Influence of PEDOT:PSS coating on screen-printed textile

DOI: 10.35530/IT.075.01.202376

SAŠA PETROVIĆ
SANDRA DEDIJER
NEMANJA KAŠIKOVIĆ
ŽELJKO ZELJKOVIĆ
VESNA GVOIĆ
IVANA JURIČ
MLADEN STANČIĆ

ABSTRACT – REZUMAT

Influence of PEDOT:PSS coating on screen-printed textile

This paper reports the impact of screen-printed PEDOT:PSS conductive ink on the optical properties of polyester fabric and colourimetric properties of yellow screen printing ink printed in a different number of layers. Yellow was chosen as one of four process colours which should theoretically suffer the most prominent changes from PEDOT:PSS overprinting. The study found that PEDOT:PSS ink significantly impacts the optical properties of the fabric and yellow ink, especially regarding the lightness and b-coordinate of the yellow ink. The acid treatment of samples, to increase PEDOT:PSS conductivity, also affected the optical characteristics through partial neutralization of the changes in the b-coordinate, especially when the sample was printed with a larger number of layers of the yellow ink and a smaller number of layers of PEDOT:PSS ink. Samples with two layers of yellow and one layer of PEDOT:PSS ink showed good conductivity results even without acid treatment, while the base colour appeared slightly darker. This change in the lightness can be compensated to some extent, proving that the aforementioned combination of PEDOT:PSS and base ink layers are the best when aspects, such as optical characteristics, conductivity, the complexity of production, production time, and limitations of the use of substrate materials are taken into account. This study provides useful insights for optimizing the printing process of PEDOT:PSS conductive inks over screen printed fabrics for various applications, including wearable electronics and smart textiles.

Keywords: *colourimetric properties, conductive ink, conductivity, acid treatment, smart textile*

Influența stratului PEDOT:PSS asupra textilelor imprimate prin serigrafie

Acest studiu raportează impactul cernelii conductoare PEDOT:PSS pentru imprimarea prin serigrafie asupra proprietăților optice ale țesăturii din poliester și proprietăților colorimetrice ale cernelii galbene pentru imprimarea prin serigrafie în număr diferit de straturi. Culoarea galben a fost aleasă drept una dintre cele patru culori de proces care ar trebui, teoretic, să sufere cele mai importante modificări de la supraimprimarea PEDOT:PSS. Studiul a constatat că cerneala PEDOT:PSS are un impact semnificativ asupra proprietăților optice atât ale țesăturii, cât și ale cernelii galbene, în special în ceea ce privește luminozitatea și coordonata b a cernelii galbene. Tratamentul cu acid al probelor, cu scopul de a crește conductivitatea PEDOT:PSS, a afectat și caracteristicile optice prin neutralizarea parțială a modificărilor coordonatei b, mai ales când proba a fost imprimată cu un număr mai mare de straturi de cerneală galbenă și un număr mai mic de straturi de cerneală PEDOT:PSS. Probele cu două straturi de galben și un strat de cerneală PEDOT:PSS au prezentat rezultate bune de conductivitate chiar și fără tratament cu acid, în timp ce culoarea de bază a apărut puțin mai închisă. Această modificare a luminozității poate fi compensată într-o oarecare măsură, demonstrând că această combinație de PEDOT:PSS și straturi de cerneală de bază este cea mai eficientă atunci când anumite caracteristici, cum ar fi cele optice, conductivitatea, complexitatea producției, timpul de producție și limitările de utilizare ale materialelor suport sunt luate în considerare. Acest studiu oferă informații utile pentru optimizarea procesului de imprimare a cernelurilor conductoare PEDOT:PSS peste țesături imprimate prin serigrafie pentru diverse aplicații, inclusiv electronice portabile și textile inteligente.

Cuvinte-cheie*: proprietăți colorimetrice, cerneală conductoare, conductivitate, tratament cu acid, material textil inteligent*

INTRODUCTION

Screen printing is a versatile printing method that can be widely applied. This technique involves pushing ink through a screen and onto a substrate, which can be textiles, paper, ceramics, plastics, and more. In addition to printing on various materials, screen printing can also be used to print on objects of different shapes and sizes, such as tennis balls, mugs, and printed electronics [1].

Screen printing is a popular method for manufacturing electronics, mainly because it allows for printing a thick layer of ink in a single pass while applying lower printing pressure, which is especially important for delicate and softer surfaces, unlike gravure printing [2]. The ink layer thickness in screen printing typically ranges from 20 to 100 µm. Various types of conductive inks, including those containing particles of silver, gold, or copper, are used for functional screen printing of electronics, circuits, and antennas for RFID tags. Some inks utilize other conductive materials, and the most commonly used opaque inks are silver- and graphene-based. However, for achieving high transparency, ITO (Indium Tin Oxide) is frequently used, but it is typically produced in the form of thin films. ITO is fragile and shows weak adhesion to polymeric materials, and in addition, the cost of indium is increasing [3].

For products where transparency is crucial, an alternative to ITO films is available in the form of conductive inks based on PEDOT:PSS polymers. These inks contain a mixture of poly(3,4-ethylene dioxythiophene) (PEDOT) and polystyrene sulfonate (PSS), which produce films that are highly transparent in the visible part of the spectrum, mechanically stable, and thermally and flexibly outstanding. However, the conductivity of these films is very low, below 1 S/cm [4], due to the presence of a thin layer of PSS chains surrounding the short, conductive PEDOT chains.

One significant advantage of PEDOT:PSS inks over ITO is that they can be printed using various techniques, commonly screen or inkjet printing. Although PEDOT:PSS ink layers may have a slightly bluish tint, they are suitable for areas requiring touchscreen capabilities, flexibility, and resistance to surface wear. Due to its conductivity and flexibility, there is a possibility that PEDOT:PSS could be used in the production of RFID antennas.

PEDOT:PSS is known for its exceptional ability to form films, high transparency, excellent thermal stability, and adjustable conductivity through the addition of secondary dopants [5, 6]. Furthermore, its conductivity can be improved by various methods such as thermal or light treatments, organic solvents, ionic liquids, surfactants, salts, dipolar ions, and acids. The mechanism behind this conductivity enhancement is based on the dissolution of the PSS component of the ink, which acts as an insulator and forms a layer around the conductive PEDOT components. This layer prevents their proper orientation and contact, which significantly limits conductivity.

