POLYPROPYLENE AND POLYAMIDE FIBRES CONTAINING PHOTOLUMINESCENT PIGMENTS

Ľudmila Balogová, Katarína Ščasníková and Mária Húšťavová

Research Institute for Textile Chemistry (VÚTCH) – CHEMITEX, spol. s r.o., Rybníky 954, 011 68 Žilina, Slovak Republic
balogova@vutch.sk

Abstract: *This article is focused on evaluating the efficiency of special protective photoluminescent pigments in polypropylene (PP) and polyamide (PA) fibres and textiles. The polypropylene and polyamide fibres have been prepared during our research by an innovative spinning technology using progressive polymer dispersions (concentrates) containing 0.01 wt.% and 0,1 wt.% of the photoluminescent organic pigment UVB, EOB3 and H-KSN. Processability of the developed fibres has been evaluated in the construction of single jersey fabrics. Degree of efficiency of the photoluminescent pigments in PP and PA fibres and fabrics has been evaluated objectively by change of color expression by means of the color coordinate b* in CIE LAB color space using ULTRASCAN XE spectrocolorimeter according to the standard STN ISO 105-J03 and by optical expression of the photoexcitation initiated by absorption of photons of electromagnetic radiation under UV lamp with a LED bulb. Intensity of optical excitation during detection under UV light creates an individual pattern enabling clear identification of the photoluminescent fibres in order to protect products against counterfeiting and ensure their authenticity and originality. There are mentioned also the results from evaluation of selected human-ecological properties of PP fibres containing the photoluminescent pigments and further possibilities of their application in the textile and clothing products.*

Keywords: *photoluminescent pigments, photoluminescent PP and PA fibres, photoexcitation, originality protection.*

1 INTRODUCTION

The long-lasting problem of the high amount of counterfeit products in the market and the growing trend of direct annual losses from infringements of intellectual property rights of trademark owners and legitimate OEMs are forcing manufacturers to look for new ways and solutions to be a step further than counterfeiters, to protect their name, brand, but especially the quality of their products. In addition to originality, counterfeits in most cases do not meet the requirements for the protection of human health, safety and quality of materials used, and in many cases are harmful to health [1, 2].

Photoluminescent dyes and pigments, which exist in organic and inorganic form, are mainly used to control the protection of the originality of the products [3]. One of the solutions is the application of photoluminescent pigments to textile fibres. These identification elements can be incorporated into textile and clothing products and will ensure the protection, originality and authenticity of products on the market. Optical excitation of photoluminescent pigments when detected under an ultraviolet (UV) lamp creates an individual spectral pattern that allows clear authentication of the product.

The effects which involve energy absorption and subsequent light emission are generally classified as luminescence [4]. Light is created as a result of the excitation of the electrons or molecules from their standard state by the radiation of this obtained excess energy during the transition of electrons to the original state. Such excitation of electrons can be caused by many ways, for example, by irradiation a textile with ultraviolet, infrared, visible or other radiation [5, 6]. For textile products made of unmodified polymer fibres, it is possible to ensure the protection of their originality by using security protection patterns made of photoluminescent polymer fibres in products, e.g. by embroidering the manufacturer's logo on the finished product, resp. by integrating the security label. Verification of patterns under a UV lamp will reveal hidden security patterns confirming the authenticity of the document [7].

This article focuses on the solution how to protect the product originality by using the polypropylene (PP) and polyamide (PA) fibres and progressive dispersions (concentrates) with a content of 0.01 and 0.1 wt.% of special protective photoluminescent (PL) blue organic pigments UVB, EOB3 and H-KSN and verification of their application in selected textile products.

