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THE INFLUENCE OF THE MECHANICAL RUB PROCESS ON THE COLOR CHANGE OF THERMOCHROMIC PRINTS ON TEXTILE SAMPLES

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Abstract: *The subject of this paper was to examine the impact of mechanical rubbing on the rate of colour change of thermochromic ink on textile samples. Textile samples made of polyester and cotton were printed using a manual screen printing technique with a reversible magenta leuco ink, with an activation temperature of 31°C. This paper aims to investigate how the process of mechanical rubbing affects the colour change of thermochromic samples during their cooling period, with varying numbers of rubbing cycles. To determine the relationship between the rubbing process and the rate of colour change, thermal, colorimetric, and spectrophotometric values were measured on the samples. The results indicate greater resistance of polyester compared to cotton, providing guidelines for improving the durability and resistance of thermochromic textile products. These findings have a significant impact on the development of more durable, functional textile products, reducing waste and costs and enhancing the sustainability of the textile industry.*

Key words: thermochromic inks, textile materials, rub resistance, smart textile.

1. INTRODUCTION

Thermochromic inks fall under the category of chromatic materials, characterized primarily by their response to thermal external stimuli, which can lead to a change or loss of colour. They are specialized inks that change colour in response to temperature variations. These inks contain microencapsulated active materials, specifically thermochromic pigments, dispersed within an appropriate binder. The active material determines the colour change, while the binder defines the printing and drying technology of the material (Rožić et al., 2017; Strižić Jakovljević et al.,2020). The colour change in thermochromic inks can be either irreversible or reversible. Irreversible inks can only change colour once, upon their initial exposure to the thermal stimulus, while reversible inks can change colour with each fluctuation in temperature (Tamrin et al., 2022, Jamnički Hanzer et al., 2023).

Thermochromic inks represent a significant innovation in the textile industry. The use of these inks on textiles provides numerous benefits, including aesthetic appeal, the ability to visually indicate temperature, and the potential for various applications in fashion and protective clothing (Strižić Jakovljević, 2022). Monitoring the resistance of materials to mechanical damage is essential for the quality and durability of textile products. Mechanical resistance directly affects the ability of the material to maintain its functional and aesthetic properties over time, especially under conditions of intensive use (Jamnički Hanzer et al., 2020). Understanding how different materials react to mechanical damages enables the development of better, more durable products that meet consumer needs and contribute to sustainability by reducing waste and costs

The use of thermochromic inks on textiles contributes to technological progress and improved product functionality and has a significant positive impact on the environment and the economy. Increasing the resistance and durability of thermochromic textile products reduces the need for frequent replacements, which contributes to the reduction of textile waste and has a positive impact on the environment. Likewise, more durable products reduce costs for consumers and producers, as they extend the life of textile items and reduce the need for purchases and production.

This research aims to examine the effect of rubbing on the rate of the colour change of thermochromic inks printed on textile samples. Specifically, it aims to quantify how different levels of mechanical rubbing affect the rate of thermochromic reactions and the time required for colour change at different temperatures. Based on the obtained results, the aim is to evaluate the resistance and durability of thermochromic inks on textiles, which will provide valuable information for their practical use and improvement in the textile industry.

2. MATERIALS AND METHODS

The samples were prepared with the manual screen-printing technique using a reversible thermochromic magenta ink based on leuco dyes. White textile materials of different raw material compositions were used as the printing substrate because the white colour of the substrate provides the best contrast with the magenta colour. A total of six samples were examined, three samples for each type of textile material, in order to calculate the arithmetic mean value of each measured characteristic. To achieve the goal of the research, the prepared textile samples were subjected to rubbing in a different number of cycles. After each rubbing cycle, during the cooling process of the samples, measurements will be performed on the printed field. Based on the measurement results, a better understanding of the resistance of thermochromic inks to mechanical damage and the identification of key factors that influence their durability on textile materials will be enabled.

