COMMUNICATIONS IN
DEVELOPMENT AND ASSEMBLING OF TEXTILE PRODUCTS

The use of phosphorescence micromaterials for commercial textile products

Boris Mahltig, **Clara Heil, Sarah Kaub, Agnes Korn, Jaydip Nareshbhai Kapadiya**

Hochschule Niederrhein, Faculty of Textile- and Clothing Technology, Mönchengladbach, Germany
*Corresponding author *E-mail address:* boris.mahltig@hs-niederrhein.de

INFO

CDAPT, ISSN 2701-939X
Peer reviewed article
2024, Vol.5, No. 1, pp. 1-10
DOI 10.25367/cdatp.2024.5.p1-10
Received: 16 November 2022
Accepted: 09 May 2023
Available online: 01 January 2024

ABSTRACT

Fluorescent textile products are manifold used. Compared to fluorescent textiles, phosphorescent textile products exhibit an afterglow effect even after the illumination is stopped. Phosphorescent textiles are less present as commercial products on the market. With this background the aim of this paper is to investigate the properties of commercially available phosphorescent textile materials. Investigations are performed by illumination under different light arrangement. Microscopy is performed by scanning electronic microscopy (SEM) and advanced light microscopy using UV light. Light emission of the samples is recorded by fluorescence spectroscopy. The chemical composition is determined by using electron dispersive spectroscopy (EDS). Depending on the type of sample, an afterglow effect can be determined up to 5 to 30 minutes after stopping the illumination with UV light. By SEM and EDS methods it is observed that the phosphorescent effects are realized by application of phosphorescent pigments, which can be best described as phosphorescent micromaterials. Depending on the product category, two different types of phosphorescent materials are used – doped strontium aluminates ($SrAl_2O_4$) and zinc sulfide (ZnS). Products based on doped strontium aluminates exhibit longer afterglow effects compared to products with ZnS pigments. However, the use of doped strontium aluminate is quite surprising for a commercial textile product, because of cost reasons. Finally, it can be stated that phosphorescent micromaterials are established materials for realization of functional textile products. These micromaterials can be found in every day products and are examples for innovative particle technology used in commercial consumer products.

Keywords
phosphorescence,
fluorescence,
luminescent,
textile,
pigment printing,
spectroscopy,
electron microscopy,
advanced light microscopy

1 Introduction

Photoluminescent textile products are luminescent in case of illumination with light. In this category it is mainly distinguished between fluorescent and phosphorescent textiles. The main difference between fluorescent and phosphorescent materials is that a phosphorescent material exhibits an afterglow effect even after the illumination is stopped. Fluorescent textile products are manifold used and offered, e.g., for whitening effects, light effects for design, protective clothing, anticounterfeit applications and UV protection [1-6]. Textiles from polyester fiber materials dyed with fluorescence dyes are available in low price consumer products as safety vests or microfiber towels [7,8]. The combination of fluorescent actives dyes with sol-gel coating agents can modify the intensity of fluorescence and improve their rubbing fastness after application on textiles [9]. Phosphorescence effects are used to functionalize textile materials for different purposes as design effects, warning elements or anticounterfeit applications [10,11]. While fluorescence textiles are widely used and realized by application of fluorescence dyes, the use of textiles with phosphorescence effect is less common and usually realized by printing phosphorescence active pigments [12,13]. Phosphorescence textile products appear regularly as special offers on the German market and are then available for moderate or low prices. These products are related mainly to the home textile sector and to children clothes. The aim of this current investigation is to give an overview on some commercial materials with the questions which type of phosphorescence materials are used and what are their performance.

2 Textile materials and analytical methods

2.1 Phosphorescent textile materials

Five different textile products with phosphorescence effect are considered for the recent investigation. These textiles are offered at medium price range with maximum 10 Euro per piece by different suppliers. The product categories are home textiles and children clothes. Phosphorescence effects are introduced by pigment print with different images like stars, unicorns or dragons. An overview on these products is given in Table 1. The information given in Table 1 related to pigment composition and pigment diameter are gained by SEM and EDS measurements as described in the sub-section analytical methods.

Table 1. Overview on investigated commercial phosphorescent textile products and properties. These products contain different phosphorescent prints.

Sample no.	**Product**	**Pigment type**	**Pigment diameter (μm)**
1	Blanket	$SrAl_2O_4$ based	50-70
2	Blanket	$SrAl_2O_4$ based	50
3	Blanket	$SrAl_2O_4$ based	100
4	T-shirt	ZnS	30
5	Rompers	ZnS	40

Photographs of these samples are provided in Figures 1 and 2. Figure 1 shows the samples under illumination with daylight. For taking the photographs in Figure 2, the samples are illuminated with UV light. The product samples 1 to 3 are blankets where the phosphorescent prints are surrounded by fleece. Samples 1 and 2 have the phosphorescent print on a white background. The sample 3 exhibits phosphorescent prints in three different colorations. The samples 4 and 5 exhibits more detailed prints. However, for these samples only view areas of the detailed prints are luminescent active, as seen under illumination with UV light (compare Fig. 2).

