

IMPREGNATION DYEING OF COTTON/POLYESTER SPUN YARN MIXTURE WITH PHOTOLUMINESCENT PIGMENTS

PAMUK/POLİESTER İPLİK KARIŞIMININ PARLAYAN PİGMENTLER İLE EMDİRME YÖNTEMİNE GÖRE BOYANMASI

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ABSTRACT

The research focuses on the technologically plain and inexpensive procedure of impregnation dyeing of spun yarn with photoluminescent pigment Speciallux TPLL-9E Yellow-Green (Special Chem, Italy). The pigment concentration was 50 and 150 g of pigment per kilogram of yarn and two binding agents were used, i.e. Elastil Transparent FG (Minerva, Italy) and Padding Binder FM/N (Minerva, Italy), as well as a mixture of both. The impregnated coating was conducted on yarns with linear density Nm 125/1 and Nm 20/1, where the mixture ratio of cotton/polyester was 50/50 and 67/33. The luminance measurements were made on the unwashed, once washed and five times washed yarns. In some cases, a high luminance level of yarns up to 500 mcd/m² was measured, which decreased only slightly after one wash, and after five washes, it dropped to 230 mcd/m². In accordance with the expectations, the luminescence decreased exponentially with time; however, the yarns could still be noticed in the darkness even after 12 hours.

Key Words: Photoluminescent pigments, Phosphorescent pigments, Photoluminescent yarn, Photoluminescence, Decorative smart textiles, Luminance.

ÖZET

İBu araştırma, eğrilmiş ipliklerin, parlayan bir pigment olan Speciallux TPLL-9E Sarı-Yeşil (Special Chem, İtalya) ile teknolojik olarak basit ve pahalı olmayan emdirme yöntemine göre boyanması prosedürü üzerine odaklanmaktadır. Çalışmada, ipliğin 1 kg'ı için 50 ve 150 g pigment içeren pigment konsantrasyonu ile çalışılmış, 2 bağlayıcı madde, Elastil Transparent FG (Mnerva, İtalya), Padding Binder FM/N (Minerva/İtalya) ve bunların karışımları, kullanılmıştır. Emdirme yöntemi ile kaplanan ipliklerin numaraları Nm 125/1 ve Nm 20/1 olup, pamuk ve poliesterin karışımındaki oranları 50/50 ve 67/33'tür. Parlaklık ölçümleri, yıkanmamış, 1 kez yıkanmış ve 5 kez yıkanmış ipliklere yapılmıştır. Bazı durumlarda, 500 mcd/m² değerlerine varan yüksek parlaklık seviyesi ölçülmüş, bu değer 1 yıkama sonrasında çok az düşmüş, 5 yıkama sonrasında ise 230 mcd/m²'ye düşmüştür. Beklentilere uygun şekilde, parlaklık, zamanla katlanarak azalmakta, ancak iplikler 12 saat sonra bile karanlıkta fark edilebilmektedir.

Anahtar Kelimeler: Parlayan pigmentler, fosforlu pigmentler, Parlayan iplikler, parlama, dekoratif akıllı tekstiller, parlaklık.

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1. INTRODUCTION

The microfibre development, which presents the new generation of synthetic fibres after 1990, began in the early 1970s in Japan. The goal was to make the properties of synthetic fibres as similar as possible to the real silk and in this way, imitate the characteristics of products from silk. Advanced research imitates the processes in nature (i.e. biomimetics)

at the very nanometric level (1). Similarly, the self-cleaning surfaces of textiles with sol-gel nanofinishes are known in the field of usable polymers, which have with their water/oil repellent nanostructure neared the superhydrophobic surface of the always remaining clean lotus leaf (2).

People have tried to mimic the light emission at night (i.e. bioluminescence) natural to fireflies, fish, fungi and

microorganisms with the help of phosphorescent pigments with a delayed emission of light. However, there is a remarkable difference between the above described processes. The luminescence of fireflies is based on a biocatalytic process where the enzyme luciferase catalyses the bioluminescence reaction in the organism of a firefly. The light emerges at the oxidation of the organic pigment of luciferase (3). On the other hand, at inorganic

phosphorescent pigments, the light emission is caused by the excitation of electrons. After the excitation of pigments with the sun light (UV rays), the electrons traverse from the excited into the ground state, whereby they emit visible light (i.e. photoluminescence) (4). Such inorganic pigments are used in the field of textiles as well. The so-called photoluminescent textiles can contribute to a more pleasant environment in our homes, not only as a decoration but also as the functional possibility of low-intensity cold lighting for improved orientation in a room by lighting up certain objects or for dealing with nyctophobia with children.