In order to achieve a thermochromic ink activation temperature of 31°C, the samples had to be heated. For this purpose, a stone was used that was placed on an induction hotplate that heated it. When the stone reached a temperature of 50°C, samples were placed on it and heated for 2 minutes so that the ink would activate, that is, lose its coloration. After heating, the samples were removed from the heated plate in order to gradually cool down and to monitor the process of returning the colour to its original state. In time intervals of 10 seconds each, thermal, spectrophotometric, and colorimetric values of prints were measured in order to determine the current temperature and colour of the printed field. After one round of measurements for each textile material, the samples were exposed to a different number of rubbing cycles, after which the same measurements were performed to determine the difference between the measurements. Within this experiment, the dry rubbing method was applied. After examining the prints, the results were analyzed and processed in order to establish the relationship between the characteristics. The ambient conditions that were present at the time of the experiment were a temperature of 22°C ± 2°C, a relative air humidity of 40% ± 2%, and an atmospheric pressure of 101 kPa ± 1 kPa.

CIE L*, a*, and b* coordinate values were obtained by colorimetric testing, for which mean arithmetic values were calculated in the data processing process for each tested sample and which were then used to calculate the absolute colour difference. The Techkon SpectroDens device is used to determine the coordinates. During the measurement, the value of the standard observer was set to 2°, the standard illumination to D50, and the polarizing filter was turned off. In the first case, the L*, a*, and b* values obtained from the first test on a certain sample are used as reference values. In the second case, the L*, a*, and b* values of each previous measurement for the same sample will be used to calculate the colour difference as a reference value. The goal of this analysis is to determine how colour has changed over time. To evaluate the mechanical degradation of the printed samples, the colour difference between the printed samples before and after the rubbing treatment was calculated using the CIE ΔE2000 formula, listed below. Each printed sample was measured 3 times at 3 different positions on the print area. The components in the formula are ΔL' difference in lightness between two colours, ΔC' difference in saturation between two colours, ΔH' difference in hue between two colours, kL, kC and kH weighting factors for lightness, saturation and hue (usually the value 1), SL, SC, and SH scalar factors to normalize lightness, saturation, and hue, and RT a rotation term that accounts for the interaction between saturation and hue. The CIE ΔE2000 formula takes into account the complex interactions between these components, providing a more accurate way to determine colour difference compared to older models.

$$\Delta E^*_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}} \tag{1}$$

Spectrophotometers use spectral analysis to measure reflectance at different wavelengths in the visible part of the spectrum. Therefore, the spectrophotometric examination of the samples obtains spectral data values, the mean values of which are presented in the form of spectral reflection curves, and the analysis of which will determine how the change in temperature over time affects the change in the degree of reflection for the range of wavelengths of the visible part of the spectrum from 400 nm to 700 nm, taking into account the influence of different printing materials and the number of rubbing cycles. Spectrophotometric measurements allow a detailed analysis of colour change therefore it is possible to quantify colour changes caused by the rubbing of samples. These changes were interpreted in

relation to the subjective visual perception, enabling a precise evaluation of the quality and durability of thermochromic inks on textiles.
Figure 1 shows the setup of the experiment, with the position of the used devices and measuring instruments when testing the samples.