2 EXPERMENTAL PART

2.1 Materials used

As part of our own research, the following types of shaped fibres with a fineness of 170 dtex were prepared:

a) *PP fibres* with content of PL blue pigment *UVB* with a concentration of 0.01 and 0.1 wt.%;

b) *PP fibres* with content of PL blue pigment *EOB3* with a concentration 0.01 and 0.1 wt.%;

c) *PA fibres* with content of PL blue pigment *UVB* with a concentration of 0.01 and 0.1 wt.%;

d) *PA fibres* with content of PL blue pigment *EOB3* with a concentration 0.01 and 0.1 wt.%;

e) *PA fibres* with content of PL blue pigment *H-KSN* with a concentration 0.01 and 0.1 wt.%;

f) shaped standard (unmodified) PP and PA fibres without photoluminescent (PL) pigment content.

PP and PA fibres were used to produce single jersey (100% quality component). An overview and designation of the prepared knitted fabrics is given in Table 1. The textile processability of the prepared PP and PA fibres was good without defects.

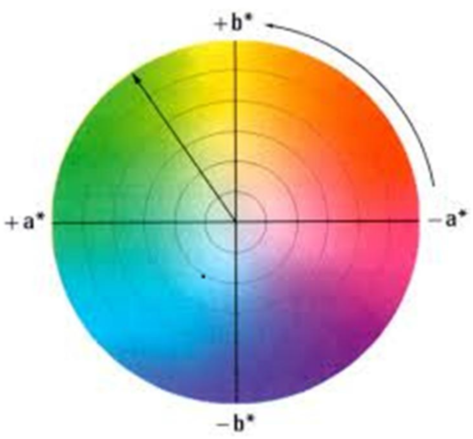
Table 1 Identification of fibres and knitted fabrics prepared from standard and photoluminescent PP and PA fibres

Fibres	Knitted fabrics
PP/FT/standard	PP/P
PP/UVB/0.01%	PP/UVB/0.01/P
PP/UVB/0.1%	PP/UVB/0.1/P
PP/EOB3/0.01%	PP/EOB3/0.01/P
PP/EOB3/0.1%	PP/EOB3/0.1/P
PA/FT/standard	PA/P
PA/UVB/0.1%	PA/UVB/0.1/P
PA/EOB3/0.1%	PA/EOB3/0.1/P
PA/H-KSN /0.1%	PA/H-KSN/0.1/P

2.2 Methods for evaluating the effectiveness of radiation intensity

The research solution for evaluating the efficiency of radiation intensity of photoluminescent blue organic pigments UVB, EOB3 and H-KSN (containing 0.01 and 0.1 wt.% of protective photoluminescent pigment) of developed PP and PA fibres and textiles prepared from them was performed by two methods:

- *objectively by changing the color expression* defined by the color coordinate b* in the CIE LAB color space on the ULTRASCAN XE according to the STN ISO 105-J03 standard. The color coordinate b* defines the shades between yellow and blue and it is a symbol for all differences between the two colors (2 color points or the coordinates of 2 color points). The intensity of the blue radiation depends on the shift of the measured value b* in the a, b diagram according to the b-axis (Figure 1a). Shifting the b* coordinate to positive values (+b*) causes the transition of the color to an area that approaches to the spectrum of yellow color. Shifting the b* coordinate to negative values (-b*) causes the color transition to an area that approaches to the blue color spectrum. The lower (more negative) the measured value of b*, the more significant the intensity of the blue light emission of the tested sample [8].
- *optical demonstration of photoexcitation* (radiation emission) initiated by the absorption of photons of electromagnetic radiation under a UV lamp with an LED lamp Nitecore CU 6 Chameleon (Figure 1b). When using a UV lamp, a physical effect is observed. The fiber / textile material containing 0.01 and 0.1 wt.% the photo-luminescent pigment emits more blue light than the pigment-free fabric.



a)

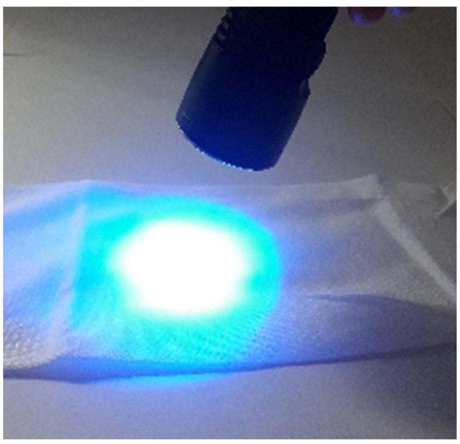

b)