Acid treatment is commonly used to enhance conductivity, with HCl and H_2SO_4 being the most frequently used strong acids for additional deposition on films. Yun et al. [7] concluded that the H_2SO_4 treatment results in conformational changes between PEDOT and PSS molecules while concurrently forming PEDOT-rich crystalline nanofibres with a drop in PSS composition, and that such transitions increase electrical conductivity and catalytic activity. Ouyang [8] investigated the use of medium, strong, and weak organic acids to improve PEDOT:PSS conductivity, with an 8M methanesulfonic acid treatment resulting in a conductivity increase to 3300 S/cm. Formic acid treatment by McCarthy et al. [9] and Mengistie et al. [10] led to a conductivity of approximately 2000 S/cm in PEDOT:PSS films.

In a study on the effect of coating on the colourimetric properties of prints conducted by Simonot and Elias [11], it was concluded that the coating layer does not significantly affect the hue but rather has more of an effect on the gloss and saturation of the samples.

Galić et al. [12] concluded in their research that UV coating not only improves the appearance of the final product and increases its mechanical resistance but also affects the colourimetric values of spot colours. In addition to the type of printing substrate and changes in gloss, changes in colourimetric values also occur due to the physical and chemical properties and interactions of spot colours and UV coating.

In the domain of integrating PEDOT:PSS with textile materials, previous studies have mainly focused on researching the electrical conductivity properties of PEDOT:PSS and the techniques used for its application on knitted and non-woven fabrics. The approaches used for textile treatment with PEDOT:PSS vary in complexity and can be categorized as conductive fibre spinning [13, 14], polymerization of PEDOT:PSS on the textile substrate [15, 16], coating/dyeing of textiles with PEDOT:PSS [17, 18], and application of PEDOT:PSS to textiles by ink-jet [19, 20] or screen printing [21, 22]. Among these methods, printing stands out as the only one that allows precise application to pre-made textiles and allows the creation of specific patterns. Screen printing is also recognized for its cost-effectiveness and practicality on an industrial scale. Previous research that applied PEDOT:PSS directly to textiles encountered difficulties in highlighting the property of transparency, which is a key differentiator from other conductive materials, due to the absorbent nature of textiles.

While some transparency analysis was conducted in research related to solar cell production using the Spin Coating method, screen printing was rendered infeasible due to the hydrophobic nature of the printing surfaces [23]. It is noteworthy that the researchers who investigated the use of PEDOT:PSS in solar cells did not measure or draw conclusions about the effects of the material on the spectral and colourimetric properties of the underlying substrates, despite considering transparency. In the textile sector, there is a lack of measurements and analyses on the influence of PEDOT:PSS on the colourimetric and spectrophotometric properties of the target samples, as this particular property of the material is impaired when applied directly to textiles.

Given the basis of previous research and the growing demand for the subsequent application of transparent electrodes, antennas, and conductive layers in the manufacture of smart textiles, there is a pronounced need for further investigation into the effects of these materials on the visual aspects of screen-printed textile designs. Therefore, the objective of this research is to establish a simple, fast, and industry-ready process for screen printing PEDOT:PSS onto pre-printed textiles. Particular attention will be paid to maximising the transparency of PEDOT:PSS while minimising any interference with the visual aesthetics of the printed textile design and reducing the visibility of printed electrodes, antennas, and conductive layers.

The scientific contribution and novelty of this study include a comprehensive evaluation of the influence of several screen-printed PEDOT:PSS layers, base yellow ink layers, and subsequent sulfuric acid treatment on changes in a variety of parameters belonging to different groups. The first group includes optical, spectrophotometric, and colourimetric parameters, while the second one is limited to the electrical conductivity properties of the samples. Furthermore, this research is expected to yield insights into the optimal production process and the ideal combination of process ink and PEDOT:PSS ink layers, encompassing all the parameters mentioned above, in contrast to earlier research that exclusively focused on conductivity properties.

MATERIALS AND METHODS

The white 100% polyester fabric with a weight of 166 g/m^2 was the chosen printing substrate.

The base ink was yellow process screen printing ink – phthalate-free Tiflex Everest (table 1). For the conductive ink, Heareus PEDOT:PSS Clevios SV4 screen printing ready ink (table 2) was chosen.

Table 1

TIFLEX EVEREST INK SPECIFICATIONS	
Property	**Value**
Appearance	Satin, yellow
Average density	1.25 g/cm^3
Rheology	Thixotropic ink
Polymerisation	2 minutes at 150–160°C
Coverage rate	25 m^2/l with 62 threads/cm mesh

Table 2

HEAREUS CLEVIOS SV4 INK SPECIFICATIONS	
Property	**Value**
Appearance	Semi-transparent, dark blue
Average density	1.06 g/cm^3
Viscosity	3.7 Pa/s
Boiling point	112°C
Sheet resistance	244 Ohm/sq
Solubility	Water soluble

Sample generation

The test chart consists of 120×40 mm solid colour fields to be printed using yellow screen printing ink and PEDOT:PSS conductive ink.

Screen development

The silk screens employed for printing featured aluminium frames and a weaving density of 68 threads/cm. The silk net was attached to the measuring aluminium frame size of 580×840 mm. After screen mesh tightening, the tensile force was 18 N/cm^2. To create the stencil, Amex Screen-Sol QT BLU emulsion was applied in two layers, measuring 40 µm in total, and exposed to UV light through a positive film with a test chart image.

Printing

During printing, the squeegee angle was maintained at 60°, and the printing speed was 150 mm/s. The distance between the stencil and the substrate was 3 mm. The thickness of the ink layer printed in one pass was limited by the stencil thickness and was approximately 40 µm. Samples were printed with varying combinations of process yellow and conductive ink layers, ranging from 0 to 3 layers.

Firstly, the yellow ink was applied to all of the samples in 1–3 layers. The ink was dried in a drying oven for 2 minutes at 150°C after applying each layer. After measuring colourimetric, spectrophotometric and surface roughness parameters, we proceeded to overprint the samples with 1–3 layers of PEDOT:PSS. To prevent mechanical deformation of the polyester printing substrate, the PEDOT:PSS ink was dried for 1.5 minutes in a hot air oven at 150 °C after each applied layer. After printing, all of the previously measured parameters were measured again to characterize the influence of PEDOT:PSS on the colourimetric and spectrophotometric properties of the samples. In addition, measurements were taken to investigate the effect of several base ink and PEDOT:PSS ink layers on conductivity.

Acid treatment

After measuring all of the parameters, the samples with PEDOT:PSS were immersed in a 1M solution of H_2SO_4 in order to increase ink conductivity. The samples were kept in acid for 10 seconds and dried in a drying oven for 2 minutes at 160°C. Afterwards, all of the measurements were repeated to see the influence of acid treatment on conductivity, colourimetric, and spectrophotometric properties.