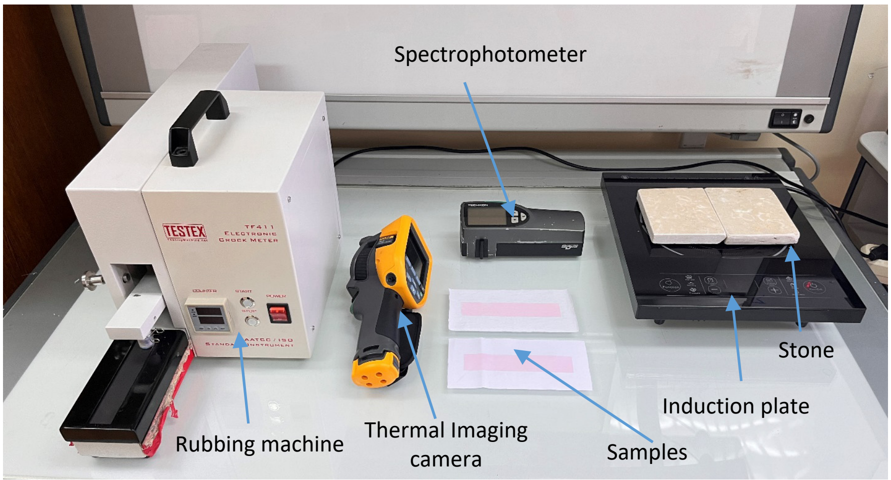

Figure 1: Experimental setup

The heating of the sample and its further measurement and analysis were performed after three cycles of 20 repetitions (20, 40, 60) of rubbing. A Testex FT411 device was used to test the color fastness of printed samples to dry rubbing. The heating was done by placing the sample on a heated stone plate, which was placed on an induction stove, at a temperature of 50°C for two minutes so that the ink would lose its color, that is, to activate it. After the ink was activated, the samples were removed from the heated plate and placed on the measuring table. Each examination was performed in a time interval of 10 s. For both one and the other type of textile material, the measurement time interval was 2 minutes due to the similar thickness of the samples.

2.1. Printing substrates

The samples were printed by manual screen-printing technique, with a 120 l/cm screen. The dimensions of the samples are 18 x 9 cm and consist of one printed field measuring 14 x 3 cm. Prints are printed on materials with different raw materials, and all samples are white. The white color was chosen because it contrasts well with the magenta printed field. The total number of samples was six, three samples each for both types of material. Two types of textile materials with different raw material composition were used. The first material used is 100% polyester (below, Sample 1). The other material that was used is 100% cotton by raw material composition (below, Sample 2). The characteristics of the samples are shown in Table 1.

Table 1: Composition and properties of water-based thermochromic leuco ink (SFXC, 2023)

Textile material	Fabric thickness mm	Fabric weight g/m^2	Number of threads per unit length threads/cm		Material composition	
			Wrap	Weft	Type	[%]
Sample 1	0,405	168,4	26	20	Polyester	100
Sample 2	0,409	150,2	28	20	Cotton	100
Standard	x	ISO 3801:1977	ISO 7211-2:2024		EN ISO 1833-1:2012	

2.2. Printing ink

Magenta reversible thermochromic water-based leuco ink was used for printing all samples, which is intended for printing with the screen-printing technique on paper, cardboard, textile, and other substrates, with an activation temperature of 31°C. The activation temperature is the temperature at which the colour changes, i.e. to discoloration. Below the activation temperature, the colour returns to its original state. The paint comes in the form of two components, binder (25 ml) and pigment (25 ml), so it is necessary to mix them in a ratio of 50:50, according to the manufacturer's instructions. After printing, the prints were dried in a COLO DRYS53A multifunctional device at a temperature of 160°C for a period of 2 minutes (SFXC, 2023).

3. RESULTS AND DISCUSSION

3.1. Thermal analysis

Temperature values for certain time intervals were obtained by thermal examination of all samples. This analysis aims to determine whether the application of mechanical damage to textile samples, such as rubbing, affects the temperature change of printed thermochromic prints during their cooling time. Figure 2 presents the results of temperature measurements for both samples before and after three rubbing cycles of 20 repetitions each (0, 20, 40, 60).