Figure 1 CIELAB color space (a) and optical expression of blue light when using a UV lamp (b)

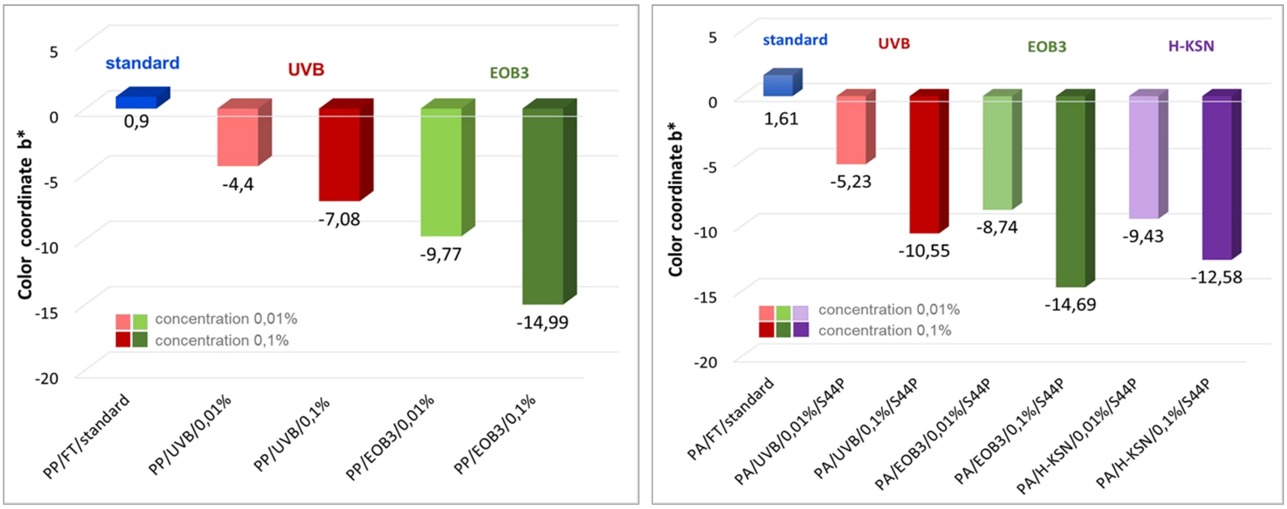
3 RESULTS AND DISCUSSION

3.1 Evaluation of the efficiency of radiation intensity of photoluminescent PP and PA fibres

The degree of effectiveness of PL pigments was evaluated in the developed PP and PA fibres without content (standard) and with a content of 0.1 and 0.01 wt.% of PL pigments UVB, EOB3 (PP fibres) and UVB, EOB3, H-KSN (PA fibres) using an objective instrumental method by determining the change in color expression which is defined by the color coordinate b* on the PP/PA fibres coils. The results are shown in Figure 2. PP fibres with a content of 0.1 wt.% PL pigment EOB3 has a 110 % higher intensity of blue light emission than PP fibres with the same content (0.1 wt.%) of PL pigment UVB and also 50% higher than PP fibres with content of 0.01 wt.% PL pigment EOB3. The most significant intensity of blue light emission was achieved in PP fibres with a content of 0.1 wt.% PL pigment EOB3. The color coordinate "b*" of these fibres is at the level -14.99.