Labelling of the samples

The samples were labelled to indicate the number of yellow ink layers as 1y, 2y, and 3y for 1, 2 and 3 layers of yellow ink respectively, and 0p, 1p, 2p, and 3p for samples printed with different numbers of PEDOT:PSS ink layers. Samples with overprinting were labelled according to the number of yellow ink layers and the number of PEDOT:PSS layers (e.g. 2y1p for samples with two layers of process yellow ink and one layer of conductive PEDOT:PSS ink). Samples that were treated with acid are marked with an asterisk (*) added to the label of the number of layers of conductive ink (e.g. 2y1p*).

Testing devices and standards

The testing and analysis of the samples involved the use of various devices and adherence to specific standards to ensure accuracy and reliability.

Substrate characterization

Substrate characterization was conducted according to ISO 1833 standards for material composition and ISO 3801 for fabric weight.

Printing equipment

The printing process was executed using the TIC ST6HB carousel screen printing machine. The squeegee used had a thickness of 5 mm and was 200 mm in length with a hardness rating of 75 Shore A. The samples were dried in the laboratory drying oven COLO DRYS53A.

Colorimetric and spectrophotometric measurements

Colourimetric and spectrophotometric measurements of the samples were conducted using the Techkon Spectrodens device with directional geometry. Colourimetric values (CIE Lab) and colour differences were measured by the settings and measurement method prescribed by EN-ISO 105-J01 and 105-F10 standards. Three layers of the same material on which the printing was done were used as a base for the measurements. Before the measurement, the device was calibrated on an absolute white plate. Measurements were performed for a 10° standard observer under D65 standard light source conditions to achieve a maximum approximation of values to how the human eye perceives colours.

Measurements were taken at 3 different locations on the surface of each sample, and the average values of the L, a, and b parameters were calculated. Based on the average values of the parameters, absolute colour differences CIE 2000 (ΔE_{00}) were calculated:

$$\Delta E_{00} = \sqrt{\frac{\Delta L'}{k_L S_L} + \frac{\Delta C'}{k_C S_C} + \frac{\Delta H'}{k_H S_H} + R_T \frac{\Delta C' \Delta H'}{S_C S_H}} \quad (1)$$

where $\Delta L' = L_1' - L_2'$ is a difference in lightness value, $\Delta C' = C_1' - C_2'$ is a difference in chromatic value, $\Delta H = 2\sqrt{C_1' C_2'} \sin\frac{\Delta H'}{2}$ is a difference in hue value, and parametric weighting factors $k_L = k_C = k_H = 1$.

In addition to absolute differences, discrete values of L, a, and b were compared to determine the direction of the changes and the influence of the different numbers of yellow and PEDOT:PSS ink layers on the CIE Lab colourimetric coordinates of the colour.

Spectral reflectance curves were generated at 10 nm intervals, covering wavelengths from 400 to 700 nm, which correspond to the visible spectrum, also under standard D65 illumination and a 10° standard observer.

Surface roughness and electrical resistance measurements

Measurements of the Ra surface roughness parameter were conducted using the Mahr M1 perthometer, following the ISO 4288-1996 standard. Gaussian filtering was applied during results processing, and average values of the Ra surface roughness parameter were calculated from 3 measurements taken longitudinal and 3 measurements taken cross-direction.

Electrical resistance measurements of the samples were carried out using a VC9208N multimeter. Measurements were taken by positioning the measuring probes 3 cm apart in the middle of the samples. Three measurements were taken and the average value was calculated.

RESULTS AND DISCUSSION

Spectral reflectance

The spectral reflectance curves corresponding to yellow printed using one, two, and three layers (as depicted in figure 1, *b–d*, respectively) reveal that an increase in the number of ink layers has an insignificant impact on the alteration in reflectance. Moreover, this increment in ink layers does not result in a substantial darkening of the colour. This observation aligns with the inherent characteristics of yellow, which is renowned for its lightness and lower density in comparison to other process colours.

The spectral reflectance curve for the unprinted textile (figure 1, *a*) demonstrates the textile's pristine white nature, characterized by a notably high whiteness index. The application of PEDOT:PSS ink elicits a notable alteration in the spectral reflectance curve (figure 1, *a*). When applied to non-absorbent materials, PEDOT:PSS ink imparts a transparent print with a slight bluish hue [24]. However, the polyester textile is absorbant [25], meaning that PEDOT:PSS cannot preserve its transparency characteristics, leading to the pronounced dying of the textile in a blueish hue. An increase in the number of PEDOT:PSS layers leads to increased ink absorption, making the textile grey, similar to dyed samples in research by Ding, Invernale and Sotzing [26].

The most substantial alterations in the spectral reflectance curve of a single layer of yellow ink manifest when one layer of PEDOT:PSS is applied. This change is most pronounced within the spectral range corresponding to wavelengths spanning from 500 to 700 nm, as illustrated in figure 1, *b*. Notably, the hue remains relatively stable, while an augmented absorption at longer wavelengths contributes to an overall darkening of the colour. This absorption occurs because one layer of yellow ink does not sufficiently prevent polyester from absorbing PEDOT:PSS. This is happening due to the porosity and high ink uptake of the fabric, similar to the findings of Figueira et al. [27].

With the progressive addition of PEDOT:PSS layers, both the transparency of PEDOT:PSS and the saturation of yellow undergo a discernible reduction. Concurrently, the presence of a blue hue becomes more conspicuous. This is notably reflected in a pronounced decline in reflectance within the wavelength range of 600 nm to 700 nm. As a consequence of these spectral changes, it can be inferred that the fundamental yellow hue experiences a perceptible shift towards a greener appearance.

The inclusion of a second layer of yellow ink demonstrates a substantial reduction in the alterations induced by the PEDOT:PSS coating (figure 1, *c*). The most prominent decline in reflectance occurs following the application of a solitary layer of PEDOT:PSS. Nevertheless, when compared to samples featuring only one layer of yellow ink, the curve's configuration more closely approximates that of pure yellow, particularly noticeable within the spectral range spanning from 510 nm to 700 nm. This phenomenon can be attributed to the substantial reduction in the likelihood of PEDOT:PSS absorption by the textile when multiple layers of base ink are applied, thereby preserving the conductive ink transparency characteristics.

The transparency of PEDOT:PSS becomes less pronounced as its number of layers increases [23], leading to a somewhat greater reduction in reflectance within the wavelength range of 620 nm to 700 nm. The disparities in reflectance between samples with one and two layers of PEDOT:PSS are more substantial compared to the distinctions between samples with two and three layers.