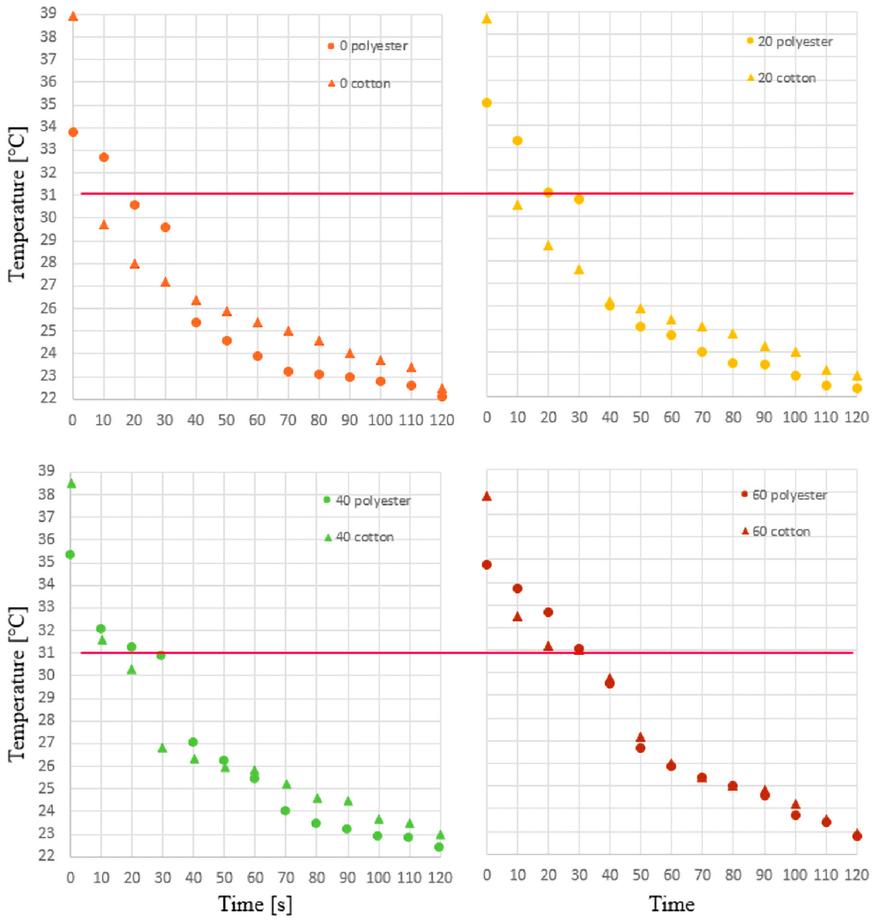

Figure 2: Comparative display of temperature dependence on cooling time for both samples

In Figure 2, it can be seen that the time to reach the activation temperature for all four states of Sample 1 and Sample 2 is different. Analyzing the temperatures on all four states of Sample 1, it is observed that the average temperature differs minimally, by about 1°C, which does not represent a significant difference. Also, it is observed that the total temperature change for the same cooling time of the samples decreases evenly, which may mean that the rate of temperature change decreases as the number of rubbing repetitions increases. The standard deviation values show that there is a relationship between the number of repetitions of rubbing and the change in temperature for individual time intervals of measurement. By analyzing the temperatures on all four states of Sample 2, it is observed that the average temperature differs minimally, by less than 1°C on the first three states and 1°C on the last state, which does not represent a significant difference. Also, it is observed that the total temperature change for the same sample cooling time decreases slightly, which also in the case of Sample 2 may mean that

the rate of temperature change decreases as the number of rubbing repetitions increases. Standard deviation values for individual measurement time intervals do not differ significantly between sample conditions, but a difference is observed before and after the last measurement cycle.
By comparing both samples in all four conditions, it is noticed that there are differences between them, although both samples have similar characteristics. Also, it is clearly observed that with an increase in the number of repetitions of rubbing, the rate of temperature change is reduced, i.e. it can be seen that the number of intervals required to reach the activation temperature is greater from the first to the last graph. Comparing Sample 1 and Sample 2, there is a noticeable difference between the recorded temperature values at the same time intervals, with the fact that this difference is not always the same, but is a little more significant in the initial measurements compared to the time after reaching the activation temperature. In addition, it can be observed that Sample 2 reaches the activation temperature faster in all four cycles, i.e. the colour change of the sample occurs faster.

3.2. Colorimetric analysis

Figure 3 shows the colour difference values for Sample 1 before and after three rubbing cycles, during a time interval of 120 seconds.