The research in the field of photoluminescent textiles dates back to the 1930s, when H. Dreyfus patented the procedure of applying photoluminescent pigments, such as zinc, cadmium, strontium, barium or magnesium sulphide on textile yarn (5). This was followed by patents for the stability improvement of the bound photoluminescent pigment on various types of fibres, from natural cellulose and protein fibres to synthetic fibres (6, 7). The photoluminescent yarns produced in this way were originally intended for theatre textiles and floor coverings, for markers in the textile industry, as well as for household textiles.

Phosphorescent pigments are crystalline organic substances (8). Today they are synthesized on the basis of rare earth metals and are a compound of oxides of strontium, aluminium, boron, europium, dysprosium and calcium (9). They are non-toxic and do not emit human-life threatening rays; nevertheless, due to the lack of knowledge, users are often distrustful of them.

The main problem of photoluminescent yarns has always been the low abrasion stability of the bound photoluminescent pigment on yarn, which prevented these yarns to be further used in the textile production. Therefore, after 1980, several patents have been issued, e.g. lamination of photoluminescent yarns (10) or extrusion of a polymer in the form of a granulate with a surface-bound photoluminescent pigment (11). The patent from 2004 describes the production procedure of

the phosphorescent masterbatch from a polymer, encapsulated phosphorescent pigments (Al, Sr, Dy and Eu oxides), a softener and dispersion agents (12).

The offer of photoluminescent yarns and textiles in the market is even today still very modest; therefore, our research studies the possibilities of using the impregnation method for the application of phosphorescent pigment on the yarn mixture from cotton/polyester fibres. The industrial procedure of impregnation dyeing with pigments is an inexpensive dyeing procedure, which comprises the impregnation, drying and condensation. Especially at drying, the migration of pigments frequently occurs, thus anti-migrants need to be added into the impregnation dyebath. In our case, when using the binder Padding Binder FM/N (Minerva, Italy) to bind the pigments Speciallux, Sinergil T (Minerva, Italy) was applied, which has the characteristics of a wetting agent. The binder Padding Binder FM/N itself is a chemical emulsion of acrylates, which already contains the softeners and cross-linkers (13). The catalyst ammonium sulphate, which is added in the composition of an impregnation bath, points to the cross-linker content in the binder.

For the preparation of printing pastes, there are already prepared agents available in the market which apart from the binder contain the cross-linkers and most likely the catalyst as well. Such a substance is Elastil Transparent FG (Minerva, Italy), which was already used along with the above described components in the bath composition for the application of phosphorescent pigments on PET yarn (14).

Impregnation dyeing with classical pigments is a procedure more appropriate for the application on textured materials (e.g. cellulose fibres) than on smooth materials (e.g. synthetic fibres). The classical pigments are 0.05–2 µm large particles. Impregnation dyebaths also contain cross-linkers which under the condensation conditions with the help of a catalyst react with hydroxyl groups of cellulose fibres and form cross-linked structures. In consequence,

such materials do not wrinkle; furthermore, the pigment particles are additionally bound. Similar behaviour was predicted with phosphorescent pigments, namely their better bonding on the cellulose component and hence better pigment stability of yarn mixture cellulose/PET if compared with PET fibres (14).

On the unwashed and several times washed samples of photoluminescent yarns, the efficiency of modern photoluminescent pigments was evaluated objectively with the measuring method of luminance and the changes in luminance with time.

2. MATERIALS AND METHODS

Impregnation dyeing

For impregnation dyeing, two spun yarns were used from a homogeneous mixture of cotton/polyester fibres (CO/PES) manufactured at the spinning mill Predilnica Litija Ltd, Slovenia:

- yarn (a): Nm 125/1; CO/PES 50/50 and
- yarn (b): Nm 20/1; CO/PES 67/33.