The application of a PEDOT:PSS coating atop three layers of yellow ink (figure 1, *d*), does not yield any substantial disparities when contrasted with samples featuring two layers of yellow ink. This is because the chance of PEDOT:PSS being absorbed by the textile, or filling the pores of the fabric is minimized already after application of the second layer of yellow ink. It can be concluded that no more than two layers of base ink are needed to ensure that PEDOT:PSS will retain its transparency characteristics.

Treating samples bearing PEDOT:PSS directly printed onto the textile with a 20% H_2SO_4 acid solution does not lead to a substantial shift in spectral reflectance, similar to the treatment of textile fibres in the experiment by Zhang et al. [14].

Upon subjecting samples with one (figure 1, *b*), two (figure 1, *c*), or three layers (figure 1, *d*) of yellow ink, each overlaid with varying numbers of PEDOT:PSS layers, to a 20% H_2SO_4 treatment, a marginal increase in reflectance becomes apparent. Similar observations were made in the research by McCarthy et al. [9] where formic acid was used for the treatment of PEDOT:PSS ink films. This increase in transparency of PEDOT:PSS is marginal because H_2SO_4 mostly removes already transparent PSS components. Furthermore, acid treatment leads to a slight reduction of conductive ink layer thickness and reorganization of the PEDOT component [9]. This allows for more light to pass through the conductive ink layer, reducing the dominance of the blue hue and allowing the yellow ink to be more prominent. As more layers of PEDOT:PSS are introduced, the observed changes become less pronounced, similar to the observations made by McCarthy et al. [9].

Lab coordinates

The introduction of PEDOT:PSS consistently results in a reduction in the lightness of the samples, attributed to incomplete transparency and the inherent bluish tint of the conductive ink. The magnitude of this reduction in lightness is less pronounced when a greater number of yellow ink layers are employed, as illustrated in figure 2, *a*. Along the "a" coordinate, a discernible shift towards a less red or more green colouration is observed, as demonstrated in figure 2, *b*. Conversely, alterations along the "b" coordinate are notably more substantial, primarily due to the presence of a blue hue within PEDOT:PSS, which significantly alters the "b" coordinate of the yellow ink (figure 2, *c*).

These changes are most prominent immediately following the application of the first layer of PEDOT:PSS. The least pronounced alterations in coordinates are observed when two layers of yellow ink are used, preventing direct contact between

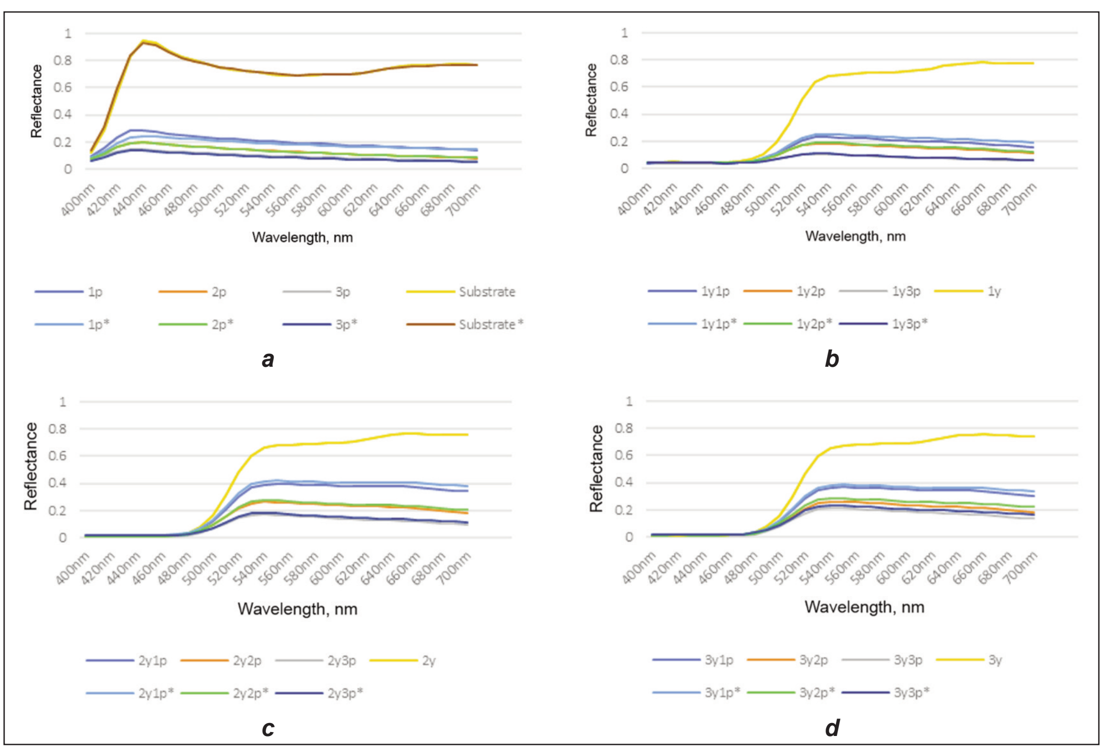

Fig. 1. The spectral reflectance curves before and after acid treatment for: *a* – substrate; *b* – one layer of yellow; *c* – two layers of yellow; *d* – three layers of yellow overprinted with one, two and three layers of PEDOT:PSS

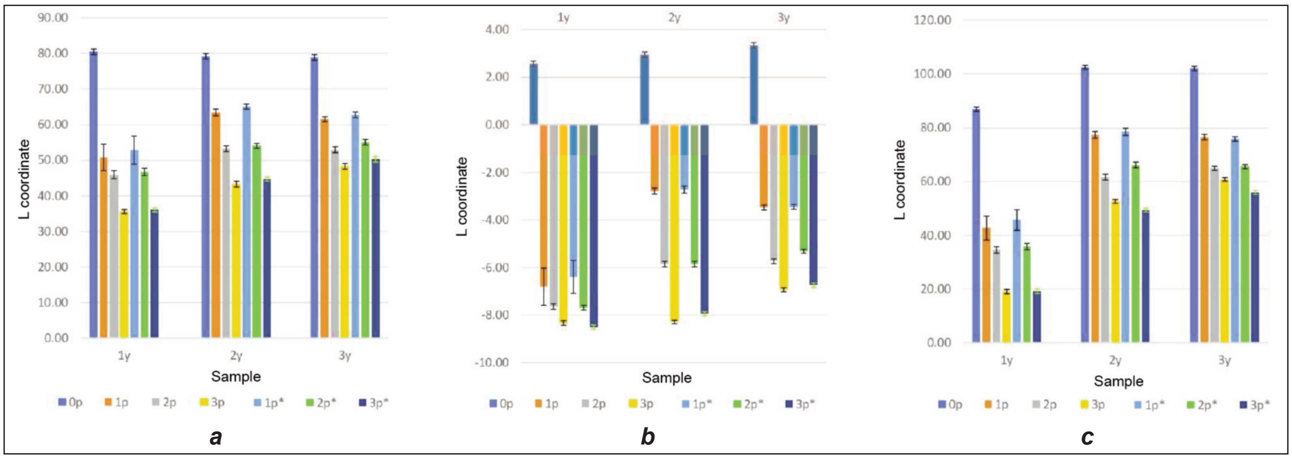

Fig. 2. Values of: *a* – lightness; *b* – a chromatic coordinate; *c* – b chromatic coordinate for all of the sample combinations before and after acid treatment

PEDOT:PSS and the textile. Conversely, the most significant changes occur with a sole layer of yellow ink, attributed to the interaction between PEDOT:PSS and the textile, as witnessed in research by Ding, Invernale and Sotzing [26].