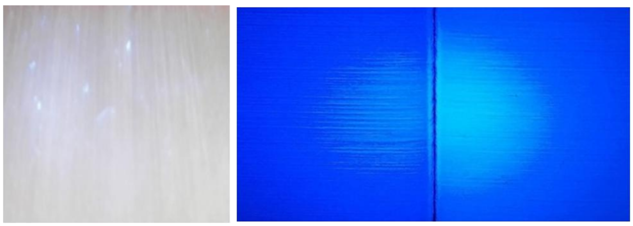
As with PP fibres, it was confirmed that the PA fiber with a content of 0.1 wt.% of PL pigment EOB3 has a higher intensity of blue light emission than PA fiber with the same content (0.1 wt.%) of PL pigment UVB (40% higher) resp. H-KSN (17% higher) and as a PA fiber with a content of 0.01 wt.% of PL pigment EOB3 (68% higher). The most significant intensity of blue light emission was achieved with PA fiber containing 0.1 wt.% of PL pigment EOB3. The color coordinate b* of this fiber is -14.69.

PP and PA fibres and fabrics with and without PL pigment are white in daylight and cannot be recognize with the naked eye. When using a UV lamp, a physical phenomenon is observed. Textile material containing PL pigment emits more light than fabrics without PL pigment. On the prepared textile materials containing PL pigment an optical excitation emitting a blue color was observed with the naked eye, which allows significant identification of the product containing the photoluminescent additives.



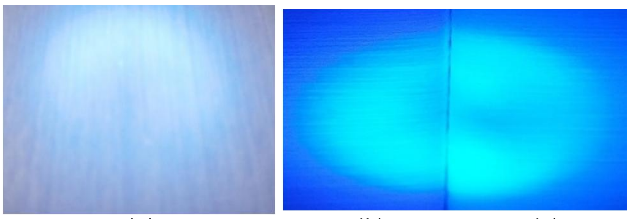
a) b)

Figure 2 Intensity of color expression of: a) PP fibres of without content (standard) and with content of 0.1 and 0.01 wt.% UVB and EOB3 photoluminescent pigments; b) PA fibres without content (standard) and with the content of 0.1 and 0.01 wt.% photoluminescent pigments UVB, EOB3 and H-KSN



3a) 3b) 3c)

Figure 3 Color intensity of PP fiber: a) standard PP fiber, b) PP fibres with a content of 0.01 wt.% PL pigment EOB3; c) PP fiber with a content of 0,1 wt.% PL pigment EOB3



4a) 4b) 4c)

Figure 4 Color intensity of PA fiber: a) standard PA fiber, b) PA fibres with a content of 0.01 wt.% photoluminescent pigment EOB3 and c) PA fibres with a content of 0.1 wt.% photoluminescent pigment EOB3

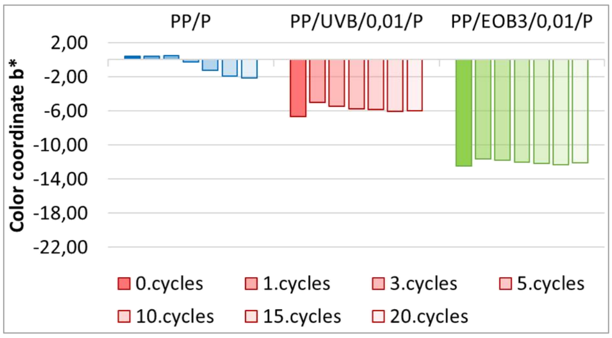
3.2 *Verification of the permeability of the efficiency of photoluminescent pigments in PP and PA fibres*

Verification of the permanence of the photoluminescent pigments UVB, EOB3 in PP and photoluminescent pigments UVB, EOB3 and HKS-N in PA fibres (concentration 0.01 and 0.1 wt.%) used in the construction of textiles (knitted fabrics) was performed after 1, 3, 5, 10, 15, 20 maintenance cycles by washing and drying, followed by evaluation of the color coordinate b* on the ULTRASCAN XE instrument and optical manifestation of photoexcitation under a UV lamp. The maintenance of textiles was performed in accordance with the standard STN EN ISO 6330: 2012 by the procedure 4N at the water temperature 40±2°C using the reference detergent 3 (ECE - phosphate-free powder detergent without optical brightener and without enzymes). Drying was performed according to procedure C: drying in a horizontal position in the spread state. The effect of washing on the change in the color coordinate b* of fabrics containing the above-mentioned PL pigments is shown in the graphs in Figure 5.