Moreover, the phosphorescent pigment Speciallux TPLL-9E Yellow-Green (Special Chem, Italy) was used, which attested at previous research as a pigment with the longest duration and the most intensive emission in the darkness [14, 15]. The impregnation was conducted at room temperature on a foulard (W. Mathis AG, Switzerland) with a 60–65% squeezing effect. The impregnated hanks of yarn were dried in a dryer (Benz, Switzerland) at 100 °C and condensed for 3 minutes at 150 °C.

The original instructions from the producer Minerva for the composition of the impregnation bath were adjusted to the composition which proved best during previous testing on pure polyester yarns from polyethylene terephthalate (14). The binding agents Elastil Transparent FG (Minerva, Italy) (ET) and Padding Binder FM/N (Minerva, Italy) (PB), as well as a mixture of both were used. With both binders, experiments with three concentrations of the binder and two concentrations of the pigment were

performed. At the use of a high- 150 g/l), only the concentrated binder composition of impregnation baths is quantity pigment concentration (i.e. or prepared paste was used. The shown in Tables 1–3.

Table 1. Composition of impregnation baths with binder Elastil Transparent FG (Minerva, Italy)

Recipe	A	B	C	D
Pigment (g/kg)	50	50	50	150
Binder ET (g/kg)	950	850	750	850
H ₂ O (g/kg)	/	100	200	/
Σ (g)	1000	1000	1000	1000

Table 2. Composition of impregnation baths with binder Padding Binder FM/N (Minerva, Italy)

Recipe	E	F	G	H
Pigment (g/kg)	50	50	50	150
Binder PB (g/kg)	894	794	694	794
(NH ₄) ₂ SO ₄ (1 : 2) (g/kg)	6	6	6	6
Sinergil T (g/kg)	50	50	50	50
H ₂ O (g/kg)	/	100	200	/
Σ (g)	1000	1000	1000	1000

Table 3. Composition of impregnation baths with mixture of binders Elastil Transparent FG (Minerva, Italy) and Padding Binder FM/N (Minerva, Italy)

Recipe	J	K
Pigment (g/kg)	50	150
Binder ET (g/kg)	750	650
Binder PB (g/kg)	100	100
H ₂ O (g/kg)	100	100
Σ (g)	1000	1000

The marks of individual samples in Figures 1–6 constitute of the mark of the used recipe (A–K) and the mark of yarn (e.g. Sample Aa is yarn (a) dyed according to the recipe A).

Luminance measurement

The luminance measurements were performed on both yarns after the impregnation with the phosphorescent pigment, and after the first and fifth wash of the impregnated yarn at 40 °C in accordance with the ISO 105 C01 standard (16). The yarn sample was evenly wound on a white cardboard carrier 2 × 2 cm in size and activated for 12 hours with fluorescent bulbs (1000 lx) with the colour temperature 5619 K. Prior to the exposure to light or activation, respectively, the samples were kept in complete darkness for 24 hours.

The luminescence testing of impregnated yarns in the darkness was first performed visually using an in-house method. Afterwards, the yarn

luminance was objectively measured with a photometer. The sample was attached in the dark chamber onto a carrier on the photometric bench 22-950 (Ealing, Great Britain). The distance between the sample and the measuring machine was 47 cm. The measurements were conducted with the photometer L 1009 (LMT, Germany, measuring field 3°, T = 23 ± 1 °C, RH = 38%) every 5 minutes for 60 minutes after the activation was completed.

3. RESULTS AND DISCUSSION

The impregnation of spun yarn from the mixture of cotton/polyester fibres in the baths with a high binder concentration and only 100 or 200 g of added water per kilogram of bath, which was conducted in this research, generally enabled very good binding of the pigment Speciallux TPLL-9E Yellow-Green on yarns. The yarn luminescence was still perceived visually after 12 hours.