The alteration in lightness after acid treatment is nearly imperceptible (figure 2, *a*). Changes along the "a" coordinate tend to approach neutral values in most instances, albeit with minimal shifts (figure 2, *b*). These shifts can be attributed to the reduction of the blueish hue introduced with the application of PEDOT:PSS. This reduction diminishes the green component obtained through the blending of blue and yellow.

In contrast, changes along the "b" coordinate are more pronounced, and post-acid treatment demonstrates a trend of reduction in the dominance of the blue hue (figure 2, *c*). This reduction occurs due to the PSS component being dissolved, thus allowing for PEDOT component reorganization. Notably, the number of layers of yellow ink does not appear to significantly impact the degree of change in the "b" coordinate.

Colour difference ΔE

When manipulating the number of layers of both the yellow and PEDOT:PSS inks, a discernible and reasonably consistent pattern emerges in the variation of colour difference. The most substantial change occurs following the initial application of PEDOT:PSS, particularly when applied on a single layer of the base yellow ink. In this scenario, the conductive ink partially dyes the textile, leading to more pronounced alterations, as demonstrated in figure 3, *a*. As additional layers of the conductive ink are applied, discrepancies in colour differences mainly stem from the profound impact of its dominant bluish hue on the "b" coordinate of the yellow.

The colour difference exhibits a decline in correspondence with an increase in the number of yellow ink layers (figure 3, *a*). This phenomenon arises from the inability of the PEDOT:PSS ink to get in contact with the textile. When employing more than one layer of yellow ink, the colour difference between samples featuring one and two layers of conductive ink is somewhat more pronounced. This effect can be attributed to the fact that the initial application of PEDOT:PSS minimally impacts the base ink, as it remains transparent due to its inability to get in contact with the textile. This leaves more space for the second layer of PEDOT:PSS to make changes, as in the case of applying several layers of transparent coating in the study by Dailliez et al. [28]. The introduction of the second layer of PEDOT:PSS leads to a more pronounced colour difference. This is due to the intensification of properties within the ink, manifesting

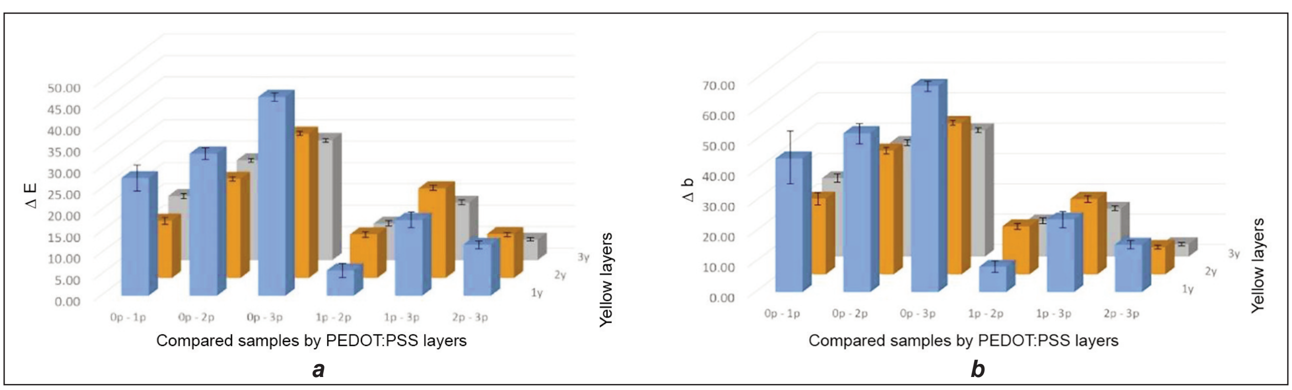

Fig. 3. Values of: *a* – Δ*E* absolute colour difference; *b* – Δ*b* b chromatic coordinate difference measured between all of the samples before acid treatment

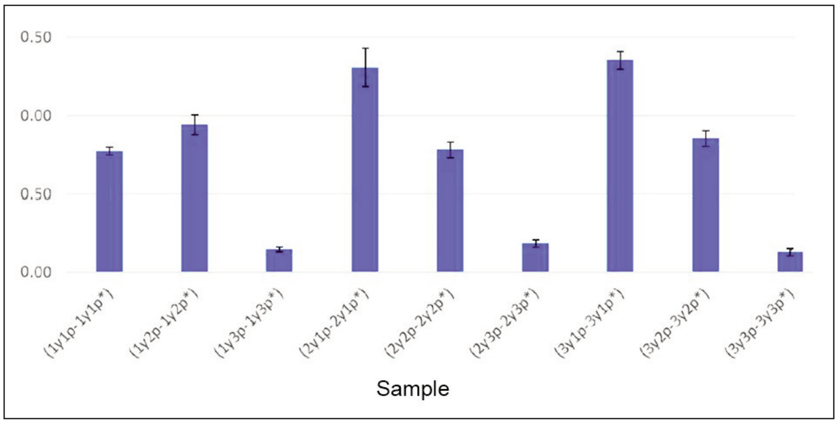

Fig. 4. Values of ΔE absolute colour difference measured between samples before and after acid treatment

as darkening and an increasingly dominant bluish hue that leads to modifications in lightness and chromatic coordinates, particularly along the "b" coordinate, as illustrated in figure 3, *b*. Subsequent applications of PEDOT:PSS ink result in relatively uniform and slightly lower changes. This happens because the ink approaches a layer thickness beyond which further alterations in transparency, and thus lightness and saturation are negligible [9, 23, 29].