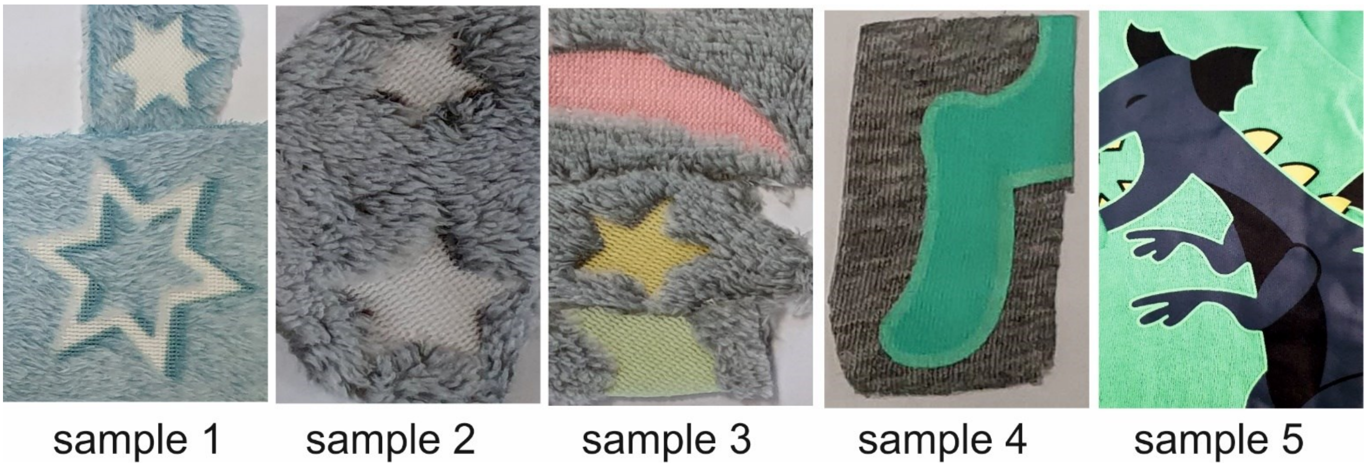

Fig. 1 Photographs of discussed samples recorded under illumination with daylight.

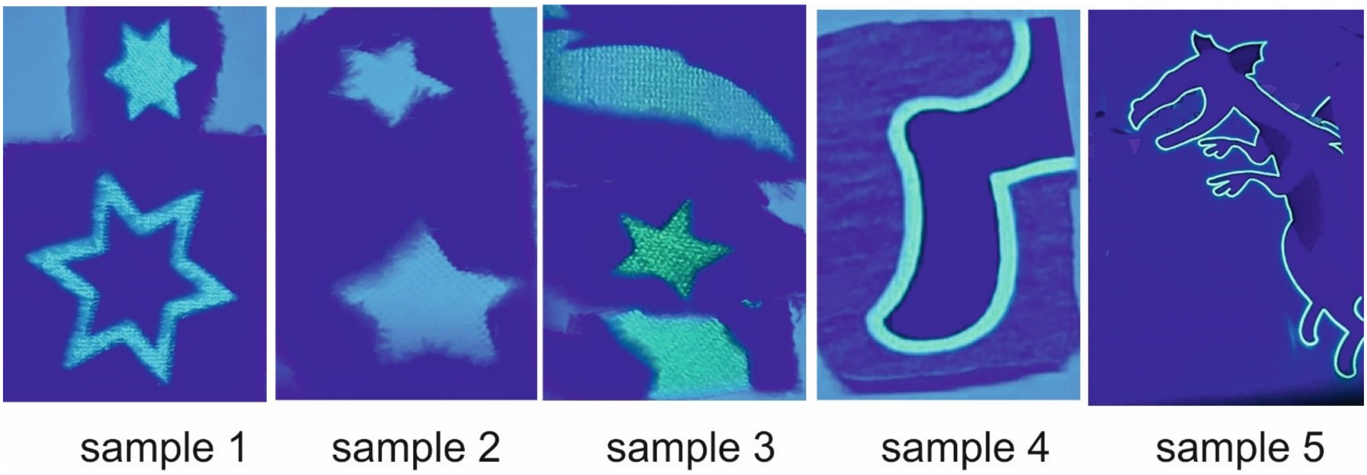

Fig. 2 Photographs of discussed samples recorded under illumination with UV light.

2.2 Analytical Methods

Microscopic investigations are done with a digital microscope PCE-MM200 using UV light for illumination. Further, scanning electron microscopy (SEM) is used (TM-3000 tabletop microscope from Hitachi, Japan). The tabletop microscope is equipped with an EDS (electron dispersive spectroscopy) unit (Quantax 70 from Bruker) allowing the identification of chemical elements on surfaces. By this EDS method the detection of the chemical element hydrogen is principally not possible [14]. The sensitivity of this method for the element nitrogen is low, so in most fiber analysis nitrogen is not clearly detected [15,16]. Optical properties and phosphorescence effects are determined by illumination in an illumination chamber Verivide using standard light D65. The standard light is related to daylight of the northern hemisphere and it contains light in the spectral range from 300 nm to 800 nm [17,18]. Also, illumination with UV light is performed. For this a UV black light lamp UV Omnilux 230V_25W is used in a dark room. For documentation of phosphorescence effect, photographs are taken after illumination for one minute with the UV lamp and afterwards storage in the dark chamber. Fluorescence emission spectra are recorded with a RF-6000 spectrofluorometer (Shimadzu, Japan). With this fluorescence spectrometer also the measurement of 2D fluorescence spectra is done.