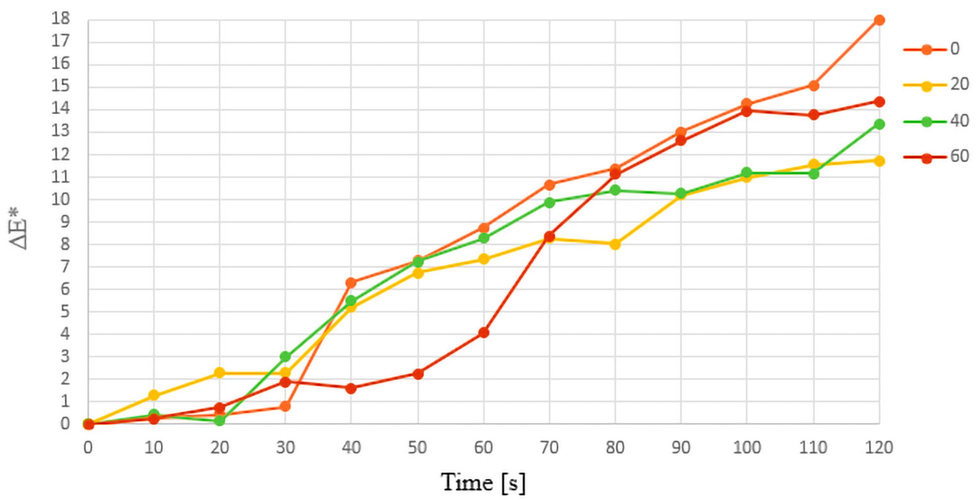

Figure 3: Comparison of the change in absolute colour difference over time for Sample 1 before and after three rubbing cycles

Analyzing the colour change values on Sample 1, it can be observed that the colour change values at the individual states of the sample are not the same and that the biggest difference in colour is observed on the sample before the rubbing process. What is also observed is that the colour changes for all sample states are in an even increase from the beginning of the measurement to the end, which is also related to the thermal measurements, because over time the temperature dropped below the activation temperature and thus the colour regained its colouring.
For the colour change values on the sample before and after the rubbing process, it was noted that there is no uniform change when observing the colour change between adjacent measurement intervals, which makes it impossible to have a relationship between those values. Also, the change values do not follow the thermal values, so that during the time immediately below the activation temperature, the biggest colour differences do not occur, but they occur randomly in some time interval for each state of the sample. It is also important to note that most of the colour differences are less than 2, which is considered a difference that is visible but still accepted as good print quality. There are also intervals where the colour difference is over 2, but even in those cases, the difference is not greater than 6. Such values suggest a clearly visible difference, but the colour does not deviate from the reference. The conclusion of this analysis is that there is no relationship between the number of times the impression is rubbed and the colour change on the same.
Analyzing the colour change values on Sample 2 from Figure 4, it can be observed that before and after the rubbing process, the colour change values on the individual states of the sample are not the same, which was expected. The biggest difference in colour is observed on the sample before the rubbing

process. It can also be observed that the colour changes for all sample states grow evenly from the beginning to the end of the measurement. This is consistent with the thermal imaging measurements, as over time the temperature dropped below the activation temperature, causing the colour to return to its original state.

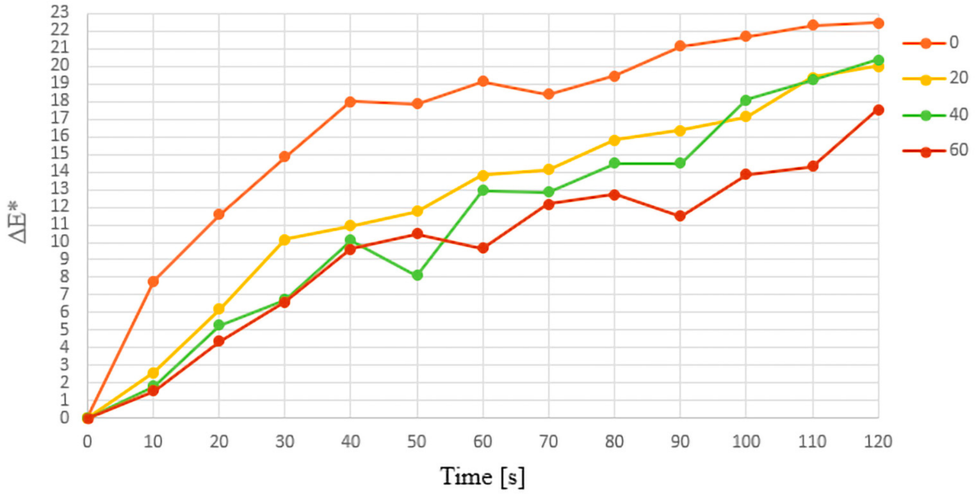

Figure 4: Comparison of the change in absolute colour difference over time for Sample 2 before and after three rubbing cycles