On the basis of the luminance measurements of unwashed samples straight after the excitation (cf. Figures 1 and 2), it can be observed that the increase in the water content in the impregnation bath and the decrease of its viscosity caused better pigment binding on the yarn (a) and consequently, higher luminance. The same applies to both binders, while the luminance was comparable regardless of the choice of the binder. An even better result was achieved with an increase in the pigment concentration in the impregnation bath, i.e. from 50 to 150 g/kg. In this case, the luminance increased especially when using the binder PB. The best result was acquired with the recipe H. The same is true for the washed samples of dyed yarns: at the Sample Ha, the luminance lowered after the fifth wash to 46% of its initial value; nevertheless, it remained above 0.23 cd/m². When using the binder ET and applying 150 g/kg of pigment (i.e. Sample Da), the luminance decreased after the fifth

wash to 59% of its initial value, which presents the smallest decrease in the luminance after the fifth wash. However, the luminance value was merely 0.18 cd/m². For the dyed yarn samples (a) (CO : PES = 50 : 50, fineness Nm 125), it can be stated that the type of binder at the pigment application 50 g/kg did not considerably influence the acquired luminance, while at the pigment application 150 g/kg, better results were achieved with the binder PB.

At the impregnation dyeing of yarn (b) (CO : PES = 67 : 33, fineness Nm 20), the increase in the amount of water did not have a positive effect on the pigment application or luminance increase, respectively (cf. Figures 1 and 2). On the contrary, when using the binder PB, the attained level of luminance lowered when increasing the water content in the impregnation

bath. Generally speaking, the luminance of samples of dyed yarn (b) when using the same dyeing recipe was lower than the luminance of samples of dyed yarn (a), which indicates that the pigment binding on yarn (b) was lower than on yarn (a) despite the larger percentage of cotton fibres. The yarn (b) namely has a 17% larger content of cotton than yarn (a). The reason for a lower binding of the pigment on yarn (b) lies mainly in the smaller specific surface of this yarn if compared with yarn (a), since yarn (b) is as many as 6-times coarser than yarn (a).

The favourable effect of the increase in the pigment concentration from 50 to 150 g/kg was found with yarn (b) as well. By applying the binder ET and 150 g/kg of pigment (i.e. Sample Db), an even higher luminance was achieved than at the application on

yarn (a) (i.e. Sample Da); however, the fastness to washing was substantially worse and after the fifth wash, the luminance of the dyed yarn (b) decreased to only 19% of its initial value.

With only one exception, better results were attained with the binder PB for the pigment application on yarn (b) than with the binder ET. The luminance was in the best case, i.e. with the application of 150 g/kg of pigment, 0.41 cd/m² (i.e. Sample Hb, cf. Figure 2) if compared to 0.34 cd/m² when using the binder ET (i.e. Sample Db, cf. Figure 1). Based on the luminance measurements of the dyed yarn (b) after washing, it can be concluded that the pigment binding on yarn (b) is lower than on yarn (a), since the luminance values decreased more after five washes.

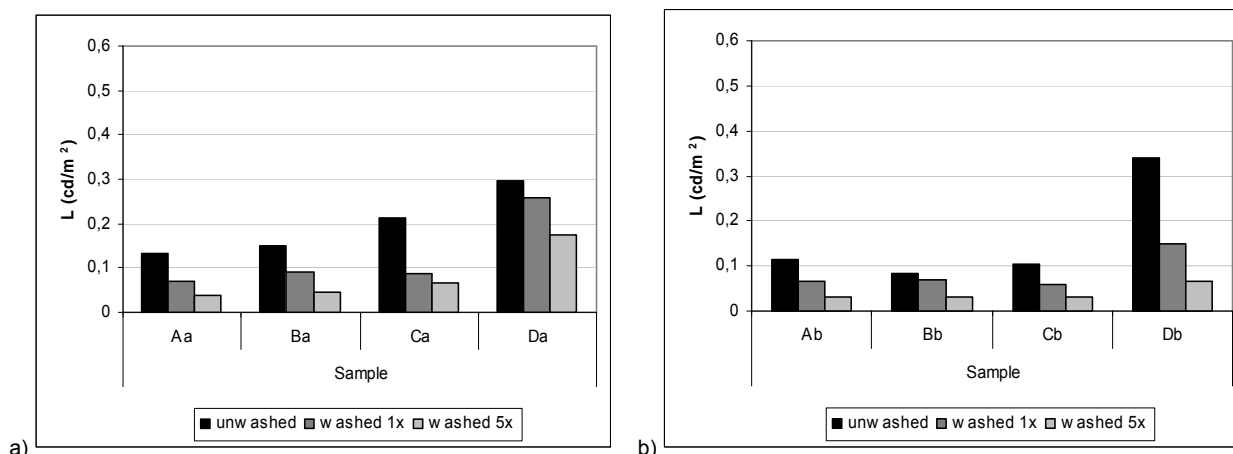


Figure 1. Luminance L (cd/m²) directly after the excitation of dyed samples of yarn (a) and yarn (b) using the binder ET in the impregnation bath