3 Results and Discussion

3.1 Material properties and composition

For first orientation, the textile products are investigated by light microscopy using UV light as light source. By this, the luminescent effect on the printed areas are identified. The luminescent pigments on the textile surface are clearly visible (Fig. 3).

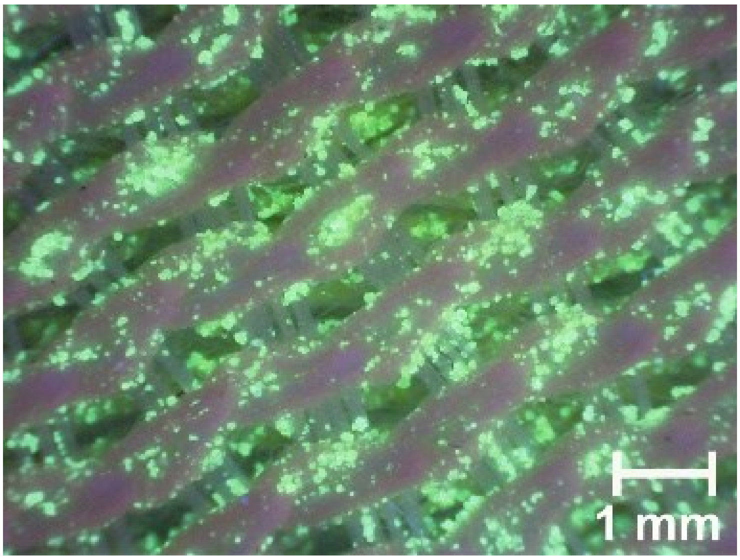

Fig. 3 Commercial phosphorescence textile print (here with sample 1) – view by light microscope under illumination with UV light.

By using SEM, the pigments on sample 1 are detected as well and in higher magnification they are identified as agglomerates of smaller micromaterials (Fig. 4). With the EDS method, the chemical composition of the pigments is identified (Fig. 4). For samples 1 to 3, the pigments are strontium aluminate ($SrAl_2O_4$) based and for samples 4 and 5 they are from zinc sulfide (ZnS). The presence of particle agglomerates of $SrAl_2O_4$ in commercial phosphorescent pigments for textile applications is reported in the literature [19]. The identification of the chemical element strontium by EDS method is not simple, because the signals according to the element silicon appear in the same region of the EDS spectrum. Further it should be remarked that in literature the application of phosphorescent $SrAl_2O_4$ based pigments on textile substrates is described. These phosphorescent pigments are doped with lanthanoids as, e.g., europium (Eu) or dysprosium (Dy) [19-21]. However, in the recent investigations the concentration of lanthanoids used for doping is probable too low to be determined by EDS-method. The preparation and application of such rare earth doped strontium aluminate pigments is intensively investigated by several groups during the last decade [22-25].