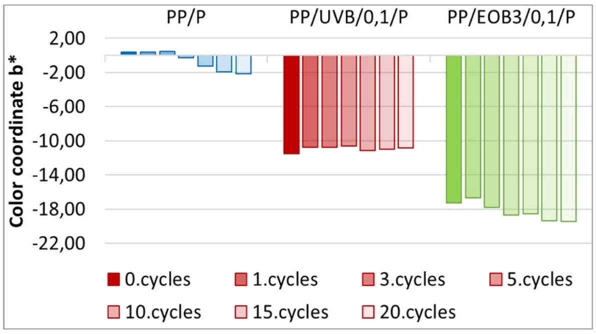
The trend of the decrease/increase in the intensity of the color expression of the photoluminescent pigment UVB in the PP fiber due to washing is comparable at both concentrations. The biggest decrease was always observed after the first washing cycle, when the photoluminescent pigment was apparently washed from the surface of the fiber. As the number of washing cycles increased, the intensity of the color expression changed continuously. After 20 cycles of washing, the decrease in the intensity of color expression was observed in the knitted PP fabrics containing PL pigment UVB at both concentration levels in the comparison with the knitted fabrics containing PL pigment EOB3. The difference in the intensity of radiation can be considered as statistically insignificant, as it could have arisen as a result of the same influences, including the influence of the fabric construction (knitted fabrics - change in density during handling).

<u>*Knitted fabrics prepared from PA fibres*</u> with a content of 0.1 wt.% of the UVB photoluminescent pigment, even after 20 washing cycles, had the same intensity of blue light emission as before washing. After 20 washing cycles of knitted fabrics prepared from PA fibres with a content of 0.1 wt.% of the photoluminescent pigment EOB-3 the color intensity increased +6% higher.

After 20 washing cycles of knitted fabrics prepared from PA fibres with a content of 0.1 wt.% of the photoluminescent pigment H-KSN the color intensity decreased -10%.



a)



b)

Figure 5 Influence of washing on the change of color coordinate b* of knitted fabrics: a) PP knitted fabrics with concentration 0.01 wt.% photoluminescent pigment UVB and EOB3 in the fiber; b) PP knitted fabrics with concentration 0.1 wt.% photoluminescent pigment UVB and EOB3 in the fiber

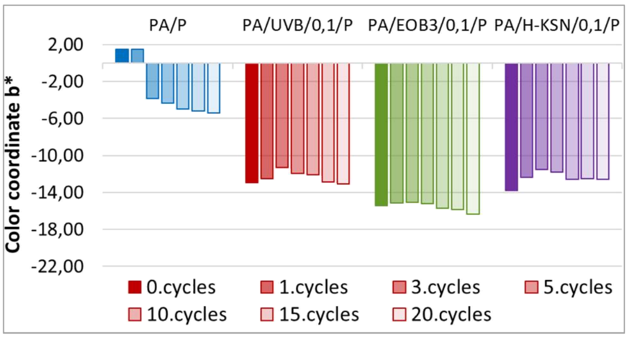


Figure 6 Influence of washing on the change of the color coordinate b* in PA knitted fabrics with a concentration of 0.1 wt.% pigment in the fiber