The colour difference before and after the treatment of samples with 20% H_2SO_4 was calculated for each pair of samples individually (figure 4). Differences are generally greatest when using one or two layers of PEDOT:PSS because PSS decomposition and PEDOT reorganization allow the yellow ink to become more pronounced, especially in samples with 2 layers of yellow. Changes in the samples with 3 layers of PEDOT:PSS are least pronounced and can only be noticed by a trained eye, especially if printed over 3 layers of yellow ink.

Conductivity

Before analysing and discussing the results of electrical conductivity (resistance) (figure 5), it is important to note that as the resistance (measured quantity) decreases, the conductivity increases because they are inversely proportional. In addition, the average values of Ra surface roughness parameter are 34.21 μm for pure textile, 19.13 μm for 1 layer of yellow, 7.68 μm for 2 layers of yellow, and 5.04 μm for three layers of yellow.

In terms of conductivity, the best results are obtained for the following samples, and in the following order:

1. 1 layer of yellow and 3 layers of PEDOT:PSS ink after acid treatment
2. 1 layer of yellow and 2 layers of PEDOT:PSS ink after acid treatment
3. 1 layer of yellow and 2 layers of PEDOT:PSS ink before acid treatment
4. 2 layers of yellow and 2 layers of PEDOT:PSS ink before acid treatment
5. 1 layer of yellow and 1 layer of PEDOT:PSS ink after acid treatment (increases conductivity up to 4 times compared to the sample before acid treatment).

The results are similar, so the sample with two layers of yellow and two layers of PEDOT:PSS ink (considering the optical characteristics, conductivity, and financial aspects) has a clear advantage because no acid treatment is required, which significantly simplifies and speeds up the process and avoids damage to the textile material caused by acid. This allows printing on cotton and other materials that would otherwise be substantially damaged by H_2SO_4 [30]. The only negative aspect is a slightly higher cost due to the application of two layers of PEDOT:PSS, as well as an additional drying time of 3 minutes after the first layer of PEDOT:PSS is applied.

Qualitative analysis of the samples

A comprehensive qualitative analysis of the samples (figure 6) reveals pronounced alterations resulting from the application of PEDOT:PSS and acid treatment. Notably, the visual impact of PEDOT:PSS on the textile is evident in the images of samples 1p and 1y1p, where the dyeing effect is apparent.

Furthermore, the images of samples 2y1p, 2y2p, and 3y1p demonstrate that two layers of base yellow ink suffice to hinder PEDOT:PSS from permeating the textile and significantly modifying the sample's colour.

Additionally, the image of sample 2y2p underscores that an increase in the number of PEDOT:PSS layers intensifies the bluish hue. Lastly, observations from the images of samples 2y1p*, 2y2p*, and 3y1p* indicate that acid treatment results in the reduction of the blue hue and an enhancement in the uniformity, especially when only one layer of PEDOT:PSS is applied.

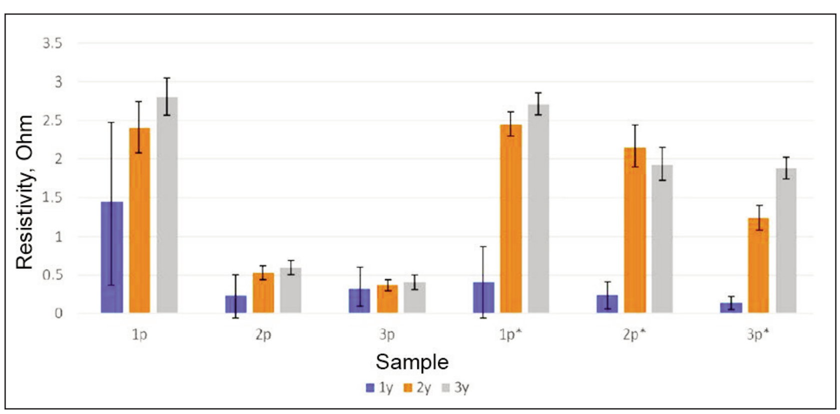

Fig. 5. Electrical resistance of all of the sample combinations before and after acid treatment

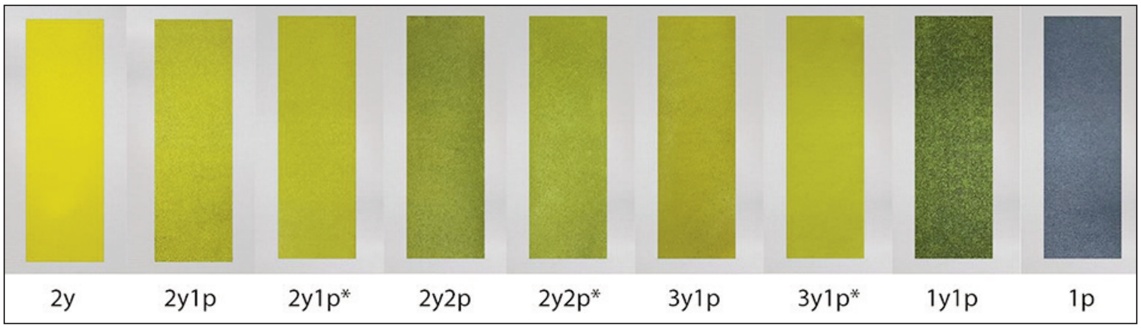

Fig. 6. Images of the samples

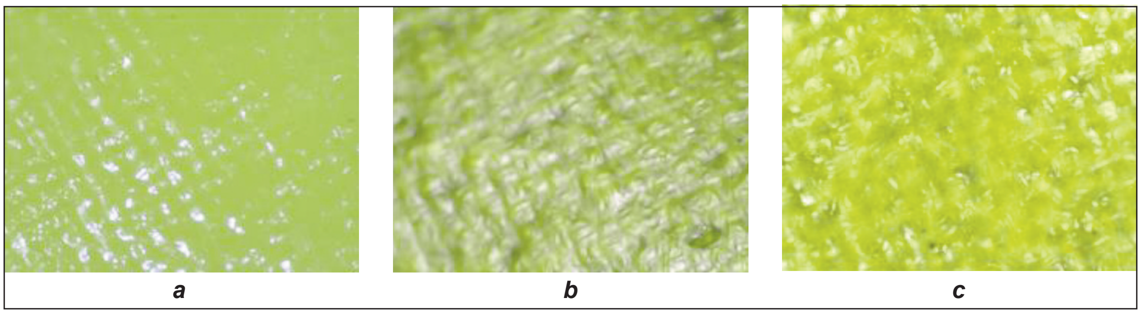

Fig. 7. Microscopic image of 400x magnified: *a* – 2y; *b* – 2y2p; *c* – 2y2p* sample

Similar observations can be made from analysis of the microscopic images of the sample with two layers of yellow ink (figure 7, *a*). The introduction of two layers of PEDOT:PSS ink (figure 7, *b*) distinctly illustrates the influence of PEDOT:PSS on the hue and lightness of the sample, rendering it bluer and darker. The subsequent acid treatment elicits a shift in the sample's characteristics, reducing its bluish tint and promoting uniformity (figure 7, *c*).