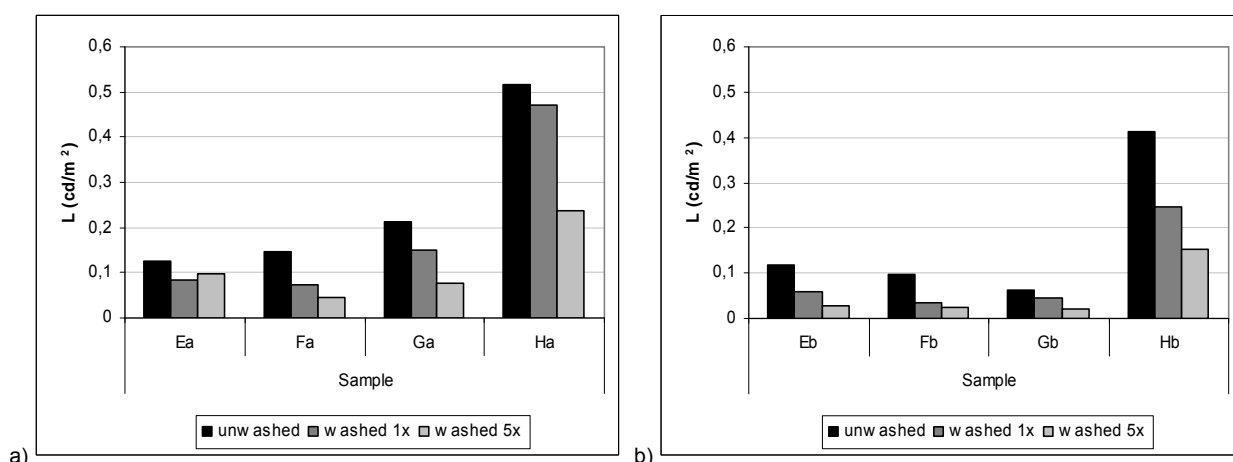


Figure 2. Luminance L (cd/m²) directly after the excitation of dyed samples of yarn (a) and yarn (b) using the binder PB in the impregnation bath

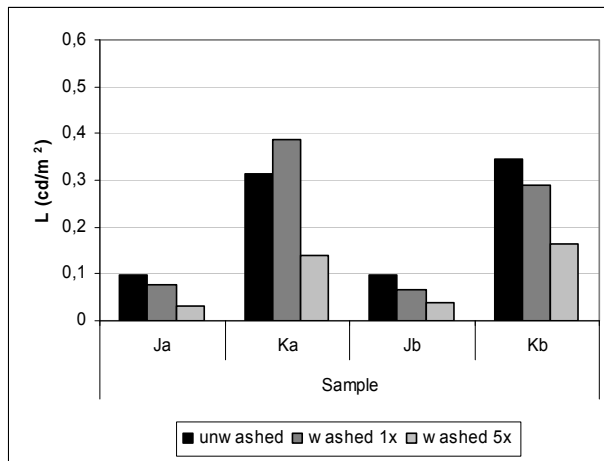


Figure 3. Luminance L (cd/m^2) directly after the excitation of dyed samples of yarn (a) and yarn (b) using the mixture of binders ET and PB in the impregnation bath