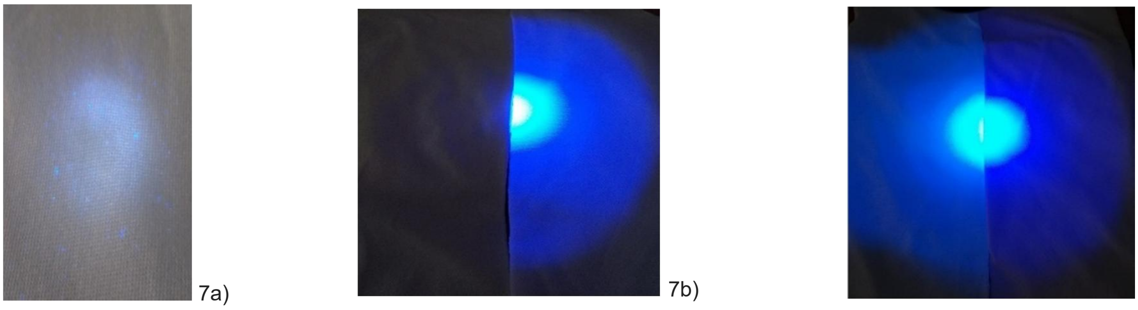


Figure 7 Intensity of color expression in PP knitted fabrics with photoluminescent pigment EOB3: a) knitted fabric of standard PP fiber; b) the standard knitted PP fabric on the left and the knitted fabric containing 0.1 wt.% pigment in the fiber on the right, c) the knitted fabric containing 0.1 wt.% pigment in the fiber on the left and on the right is a knitted fabric containing 0.01 wt.% pigment in the fiber

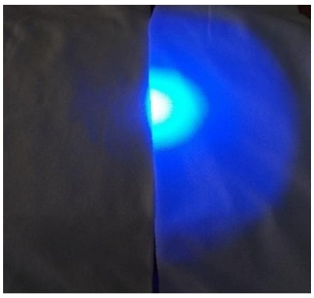


Figure 8 Intensity of color expression of PA knitted fabrics with photoluminescent pigment EOB3: on the left is a knitted fabric made of standard PA fiber, on the right is a knitted fabric containing 0.1 wt.% pigment in the fiber

The optical effect of photoexcitation in textiles (knitted fabrics) with the highest intensity of blue light emission under a UV lamp is shown in Figures 7 and 8.

3.3 The evaluation of human-ecological properties of PP and PA photoluminescent fibres

In order to demonstrate health safety, a set of analysis was performed on photoluminescent PP and PA fibres to verify the human-ecological properties and to confirm the health safety of developed PP and PA fibres with PL pigments according to the test methods of the international association OEKO-TEX® Standard 100. Analyzes were performed by 3 methods:

- by liquid chromatography (HPLC Agilent 1260 LC, 6120 MS) with diode and mass detector (LC/DAD/MS). *Alkylphenols* and *alkylphenol-ethoxylates* were determined according to OEKO-TEX® M-25 & ML-25. The analyzed samples of developed PP and PA fibres meet the required limits according to STANDARD 100 by OEKO-TEX®.
- Subsequently, the content of UV stabilizers was determined on samples of developed PP and PA fibres without and with a content of 0.1 wt.% photoluminescent pigment according to OEKO-TEX® M-28 & ML-28. The presence of forbidden UV stabilizers was not detected in any of the analyzed samples of developed PP and PA fibres and they meet the required limits according to STANDARD 100 by OEKO-TEX®.
- by atomic absorption spectrometry (SPECTRA DUO AA 240Z, AA 240 FS; AMA 254). The content of *extractable heavy metals* was determined in the samples of developed PP and PA fibres without and with a content of 0.1 wt.%. photoluminescent pigment UVB, EOB-3 (PP fibres) and UVB, EOB-3 and H-KSN (PA fibres) according to OEKO-TEX® M10 & ML-10. The performed analyzes confirmed that the laboratory samples of the developed photoluminescent PP and PA fibres do not contain harmful substances and meet the required limits according to STANDARD 100 by OEKO-TEX®.
- by gas chromatography with a mass detector (GC/MS). Determination of *polycyclic aromatic hydrocarbons (PAH)* in the samples of developed PA and PP fibres without/with content of 0.1 wt.% photoluminescent pigment UVB, EOB-3 (PP fibres) and UVB, EOB-3 and H-KSN (PA fibres) according to OEKO-TEX® M-23 & ML-23. The determined amount of PAH was below the detection limit (less than 0.3 mg/kg). According to the performed analyzes, it is clear that the analyzed textile samples do not contain harmful polycyclic aromatic hydrocarbons. Determination of *phenol, chlorinated phenols and*

orthophenylphenol (OPP) in the samples of developed PA and PP fibres without/with content of 0.1 wt.% PL pigment according to OEKO-TEX® M-7. The determined amount of chlorinated phenols was below the detection limit (for trichlorophenols, monochlorophenols and OPP less than 0.1 mg/kg and for tetrachlorophenols, dichlorophenols and PCP less than 0.05 mg/kg). The results of analyzes of the determination of OPP and chlorinated phenols indicate that these dangerous substances are not present in the tested samples.