CONCLUSIONS

The influence of the PEDOT:PSS ink on the optical properties is such that the lightness of the base yellow ink changes the most, of course in addition to the b-coordinate as it is opposite to the b coordinate of the PEDOT:PSS ink. The a-coordinate of the base yellow ink also changes in correlation with the change in the b-coordinate caused by the application of PEDOT:PSS.

Samples with a combination of two layers of yellow and one layer of PEDOT:PSS ink give the best optical results. This is due to the inability of PEDOT:PSS to make contact with the fabric and dye it. In addition, the lightness and saturation of two layers of yellow are higher than those of the samples with three layers of yellow, making it more able to compensate for the changes caused by PEDOT:PSS. The acid treatment of samples, which aims to increase conductivity, affects the optical characteristics through partial neutralization of the changes in the b-coordinate. This is especially apparent when the sample is printed with a larger number of layers of the base yellow ink and a smaller number of layers of the conductive ink.

As for conductivity, the discovery that the number of layers of both PEDOT:PSS and the base yellow ink affects it opens up the possibility of finding the "golden middle", which represents the best combination of the number of layers of the base yellow and conductive PEDOT:PSS inks, while providing good conductivity results. When choosing the best combination, it is also important to pay attention to the optical and financial aspects, as well as the complexity of production, limitations on the use of substrate materials, and production time.

Samples with a combination of two layers of the base yellow and two layers of PEDOT:PSS ink give good conductivity results even without acid treatment. In contrast, the surface of the samples is uniform and without a grainy structure. However, the yellow in this case appears darker, which can be compensated to some extent, so this combination could be chosen as the best if all of the previous aspects are taken into account. All of the previous findings can be applied to other base colours, as most of them are less prone to the changes by the PEDOT:PSS blueish hue than yellow. Future research on this topic could go in the direction of printing and analysing the impact of other transparent conductive inks, such as silver nanowire inks, or even a combination of several types of transparent inks.

ACKNOWLEDGEMENTS

This research (paper) has been supported by The Ministry of Science, Technological Development and Innovation through project no. 451-03-47/2023-01/200156 “Innovative scientific and artistic research from the FTS (activity) domain”.

REFERENCES

[1] Novaković, D., Kašiković, N., *Propusna štampa*, FTN Izdavaštvo, Novi Sad, 2013

[2] Suganuma, K., *Introduction to Printed Electronics*, Springer, New York, 2014, 129, https://doi.org/10.1007/978-1-4614-9625-0

[3] Tao, C.S., Jiang, J., Tao, M., *Natural resource limitations to terawatt-scale solar cells*, In: Solar Energy Materials and Solar Cells, 2011, 95, 12, 3176–3180, https://doi.org/10.1016/j.solmat.2011.06.013

[4] Wei, H.Y., Huang, J.H., Hsu, C.Y., Chang, F.C., Ho, K.C., Chu, C.W., *Organic solar cells featuring nanobowl structures*, In: Energy & Environmental Science, 2013, 6, 4, 1192–1198, https://doi.org/10.1039/C3EE24128A

[5] Pillai, A.S., Chandran, A., Peethambharan, S.K., *MWCNT Ink with PEDOT:PSS as a multifunctional additive for energy efficient flexible heating applications*, In: Applied Materials Today, 2021, 23, https://doi.org/10.1016/j.apmt.2021.100987

[6] Nguyen, V.A., Kuss, C., *Review – Conducting Polymer-Based Binders for Lithium-Ion Batteries and Beyond*, In: Journal of The Electrochemical Society, 2020, 167, 6, https://doi.org/10.1149/1945-7111/ab856b

[7] Yun, D.J., Ra, H., Kim, J.M., Lee, J.H., Park, S.H., Hwang, J., Chung, J.G., Kim, S.H., Kim, Y.S., Jeong, Y.J., Lee, S.H., *A study on distinctive transition mechanism of sulfuric acid treatment on performance enhancement of poly(3,4-ethylenedioxythiophene): Polystyrene based electrodes depending on multiwall carbon nanotube dose*, In: Applied Surface Science, 2019, 487, 480–487, https://doi.org/10.1016/j.apsusc.2019.05.125

[8] Ouyang, J., *Solution-Processed PEDOT:PSS Films with Conductivities as Indium Tin Oxide through a Treatment with Mild and Weak Organic Acids*, In: ACS Applied Materials & Interfaces, 2013, 5, 24, 13082–13088, https://doi.org/10.1021/am404113n

[9] McCarthy, J.E., Hanley, C.A., Brennan, L.J., Lambertini, V.G., Gun'ko, Y.K., *Fabrication of highly transparent and conducting PEDOT:PSS films using a formic acid treatment*, In: Journal of Materials Chemistry C, 2014, 2, 4, 764–770, https://doi.org/10.1039/C3TC31951B

[10] Mengistie, D.A., Ibrahem, M.A., Wang, P.C., Chu, C.W., *Highly Conductive PEDOT:PSS Treated with Formic Acid for ITO-Free Polymer Solar Cells*, In: ACS Applied Materials & Interfaces, 2014, 6, 4, 2292–2299, https://doi.org/10.1021/am405024d

[11] Simonot, L., Elias, M., *Colour change due to a varnish layer*, In: Colour Research & Application, 2004, 29, 3, 196–204, https://doi.org/10.1002/col.20008

[12] Galić, E., Ljevak, I., Zjakić, I., *The Influence of UV Varnish on Colorimetric Properties of Spot Colours*, In: Procedia Engineering, 2015, 100, 1532–1538, https://doi.org/10.1016/j.proeng.2015.01.525

[13] Zhou, J., Li, E.Q., Li, R., Xu, X., Ventura, I.A., Moussawi, A., Anjum, D.H., Hedhili, M.N., Smilgies, D.-M., Lubineau, G., Thoroddsen, S.T., *Semi-metallic, strong and stretchable wet-spun conjugated polymer microfibres*, In: Journal of Materials Chemistry C, 2015, 3, 11, 2528–2538, https://doi.org/10.1039/C4TC02354D