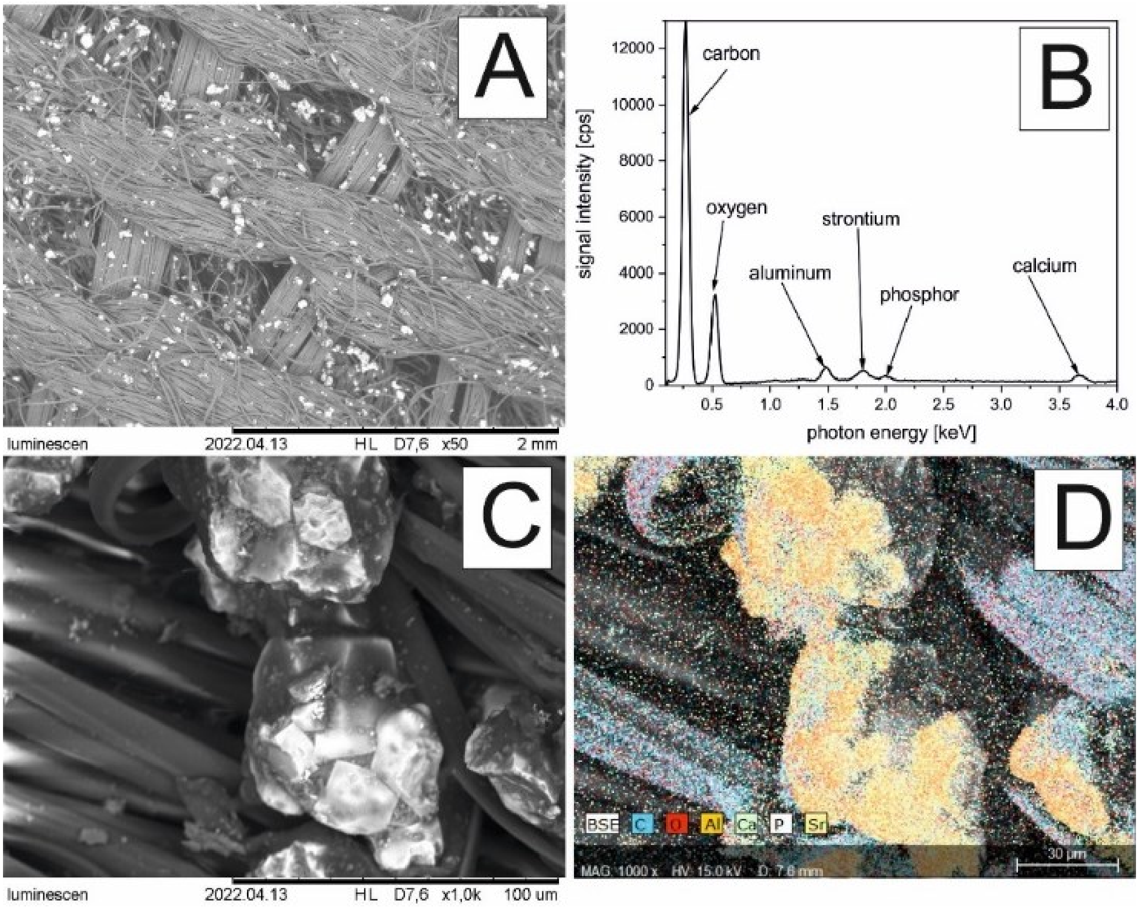

Fig. 4 Analysis of commercial phosphorescence textile print (here as example sample 1) – (A) overview SEM image in low magnification; (B) EDS spectrum with element analysis; (C) SEM in high magnification; (D) EDS mapping with detected chemical elements.

The particle size and shape for samples 2 to 5 are investigated by application of SEM in higher magnification (Figure 5). Please compare to the images of sample 1 shown in Figure 4. For the ZnS containing samples 4 and 5 regular shaped particles of nearly the same size are determined. These particles are surrounded by the binder layer. For the samples 2 and 3 with the $SrAl_2O_4$ based particles, the particle geometries are less regular. Here also larger agglomerates formed by smaller particles are detected. It can be stated that even the samples 1 to 3 contain $SrAl_2O_4$ based phosphorescent pigments, the used pigments are not the same due to different particle size and shape.

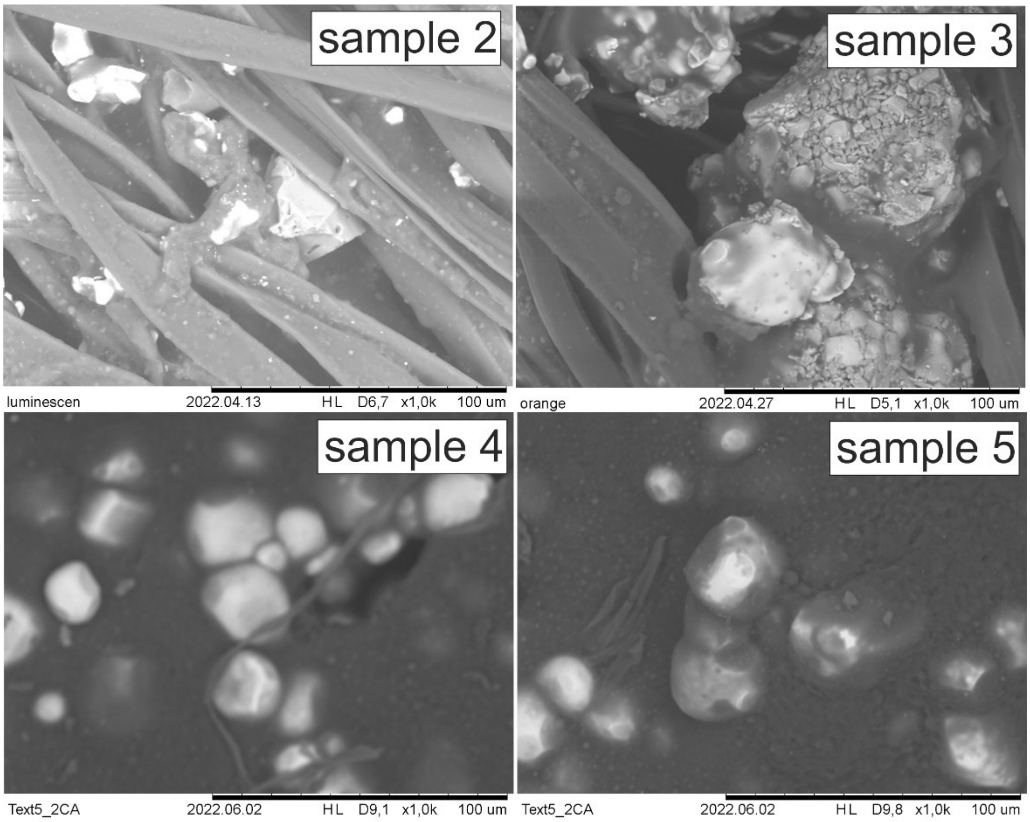

Fig. 5 SEM images of different samples in high magnification.