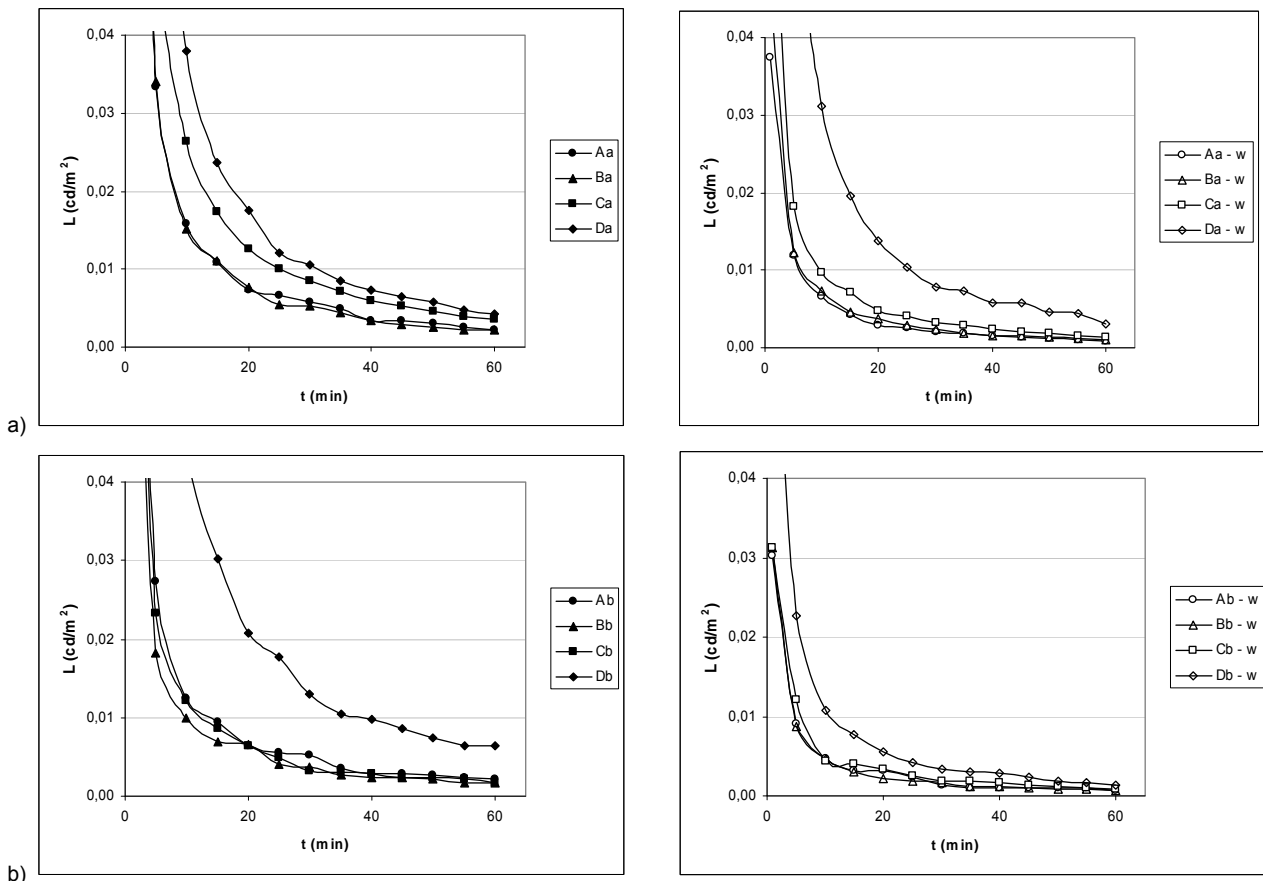


Figure 4. Luminance change for unwashed (left) and five times washed (right) samples with binder ET on yarn (a) or yarn (b) in dependence of time

By mixing the two binders (ET + PB), no better results were acquired on either of the used yarn (cf. Figure 3) as when using one binder only. The latter was discovered even in the case of the pigment concentration increase to 150 g/kg (i.e. Samples Ka and Kb). The luminance was higher regarding the samples with lower pigment content;

however, with the exception of one sample (i.e. Sample Da), it did not achieve the same value as when using individual binders. On the other hand, a relatively low decrease in the luminance was measured after five washes when using the mixture of the two binders and a high-quantity pigment application. The luminance

value on yarn (a) decreased to 45% of the initial value (i.e. Sample Ka) and on yarn (b) to 48% of the initial value (i.e. Sample Kb).

For the majority of samples, the mixture of both binders (ET + PB) proved in comparison with an individual binder as the least efficient.

