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STABILITY OF SILVER BASED CONDUCTIVE FILMS ON CELLULOSE BASED SUBSTRATES

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Abstract: *The possibility of integrating printed flexible electronic components into visual solutions that interactively communicate with the consumer represents a new direction in the development of sustainable solutions accessible to all target groups. Flexible electronic thin films are becoming one of the integral elements of visual communication, which means they must be incorporated into the design itself rather than being hidden beneath another element. Today's trends are increasingly directed towards the use of cellulose materials as more acceptable in packaging and other graphic products. In this regard, it was necessary to examine the mechanical, electrical, and colour stability of conductive thin films printed on cellulose substrates. This study examined the possibility of applying conductive silver-based film on cellulose based substrate through the examination of the electric conductivity of silver-based thin films by comparing the quality of prints on two substrates. Additionally, the resistance of printed thin films to double bending and rubbing was investigated. The values of electrical conductivity before and after mechanical testing were compared to explore the potential application of conductive inks in creating visually attractive and mechanically resistant silver-based conductive films. The research has shown that the substrate selection significantly affects the mechanical resistance of prints to bending. Additionally, despite significant visual changes in the conductive thin films, the electrical conductivity of the thin films did not change significantly.*

Key words: Conductive ink, cellulose based substrate, functional printing, mechanical resistance

1. INTRODUCTION

Printed sensors, including capacitive sensors, electrochemical sensors, and printed radio frequency identification tags, are some of the key beneficiaries of printing technologies, owing to their ability to be produced at low cost, on flexible substrates, and at high volumes. These sensors offer significant advantages in various industries, such as healthcare, environmental monitoring, logistics, and consumer electronics, where lightweight, compact, and easily deployable sensing solutions are required. The versatility of printing methods allows for the integration of these sensors into diverse applications, enabling the development of smart, connected devices and the expansion of the Internet of Things.

Various printing techniques are currently employed in the fabrication of electronic devices, including printed diodes (Ahmad et al., 2023), transistors (Arias et al., 2004), sensors (Shkodra et al., 2020), and antennas (Wiklund et al., 2021). Flexography, gravure, and inkjet printing utilize low-viscosity liquid inks, whereas offset, screen, and pad printing employ high-viscosity, paste-like inks (Izdebska 2016).

Printed thin films are created by depositing thin layers of functional inks onto a low-cost substrate that may be recyclable or biodegradable. The production process consists of three main stages: material selection, printing, and post-printing (Wiklund et al., 2021). The key materials used in printed thin films include inks with conductive, semiconductive, or dielectric properties, along with substrates typically made from synthetic or natural polymers.

Conductive inks on paper open new possibilities in the field of printed electronics, enabling the development of innovative and adaptable electronic solutions. This technology combines the advantages of paper materials with the electrical properties of conductive inks, allowing for the creation of flexible and lightweight electronic components that can be easily integrated into various applications. The use of conductive inks on paper can be applied in diverse areas, including environmental monitoring sensors, flexible circuits in wearable devices, and interactive applications in education and marketing.

One of the key benefits of this technology is the reduction in production costs, which facilitates faster and more economical prototyping and product manufacturing. Additionally, this innovation contributes to sustainability by using eco-friendly materials, which is particularly important in the context of the growing demand for sustainable electronic solutions. With the introduction of conductive inks on paper, we can anticipate advancements in the development of smart packaging, health monitoring devices, and other functional products that combine electronics with traditional materials, paving the way for new innovations and creative solutions in the industry.

Previous studies examined the performance variability of paper-based printed antennas, focusing on the effects of the printing process, changes in permittivity due to ink carrier absorption, and temperature. Surface roughness, thickness, and reflection coefficient were evaluated, with the screen-printed antenna showing the best performance (Ahmad et al., 2023). The impact of altered permittivity from ink absorption and temperature was also explored.

Advantages of eco-design in printed electronics are numerous, including more efficient material utilization, reduced energy consumption during both manufacturing and operation, decreased reliance on hazardous substances, and enhanced recyclability (Kunnari et al., 2009). In that sense the aim of this work is to explore the possibility for using conductive silver-based films on cellulose substrates by evaluating the electrical conductivity of these thin films and comparing the print quality on two different substrates. The research also assessed the resistance of the printed thin films to double bending and rubbing. The electrical conductivity values were compared before and after mechanical testing to investigate the feasibility of using conductive inks for producing visually appealing and mechanically durable silver-based conductive films.