3.2 Fluorescence properties

The fluorescence properties of the samples are at first determined by 2D fluorescence measurements to support an overview on the complete fluorescence properties. An example for such a 2D fluorescence spectrum is given for sample 2 in Figure 6. The diagonal areas with high emission intensity are not related to the measurement of the textile sample. Instead, they are caused by the measurement arrangement. For sample 2, a clear region of fluorescent activity can be determined. The maximum of excitation is around 380 nm, while the emission maximum is around 440 nm. By this fluorescence effect, UV light is transferred mainly into visible blue light. The exciting UV light in the range of 350 to 380 nm refers to the emission to the sun light and commercially available black light and standard lamps [17,26-28].

Due to the high relevance of UV light in the spectral region around 380 nm, the fluorescence properties for all five samples are evaluated under excitation with UV light of 380 nm (Figure 7). In this comparison, sample 2 exhibits the strongest fluorescence intensity. The measurements at samples 1, 3 and 5 lead to a peak signal around 425 nm, which is probable related to the measurement arrangement and not caused by the fluorescent properties of investigated textile samples. The main maximum for fluorescence light of all samples (beside sample 2) is around 530 nm, which is related to yellow/green light [17].

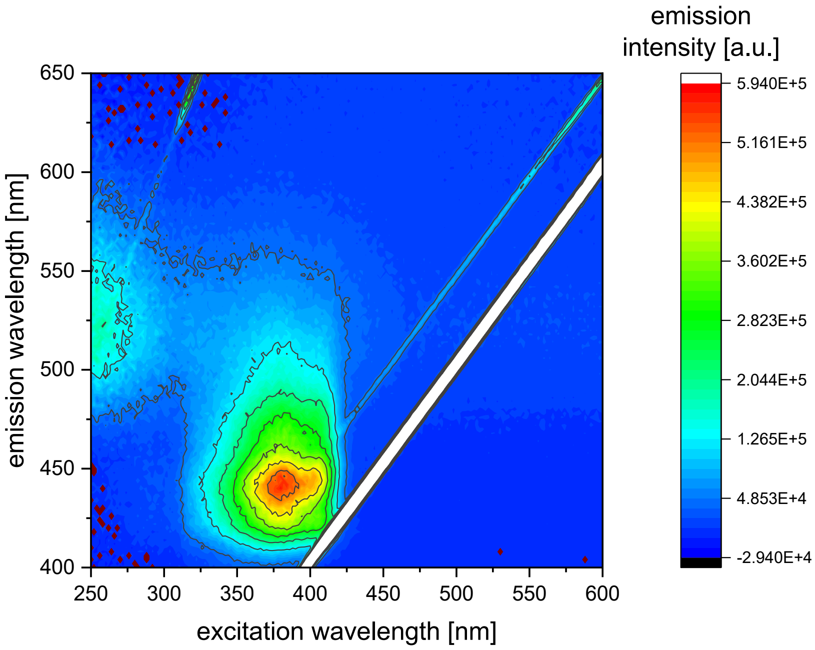

Fig. 6 2D fluorescence spectrum of evaluated sample no. 2.

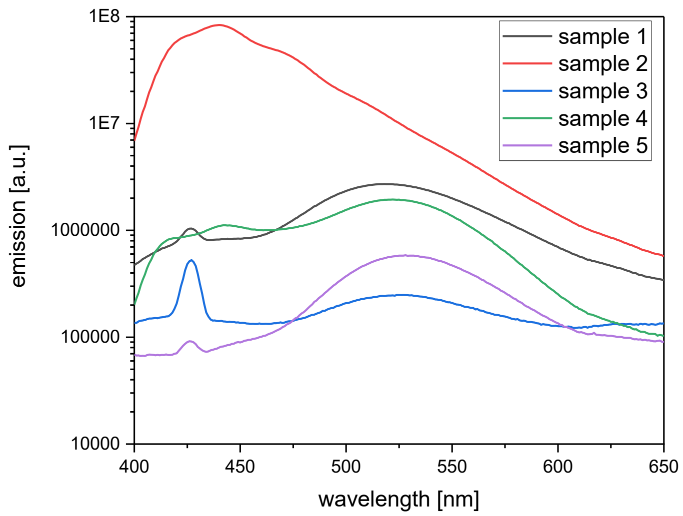

Fig. 7 Fluorescence emission spectra of evaluated samples – excitation performed with light of 380 nm.

3.3 Phosphorescence properties

The phosphorescence properties are evaluated after illumination with UV light for one minute or artificial daylight D65 for five minutes in a dark chamber. Figure 8 illustrates these results on sample 2 by photographs, while in Figure 9 the decrease in luminescence is given as function of time for all five investigated samples. Short time after illumination the luminescent effect is clearly visible but it strongly decreases as function of time. The three samples containing $SrAl_2O_4$ based pigments exhibit longer effects with more than 10 minutes (Fig. 9). Both samples with ZnS pigments show after 10 minutes low effects of less than 4% intensity.

