photochromic, and there are very few compounds that are also photochromic in the solid (crystalline) phase - photochromic pigments. For dispersion dyes, it is assumed that inside the hydrophobic fiber is a form of "solid solution"; so that photo-chromic effect is present in individual molecules. On the contrary, pigments are dispersions of crystals inside (or on the surface) of the hydrophobic fiber. So I'll start with an explanatory question. The author used three photochromic compounds, MPB, MPP and MPY in his experiments. Are these compounds photochromic if they are just poured on the surface of the fabric? For polypropylene coloration in mass, the author writes that the pigment has been blended into molten polypropylene (page 35). Has a solution or dispersion been formed? On the contrary, in sol-gel technology (page 89), the author writes that a clear solution has formed which he applied to the surface of PET fabric. If this is true, this suggests that it is a "solid solution" where it is a photochromic of individual molecules.

In the scheme 2 (page 15) is a small error, the product of homolytic cleavage being two radicals.



The question of whether the pigment or dispersion dye is completely fatal for the photoresistance (lightfastness) of these photochromic colorants, which is a major problem with the current photochromic compounds. By the way, due to the formation of a triplet excited state.

As for recommendations for future work in this field. And I'll start asking. Did the author of this dissertation work meet the dyes for natural (hydrophilic) fibers that would be soluble in water and would be photochromic after application to these fibers? This is one direction. The second direction is the photochromic of the pigment (photochromic effect in the solid state), as this could solve the problem of low lightfastness.

In conclusion, I can say that the work is very good and I therefore strongly recommend the work for the defense.

In Pardubice on 9.10.2018

Prof. Ing. Radim Hrdina, CSc.

Aravin Prince Periyasamy, M.Tech.

PhD. Dissertation:

PROPERTIES OF PHOTOCHROMIC TEXTILES

Review

Dissertation submitted is divided into eight parts. The bottom-line of all of them is the extensive study of photochromic dyes. There are two materials thoroughly studied in the Dissertation. The first one, polypropylene, was used as the polymeric matrix. It was mixed with three commercial photochromic dyes (one with spiropyran skeleton and two with spirooxazine structures) shown on page 33. It is known, that polypropylene can be colored only through mass or spin coloration techniques. The second material to be coloured was PET fabrics using thin surface layer prepared from one photochromic pigment with the help of the sol-gel method.

To keep my review acceptably short, I will concentrate on the chemistry behind the coloration process dealing with the sol-gel photochromic fabric. This part is much more chemistry oriented and it is what I was looking for. It should be stressed that Disertation reports on immense amount of experimental work, mainly connected with the colorationm itself.

Consequently, I have several questions and remarks that follow.

- 1. The first remark is that I am missing very badly the detailed description of experixments that is usually called experimental part. Such part allows any reader to perform experiments successfully which should summarise the all experimental procedures. On page 35 and 89 we can find something called "process sequence" and "sequencing process. These descriptions of both types of experiments are not sufficient. The same is true for description of dip coating method on page 85. Expression like "constant speed" and "for a while" can be found there.
- 2. On page 84, there are schematic representation of sol-gel coating method, followed by short description of chemistry behind it on pages 86 88 and finally, the whole process on page 89. The chemistry described is shown for dimers only. Is it so, that reaction goes to dimers stage and stops there? Could you show chemical reactions going on in the each step depicted there.
- 3. It would be also very important to fill all these reaction precisely up to the stage of polymers.
- 4. There are substantial difference between the structure of photochromic material based on polypropylene and PET as far as the bonds formed are concerned. Could you discuss this in more details.

- 5. On page 117 the surface roughness characteristics of coated fabric are given. Frankly, I am unable to see any substantial changes among figures 78A 78F. Could you also estimate, how many molecules of MPP photochromic dyes would fit to max. peak hight shown in Table 16.
- 6. Could the theoretical (quantum) chemistry be of some help in the study you have described in Dissertations?

Finallly, I can conclude, that Dissertation reports on many experiments done, most of them are carefully interpreted and used for building up the general picture of photochromic textile preparation, structure and application potential.

I am in the position to recommend the Dissertation in question for further process leading to PhD degree.

In Liberec, 29. 10. 2018

Prof. Ing. Ivan Stibor, CSc.

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