The luminance measurement results on the washed samples (cf. Figures 1–3) show that the use of the mixture of the two binders was efficient only at the pigment application on yarn (b), for the results were better than at the use of the binder ET, but worse than at the use of the binder PB.

At the high-quantity pigment application, the luminance on the dyed

yarn (a) lowered substantially only after five washes, and on the dyed yarn (b) already after the first wash, which again leads to lower pigment binding on yarn (b) (i.e. Samples Da, Db, Ha, Hb). This occurrence was less obvious at the lower-quantity pigment application, but it can nevertheless be noticed that with the same recipe (A, B, C, E, F or G) on yarn (a) after the

first wash, higher luminance levels were obtained than on yarn (b), since the initial luminance values were higher as well.

Figures 4, 5 and 6 demonstrate the changes in the luminance of samples with time.

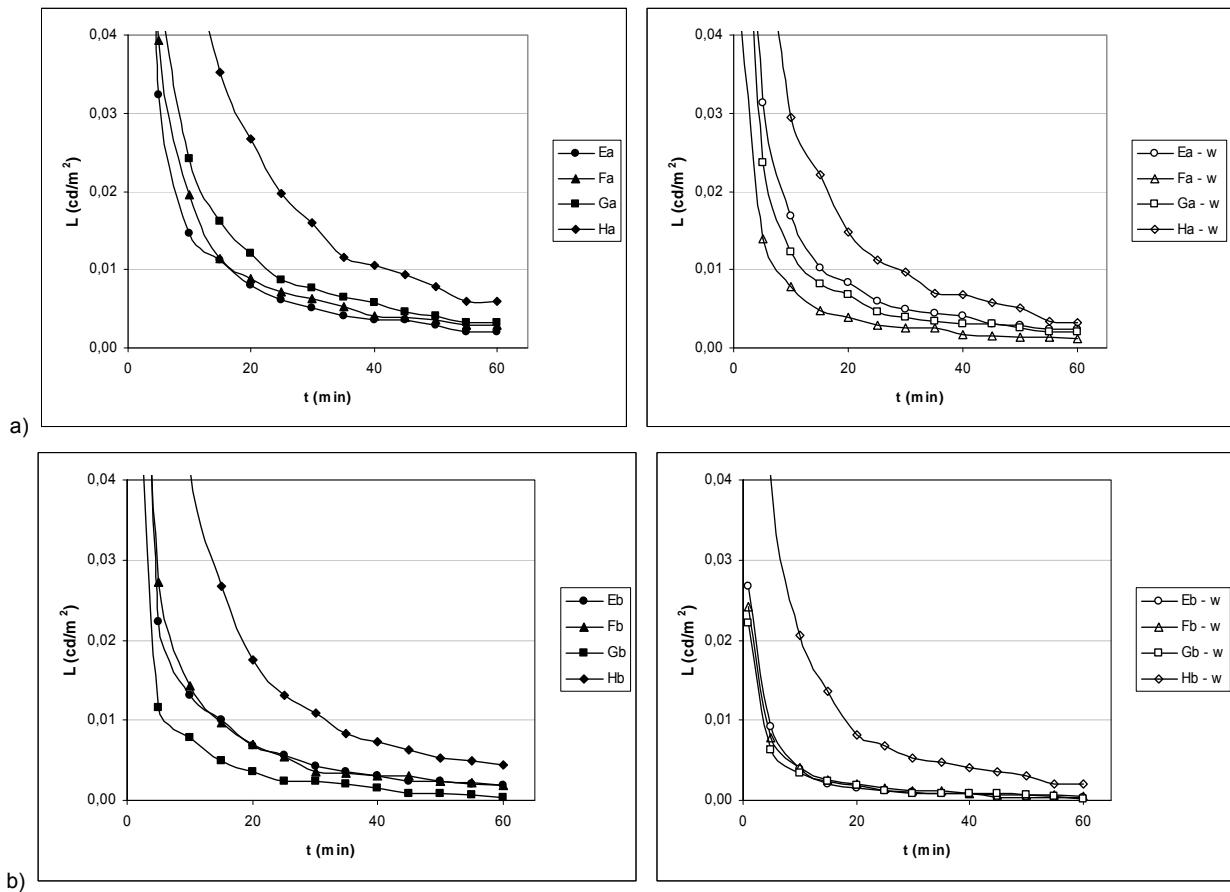


Figure 5. Luminance change for unwashed (left) and five times washed (right) samples with binder PB on yarn (a) or yarn (b) in dependence of time