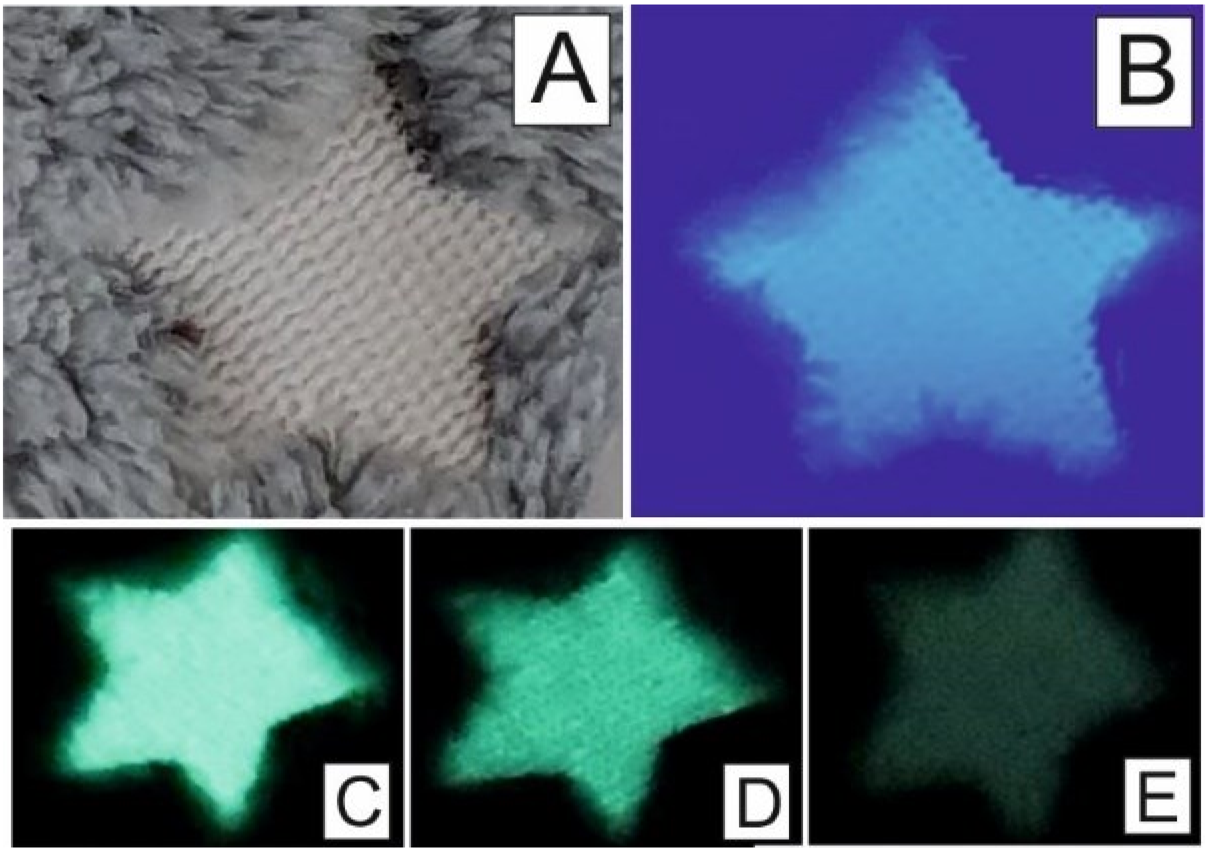

Fig. 8 Commercial phosphorescence textile print (sample 2) – (A) under day light; (B) under UV lamp; (C) in dark chamber after 1 min UV illumination; (D) in dark chamber 1 min. after UV illumination; (E) in dark chamber 4 min. after UV illumination.

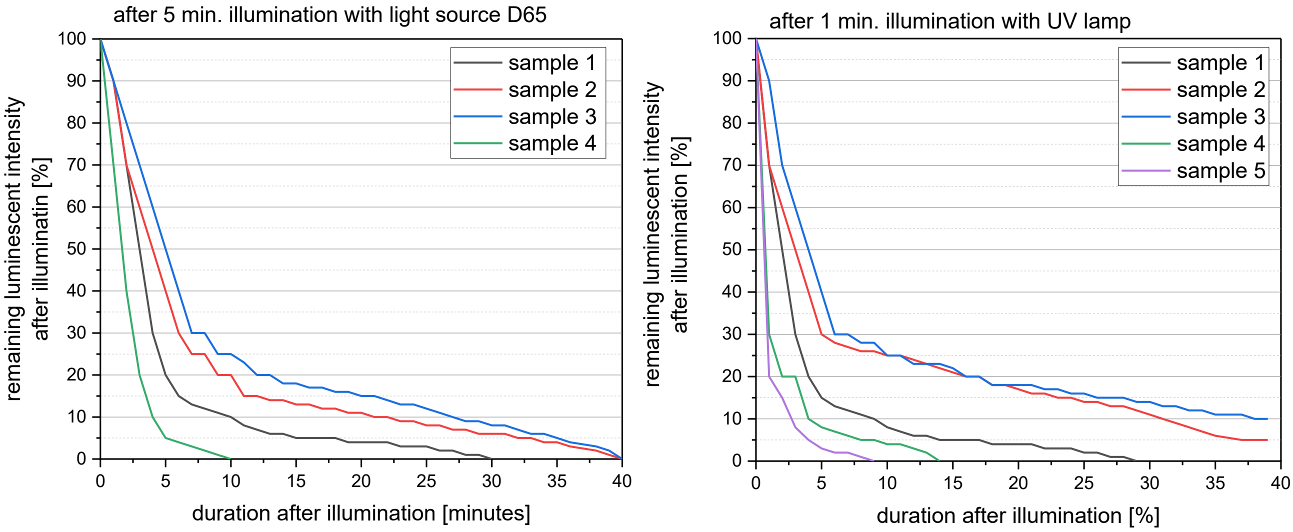

Fig. 9 Remaining luminescent intensity after the external illumination is stopped as function of time after stopping illumination. The external illumination is done for 5 minutes with the daylight source D65 (left image) or for 1 minute with the UV lamp Omnilux (right image).