In contrast to the values measured on Sample 1, with Sample 2, a colour change is observed that is related to the number of rubbing cycles of the sample, that is, the number of rubbing cycles applied to the sample affects the colour change values on the sample during the measurement time of 120 seconds. The highest values of colour change were recorded on the sample before rubbing, where most values are between 1 and 2, which is characterized as a small difference. Also, the highest values were recorded around the interval when the activation temperature was reached. After the first and second rubbing cycle, the colour change value between the measurement intervals is less than 6, so the difference is visible but the colour tone is still not changed. In the case of the sample after the third rubbing cycle, the difference is, in most cases, less than 3, which is characterized as a difference that can be seen even by the untrained eye. Common to all conditions is that the greatest changes occur precisely between the intervals around reaching the activation temperature.

3.3. Spectrophotometric analysis

Spectral reflectance curves were obtained from spectral data obtained by spectrophotometric testing of samples. The analysis of the curves will determine what effect the change in the condition of the sample before and after three cycles of dry rubbing has on the change in the degree of reflection of prints for the range of wavelengths of the visible part of the spectrum.

With Sample 1, it can be seen that before the rubbing process, the maximum reflection was 74,95%, while the lowest percentage of reflection was 17,39%. The percentage difference between the maximum and minimum reflectance of the sample after the first rubbing cycle is 55,38. These results indicate that there is no decrease in reflection as the number of rubbing cycles increases; that is, 60 repetitions in three rubbing cycles do not have a particular effect on the degree of reflection of the sample. However, if we observe the moment of reaching the activation temperature, which is the main moment for evaluating the properties of thermochromic ink, in that case we see that the reflection decreases as the number of rubbing cycles increases. The only deviation occurs at the last rubbing cycle when the spectral data is higher than expected. Figure 5 shows the spectral reflectance curves (at the beginning and at the end of the measurement) for Sample 1 before and after three cycles of rubbing the material.