4 CONCLUSION

The processability of the selected laboratory samples of photoluminescent PP and PA fibres into the construction of single jersey fabrics was confirmed in the laboratory. The textile processability of the developed photoluminescent PP and PA fibres into the assortment of knitted fibres was at a good level, without registration of any errors or without possible exclusion of the fiber sample. The degree of efficiency of photoluminescent pigments in developed PP and PA fibres and fabrics prepared from them was evaluated after the 20th cycle of washing by instrumental method determining color change defined by color coordinate b* and optical demonstration of photoexcitation initiated by photon absorption of electromagnetic radiation under UV lamp with LED lights. The most significant intensity of blue light emission was achieved with PP and PA fibres with a content of 0.1 wt.% photoluminescent pigments EOB3.

The measured color coordinates b* of knitted fabrics samples prepared from photoluminescent PP and PA fibres confirmed the results measured in PP and PA fiber coils in terms of selecting the most suitable type of photoluminescent pigment (EOB3) and its concentration (0.1 wt.%) in the fiber. PP and PA fibres and textiles with PL pigments as well as textiles without photoluminescent pigment are white in daylight and are not recognizable to the naked eye of the observer. When using a UV lamp, a physical phenomenon is observed. The textile material containing a photoluminescent pigment emits more light than a fabric without a photoluminescent pigment. In the prepared textile materials containing photoluminescent pigment, an optical excitation emitting a blue color was observed with the naked eye, which allows significant identification of the product containing the used photoluminescent additives. Based on the measurement of the results of human-ecological properties, the performed analyzes confirmed that the laboratory samples of the developed photoluminescent PA fibres do not contain harmful substances and meet the required limits according to STANDARD 100 by OEKO-TEX®.

ACKNOWLEDGEMENT: *This work was supported by the Slovak Research and Development Agency under the Contract no. APVV-18-0187.*

5 REFERENCES

1. Purvis C.: Challenges in the global man-made fibres market, Proceedings of 49th Dornbirn Man-Made Fibres Congress, 15-17 September 2010, Austria, p. 48
2. https://www.cas.sk/clanok/618514/colnici-zlikvidovali-napodobneniny-hraciek-a-textilu-v-ohni-skoncilo-21-tisic-fejkov/
3. Bamfield P.; Hutchings M.G.: Chromic Phenomena, Technological Applications of Color Chemistry, 2nd Ed., The Royal Society of Chemistry, Cambridge, 2010, ISSN 978-1-84755-868-8
4. Kitai A.: Luminescent Materials and Application, John Wiley & Sons, Ltd, 2008, ISBN: 978-0-470-058 18-3, Available from: http://kirchhoff.weebly.com/uploads/1/6/3/0/1630371/xandrea.pdf, Accessed: 2018-01-18
5. Krasovitskii B.M.; Bolotin B.M.: Organic Luminescent Materials, Weinheim NY, VCH, 2002
6. Bala R., Eschbach R., Zang Y.: Substrate Fluorescence: Bane or Boon, In Proc. 15th IS&T/SID Color Imaging Conference, Nov.2007, Albuquerque, NM, pp.12-17
7. Rossier R.; Hersch R.D.: Hiding patterns with daylight fluorescent inks, 19th Color and Imaging Conference, 2011, pp. 223-228
8. Berns R.S.: Billmeyer and Saltzman´s Principles of Color Technology, 3rd Ed., New York: John Wiley, 2000, 247 p., ISBN 04-711-9459-X