4 Conclusions

Five commercially available functional textile materials with phosphorescence properties are evaluated. The phosphorescence properties are realized by pigment prints using $SrAl_2O_4$ based pigments or ZnS pigments. Identified $SrAl_2O_4$ pigments are built up by clusters of smaller micromaterials and are probable also containing a doping with rare-earth materials. With regard to the duration of the phosphorescence effect, the ZnS pigment containing products exhibit weaker performance. The main influence on the phosphorescence is obviously the composition of the used pigments and not the shape or size of pigment particles. The used textile material or the binder system used for the print may have an additional effect but such an influence can not be verified by the here presented results. Especially surprising is the use of phosphorescent pigments based on $SrAl_2O_4$, because this material is quite expensive as pure substance and here detected on a commercial product offered for moderate price.

Author Contributions

Clara Heil, Sarah Kaub, Agnes Korn and Jaydip Nareshbhai Kapadiya: illumination experiments, spectroscopic measurements and microscopic investigations. Boris Mahltig: supervision, writing, review, editing, spectroscopic and microscopic measurements.

Acknowledgements

All product and company names mentioned in this article may be trademarks of their respected owners, even without labeling. There is no conflict of interest and no funding for the presented research.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Grancaric, A. M.; Tarbuk, A.; Botteri, L. Light conversion and scattering in UV protective textiles. *AUTEX Research Journal* **2014**, *14*, 247-258. DOI: doi.org/10.2478/aut-2014-0025.
2. Baatout, K.; Saad, F.; Baffoun, A.; Mahltig, B.; Kreher, D.; Jaballah, N.; Majdoub, M. Luminescent cotton fibers coated with fluorescein dye for anti-counterfeiting applications. *Materials Chemistry and Physics* **2019**, *234*, 304-310. DOI: doi.org/10.1016/j.matchemphys.2019.06.007.
3. Liu, M. O.; Lin, H. F.; Yang, M. C.; Lai, M. J.; Chang, C. C.; Liu, H. C.; Shiao, P.-L., Chen, I.-M. Chen, J. Y. Thermal and fluorescent properties of optical brighteners and their whitening effect for pelletization of cycloolefin copolymers. *Materials Letters* **2006**, *60*, 2132-2137. DOI: doi.org/10.1016/j.matlet.2005.12.112.
4. Saad, F.; Baffoun, A.; Mahltig, B.; Hamdaoui, M. Polyester Fabric with Fluorescent Properties Using Microwave Technology for Anti-Counterfeiting Applications. *Journal of Fluorescence* **2022**, *32*, 327-345. DOI: doi.org/10.1007/s10895-021-02845-7.
5. Dalponte, E.; Mahltig, B.; Breckenfelder, C. Luminous Textiles for UV-Protection and Light Effect Application. Book chapter. In: *Textiles: Advances in Research and Applications*; Mahltig, B. (Ed.), Nova Science Publishers Inc., New York, USA, 2018; pp. 167-182.
6. Szuster, L.; Kaźmierska, M.; Król, I. Fluorescent dyes destined for dyeing high-visibility polyester textile products. *Fibres & Textiles in Eastern Europe* **2004**, *1*, 70-75.
7. Mahltig, B.; Leuchtges, G.; Holstein, P. T-Shirts – an overview and comments on price range, functional materials and European production. *Tekstilna Industrija* **2022**, *70*, 4-13. DOI: 10.5937/TEKSTIND2204004M.
8. Mahltig, B.; Ernst, V.; Schröder, L. Exemplarily view on selected fluorescence textile products. *Communications in Development and Assembling of Textile Products CDATP* **2023**, *4*, 61-69. DOI: 10.25367/cdatp.2022.4.p61-69.
9. Yuan, Y.; Grethe, T.; Mahltig, B. Sol-gel coatings with the fluorescence dye Rhodamine B for the optical modification of cotton. *Communications in Development and Assembling of Textile Products CDATP* **2023**, *4*, 1-17. DOI; 10.25367/cdatp.2022.4.p1-17.
10. Vik, M.; Vikova, M.; Kasparova, M. Decay of Phosphorescent Warning Design on Textile Substrates. *Applied Mechanics and Materials* **2014**, *440*, 112-117. DOI: doi.org/10.4028/www.scientific.net/AMM.440.112.
11. Mokhtar, O. M.; Attia, Y. A.; Wassel, A. R.; Khattab, T. A. Production of photochromic nanocomposite film via spray-coating of rare-earth strontium aluminate for anti-counterfeit applications. *Luminescence* **2021**, *36*, 1933-1944. DOI: doi.org/10.1002/bio.4127.
12. Christie, R.M. Fluorescent dyes. In: *Handbook of Textile and Industrial Dyeing*; Clark, M. (Ed.), Woodhead Publishing, 2011; pp. 562-587. DOI: doi.org/10.1533/9780857093974.2.562.
13. Ahmed, E.; Maamoun, D.; Hassan, T.M.; Khattab, T.A. Development of functional glow-in-the-dark photoluminescence linen fabrics with ultraviolet sensing and shielding. *Luminescence* **2022**, *37*, 1376-1386. DOI: doi.org/10.1002/bio.4310.
14. Colliex, C.; Kohl, H. *Elektronenmikroskopie*, Wissenschaftliche Verlagsgesellschaft mbH, 2008.