[14] Zhang, J., Seyedin, S., Qin, S., Lynch, P.A., Wang, Z., Yang, W., Wang, X., Razal, J.M., *Fast and scalable wet-spinning of highly conductive PEDOT:PSS fibres enables versatile applications*, In: Journal of Materials Chemistry A, 2019, 7, 11, 6401–6410, https://doi.org/10.1039/C9TA00022D

[15] Allison, L., Hoxie, S., Andrew, T.L., *Towards seamlessly-integrated textile electronics: methods to coat fabrics and fibres with conducting polymers for electronic applications*, In: Chemical Communications, 2017, 53, 7182–7193, https://doi.org/10.1039/C7CC02592K

[16] Bashir, T., Skrifvars, M., Persson, N.-K., *High-strength electrically conductive fibres: Functionalization of polyamide, aramid, and polyester fibres with PEDOT polymer*, In: Polymers for Advanced Technologies, 2017, 29, 1, 310–318, https://doi.org/10.1002/pat.4116

[17] Lund, A., Darabi, S., Hultmark, S., Ryan, J.D., Andersson, B., Ström, A., Müller, C., *Roll-to-Roll Dyed Conducting Silk Yarns: A Versatile Material for E-Textile Devices*, In: Advanced Materials Technologies, 2018, 3, 12, https://doi.org/10.1002/admt.201800251

[18] Tadesse, M.G., Mengistie, D.A., Chen, Y., Wang, L., Loghin, C., Nierstrasz, V., *Electrically conductive highly elastic polyamide/lycra fabric treated with PEDOT:PSS and polyurethane*, In: Journal of Materials Science, 2019, 54, 9591–9602, https://doi.org/10.1007/s10853-019-03519-3

[19] Guo, Y., Otley, M.T., Li, M., Zhang, X., Sinha, S.K., Treich, G.M., Sotzing, G.A., *PEDOT:PSS "Wires" Printed on Textile for Wearable Electronics*, In: ACS Applied Materials & Interfaces, 2016, 8, 40, 26998–27005, https://doi.org/10.1021/acsami.6b08036

[20] Kye, M.J., Cho, J., Yu, J. C., Chang, Y.-W., Han, J., Lee, E., Lim, H.S., Lim, J.A., *"Drop-on-textile" patternable aqueous PEDOT composite ink providing highly stretchable and wash-resistant electrodes for electronic textiles*, 2018, 155, 150–158, https://doi.org/10.1016/j.dyepig.2018.03.024

[21] Sinha, S.K., Noh, Y., Reljin, N., Treich, G.M., Hajeb-Mohammadalipour, S., Guo, Y., Chon, KH., Sotzing, G. A., *Screen-Printed PEDOT:PSS Electrodes on Commercial Finished Textiles for Electrocardiography*, In: ACS Applied Materials & Interfaces, 2017, 9, 43, 37524–37528, https://doi.org/10.1021/acsami.7b09954

[22] Tseghai, G.B., Malengier, B., Fante, K.A., Nigusse, A.B., Van Langenhove, L., *Development of a Flex and Stretchy Conductive Cotton Fabric Via Flat Screen Printing of PEDOT:PSS/PDMS Conductive Polymer Composite*, In: Sensors, 2020, 20, 6, https://doi.org/10.3390/s20061742

[23] Pali, L.S., Jindal, R., Garg, A., *Screen printed PEDOT:PSS films as transparent electrode and its application in organic solar cells on opaque substrates*, In: Journal of Materials Science: Materials in Electronics, 2018, 29, 11030–11038, https://doi.org/10.1007/s10854-018-9185-y

[24] Kawahara, J., Andersson Ersman, P., Engqist, I., Berggren, M., *Improving the colour switch contrast in PEDOT:PSS-based electrochromic displays*, In: Organic Electronics, 2012, 13, 3, 469–474, https://doi.org/10.1016/j.orgel.2011.12.007

[25] Yousef, M., Othman, H., Hassabo, A.G., *A Recent Study for Printing Polyester Fabric with Different Techniques*, In: Journal of Textiles, Colouration and Polymer Science, 2021, 18, 2, 247–252, https://doi.org/10.21608/jtcps.2021.84754.1072

[26] Ding, Y., Invernale, M.A., Sotzing, G.A., *Conductivity Trends of PEDOT-PSS Impregnated Fabric and the Effect of Conductivity on Electrochromic Textile*, In: ACS Applied Materials & Interfaces, 2010, 2, 6, 1588–1593, https://doi.org/10.1021/am100036n

[27] Figueira, J., Bonito, R. M., Caravlho, J.T., Vieira, E.M.F., Gaspar, C., Loureiro, J., Correia, J.H., Fortunato, E., Martins, R., Pereira, L., *Screen-printed, flexible, and eco-friendly thermoelectric touch sensors based on ethyl cellulose and graphite flakes inks*, In: Flexible and Printed Electronics, 2023, 8, 2, https://doi.org/10.1088/2058-8585/acc114

[28] Dailliez, F., Hébert, M., Blayo, A., Chagas, L., Fournel, T., *Impact of a Transparent Coating on the Reflectance of a Line Halftone Pattern*, In: Coatings, 2021, 11, 12, https://doi.org/10.3390/coatings11121465

[29] Pang, Y.C., Li, Z.J., Shi, L.L., *Study on Relationship of Ink Thickness and Colour Saturation*, In: Applied Mechanics and Materials, 2015, 731, 295–299, https://doi.org/10.4028/www.scientific.net/AMM.731.295

[30] Paul Dauglas Vincent, B.A., *The effect of treatment with sulphuric acid on the breaking load of cotton*, In: Journal of the Textile Institute Transactions, 1924, 15, 5, T281–T290, https://doi.org/10.1080/19447022408661302

Authors:

SAŠA PETROVIĆ[1], SANDRA DEDIJER[1], NEMANJA KAŠIKOVIĆ[1], ŽELJKO ZELJKOVIĆ[1], VESNA GVOIĆ[1], IVANA JURIČ[1], MLADEN STANČIĆ[2]

[1]University of Novi Sad, Faculty of Technical Sciences, Department of Graphic Engineering and Design, Trg Dositeja Obradovića 6, 21000, Novi Sad, Serbia
e-mail: petrovic.sasa@uns.ac.rs, dedijer@uns.ac.rs, knemanja@uns.ac.rs, kecic@uns.ac.rs, rilovska@uns.ac.rs

[2]University of Banja Luka, Faculty of Technology, Department of Graphic Engineering and Design, Bulevar Vojvode Stepe Stepanovića 73, 78000, Banja Luka, Bosnia & Herzegovina
e-mail: mladen.stancic@tf.unibl.org

Corresponding author:

ŽELJKO ZELJKOVIĆ
e-mail: zeljkoz@uns.ac.rs