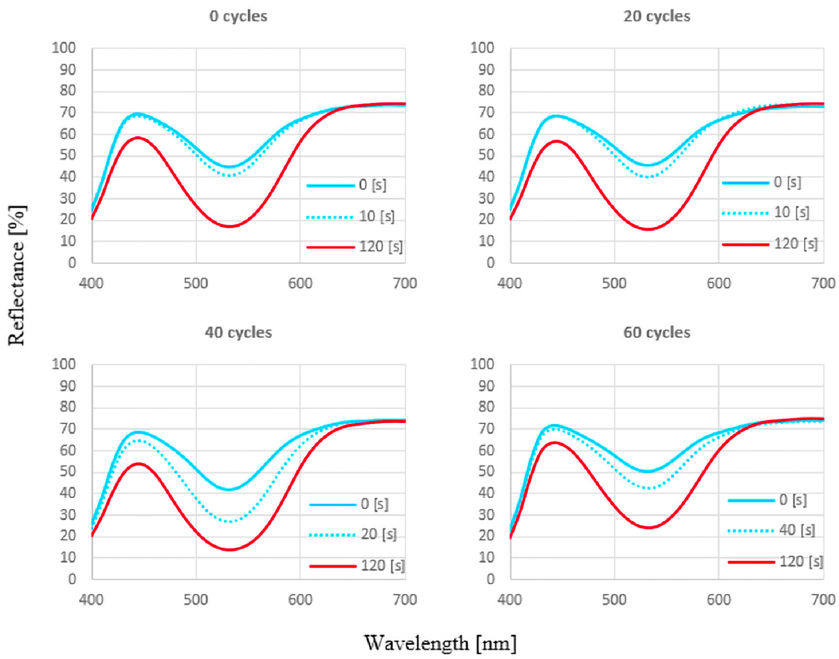

Figure 5: Comparison of maximum and minimum spectral reflectance for Sample 1

In Figure 6, it can be seen that on all four states of Sample 2, the spectral curve retains the same shape and that the obtained results are in accordance with thermal measurements because the shape of the curve shows that the reflection decreases over time. Such behaviour of the curves over time was expected, considering that over time the colouring of the thermochromic colour returns, i.e. the print on the sample is getting darker. With Sample 2, it can be seen that before the rubbing process, the maximum reflection was 77,12%, while the lowest percentage of reflection was 13,50%. The percentage difference between the maximum and minimum reflectance of the sample after the first rubbing cycle is 59,22. Observing the reflectance at the moment of reaching the activation temperature, the reflectance decreases, which was expected and suggests that there is a relationship between the reflectance and the number of repetitions of the rubbing cycle.

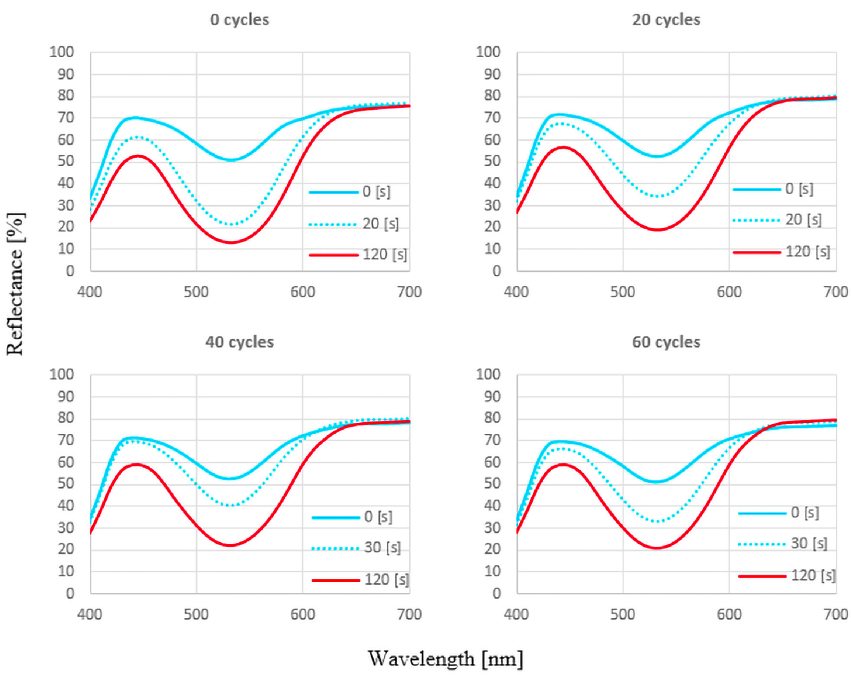

Figure 6: Comparison of maximum and minimum spectral reflectance for Sample 2

4. CONCLUSION

The investigation of the effect of wear and friction on the colour change of the thermochromic dye was carried out on textile samples made of polyester and cotton. The results showed different effects of wear and friction on these two materials. A slight degradation of the material due to wear was observed on cotton, which indicates a certain sensitivity of cotton to physical influences. In contrast, for polyester, no significant relationship was observed between colour deterioration and the number of rubbing cycles, suggesting that polyester is more resistant to abrasion and that the rate of thermochromic colour change does not depend on mechanical damage to the sample compared to cotton.
These results indicate that polyester is a more suitable material for the use of thermochromic paints in conditions where intense wear is present, while cotton can be used in applications where wear is less pronounced. Further research can focus on improving the wear resistance of cotton or on the development of new material blends that combine the best properties of both materials, which would expand the application possibilities of thermochromic dyes in the textile industry.

5. ACKNOWLEDGMENTS

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