15. Mahltig, B.; Grethe, T. High-Performance and Functional Fiber Materials — A Review of Properties, Scanning Electron Microscopy SEM and Electron Dispersive Spectroscopy EDS. *Textiles* **2022**, *2*, 209-251. DOI: doi.org/10.3390/textiles2020012.
16. Flesner, J.; Mahltig, B. Fibers from Natural Resources. Book chapter. In: *Handbook of Composites from Renewable Materials, Volume 4 – Functionalization*; Thakur, V.K.; Thakur, M.K.; Kessler, M.R. (Eds.), Scrivener Publishing Wiley, Hoboken, New Jersey, USA, 2017; pp. 287-310.
17. Lübbe, E. Farbempfindung, Farbbeschreibung und Farbmessung, Springer Vieweg, 2013.
18. Tang, J.; Guo, Y.; Xu, C. Light Pollution Effects of Illuminance on Yellowish Green Forsterite Color under CIE Standard Light Source D65. *Ekoloji* **2018**, *27*, 1181-1190.
19. Sayeb, S.; Debbabi, F.; Horchani-Naifer, K. Optical Characterisation of Commercial Photoluminescent Rare Earth Pigments Used in Textile Industry. Book chapter. In: *International Conference of Applied Research on Textile and Materials*; Mhsahli, S.; Debbadi, F. (Eds.), Springer, 2022; pp. 36-42. DOI: doi.org/10.1007/978-3-031-08842-1_8.
20. Khattab, T.A.; Rehan, M.; Hamdy, Y.; Shasheen, T.I. Facile Development of Photoluminescent Textile Fabric via Spray Coating of Eu(II)-Doped Strontium Aluminate. *Ind. Eng. Chem. Res*. **2018**, *57*, 11483-11492. DOI: doi.org/10.1021/acs.iecr.8b01594.
21. Khattab, T. A.; Fouda, M.M.G.; Abdelrahman, M.S.; Othman, S.I.; Bin-Jumah, M.; Alqarawi, M.A.; Fassam, H.A.; Allam, A.A. Development of Illuminant Glow-in-the-Dark Cotton Fabric Coated by Luminescent Composite with Antimicrobial Activity and Ultraviolet Protection. *Journal of Fluorescence* **2019**, *29*, 703-710. DOI: doi.org/10.1007/s10895-019-02384-2.
22. Wu, Y.; Gan, J.; Wu, X. Study on the silica-polymer hybrid coated $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphor as a photoluminescence pigment in a waterborne UV acrylic coating. *Journal of Materials Research and Technology* **2021**, *13*, 1230-1242. DOI: doi.org/10.1016/j.jmrt.2021.05.035.
23. Katsumata, T.; Sasajima, K.; Nabae, T.; Komuro, S.; Morikawa, T. Characteristics of Strontium Aluminate Crystals Used for Long-Duration Phosphors. *J. Am. Ceram. Soc*. **1998**, *81*, 413-416.
24. Ghahari, M.; Arabi, A.M. Preparation of Persisted Luminescence Pigment and Investigation in Glaze Compatibility. *Prog. Color Colorants Coat*. **2012**, *5*, 55-63.
25. Shafia, E.; Aghaei, A.; Davarpanah, A.; Bodaghi, M.; Tahriri, M.; Alavi, S.H. Synthesis and Characterization of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} Nanocrystalline Phosphorescent Pigments. *Trans. Ind. Ceram. Soc*. **2011**, *70*, 71-77.
26. Setlow, R.B. The Wavelengths in Sunlight Effective in Producing Skin Cancer: A Theoretical Analysis. *Proc. Nat. Acad. Sci. USA* **1974**, *71*, 3363-3366.
27. Yoon, J.H.; Lee, C.-S.; O´Connor, T.R.; Yasui, A.; Pfeifer, G.P. The DNA Damage Spectrum Produced by Simulated Sunlight. *J. Mol. Biol*. **2000**, *299*, 681-693. DOI: 10.1006/jmbi.2000.3771.
28. Böttcher, H.; Mahltig, B.; Sarsour, J.; Stegmaier, T. Qualitative investigations of the photocatalytic dye destruction by TiO_2-coated polyester fabrics. *J. Sol-Gel Sci. Technol*. **2010**, *55*, 177-185. DOI: doi.org/10.1007/s10971-010-2230-9.