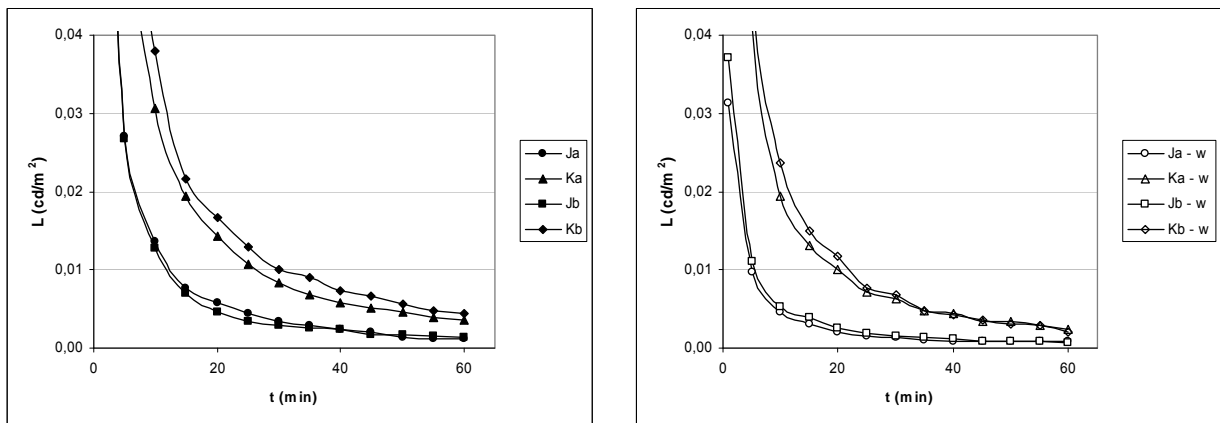


Figure 6. Luminance change for unwashed (left) and five times washed (right) samples with mixture of binders ET and PB on yarn (a) or yarn (b) in dependence of time

Figures 4–6 show that the luminance after the excitation or the removal of the light source, respectively, decreases rapidly, which is in accordance with the expectations and is typical of such samples (17). This applies to the samples of impregnated unwashed dyed yarns and even more to the washed samples, for the initial values of the latter are lower. The slowest decrease can be noticed at samples with a high-quantity pigment application, regardless of the used binder or type of yarn.

The yarns with a high-quantity (i.e. 150 g/kg) pigment application with the binder ET retained on average 15% of their initial luminance value 10 minutes after the removal of the light source, and with the binder PB as well as with the mixture ET + PB 12% of their initial value. With the use of the binder ET or the mixture ET + PB, the decrease in the luminance of five times washed samples was relatively lower than with the use of the binder PB. The

luminance lowered with all dyed yarns regardless of the used binder and type of yarn to 1–2% of the initial luminance value 60 minutes after the removal of the light source or after the pigment excitation, respectively, and did not exceed 0.007 cd/m². This indicates that the intensive luminescence in the darkness was relatively short-lived despite the yarn luminescence being visible with the naked eye even up to 12 hours.

4. CONCLUSIONS

The research results indicate that the photoluminescent pigment application with impregnation dyeing is more efficient on yarn mixtures CO/PES 50/50 (i.e. yarn a) than on yarn mixtures CO/PES 67/33 (i.e. yarn b). The research confirms better pigment binding on finer yarns. Among the tested binders, the binder Padding Binder FM/N (Minerva, Italy) proved best. The initial luminescence of photoluminescent yarn is strongly

dependent on the concentration of the used pigment. At a high-quantity pigment application, the luminance on the dyed yarn (a) considerably lowered only after five washes, while on the dyed yarn (b) already after the first wash. In the darkness or after the removal of the light source, respectively, the luminescence decreased rapidly. The slowest luminescence decrease can be observed with samples with a high-quantity pigment application, regardless of the used binder or the type of yarn.

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