2. MATERIALS AND METHODS

2.1 Materials

Since the goal is for the antenna to become an integral part of the design, atypical shapes to test their stability were created. The patterns for printing were prepared in Adobe Illustrator (Figure 1).

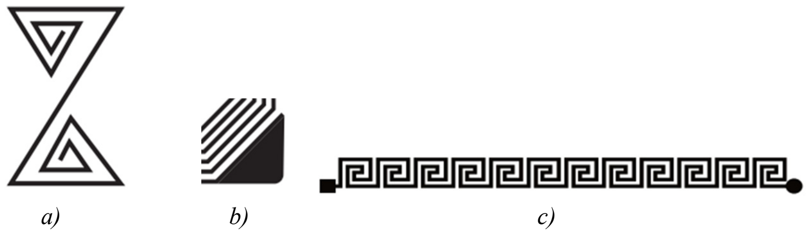

Figure 1: Patterns for printing a) sample for resistance measurement, b) sample for rub test, c) sample for double folding test

The screen-printing technique was used for printing, utilizing a capillary photosensitive film. The mesh used for creating the printing form in this study is SEFAR PME mesh with a mesh count of 140 lines per cm, and the base material is polyester, specifically poly(ethylene terephthalate). The form was exposed for 2 minutes in a screen-printing exposure machine. In this study, Saral HSCSilver 600 high-conductivity ink with a high solid content of 86% silver was used (Thermo Fischer 2012). The silver particles are dispersed in a solvent based on diethylene glycol monoethyl ether. The ink density is 3.7 g/cm^3. This ink is designed for screen printing, with a recommended mesh count of 61 lines/cm and a thread diameter of 64 µm. It is suitable for printing mainly on polymer materials. This ink dries at a relatively low temperature (Thermo Fischer 2012). In this study the ink was cured (sintered) at 70°C for 10 minutes. The thickness of the dry ink layer is 19 µm. Prints were made on two different types of paper with the same weight, i.e., 200g/m^2, one being satin-finished and the other coated paper from the same manufacturer. Ten prints with the same patterns were made on each type of paper.

2.2 Electric resistance testing

Two-point resistance measurement with a multimeter was conducted on all line prints. Two-point resistance measurement is a straightforward technique used to determine the electrical resistance of a component by connecting two probes directly to its terminals. A small current is passed through the component, and the voltage drop across it is measured, allowing resistance to be calculated using Ohm's Law. This method is commonly employed due to its simplicity and effectiveness in providing quick resistance values. Electric resistance testing was conducted on samples printed with patterns in Figure 1a.

2.3 Mechanical testing

Two mechanical tests, resistance of paper substrates and prints to double bending and rub and abrasion tests, were conducted. The test is conducted by measuring the number of double bends a sample of specific dimensions (15 x 100 mm) can withstand before breaking. The paper sample is secured in clamps so that it passes through a vertical slit in a metal plate and is loaded with 9.81 N. Moving the plate back and forth causes the sample (specimen) to undergo double bending. Double bend testing was conducted on samples printed with patterns in Figure 1c.

By testing the resistance of prints to abrasion, the resistance of the finished (dry) print to the removal of the ink layer due to friction is determined. This occurs either from rubbing two prints together or from rubbing the test print against another material. For the preparation of the test, circular paper samples are cut, with the substrate having a diameter of 115 mm and the printed sample having a diameter of 50 mm. the prints were subjected to a rub resistance test using a Hanatek Rub and Abrasion Tester in accordance with the BS 3110 standard. Rub resistance test was performed on samples printed with patterns in Figure 1b.

The core of the device consists of two disks with different radii that are in contact over their entire surfaces. Driven by an electric motor, the disks rotate at the same angular speed. During testing, the sample and the substrate made of the same material are placed on the disks, and the pressure between them is regulated by placing weights of different masses on the top disk. The ink removed from the surface of the print due to rubbing is transferred to the abrasion substrate. An air supply tube removes the particles of dislodged ink from the sample during the test, preventing additional abrasive action of the dislodged particles on the sample. After a specified number of abrasions (10, 20, and/or 40), the device stops. The samples (prints) and the abrasion papers are visually assessed to determine whether the resistance to abrasion is satisfactory. The assessment is carried out by comparing the transfer of printing ink from the tested sample to the abrasion substrate. The samples are then evaluated with scores from 1 to 5, where 1 is the highest score and is awarded to the sample with the greatest resistance, and 5 to the sample with the least resistance, according to the following scale:1 - no visible fingerprint smudging (no smudging) 2 - slight signs of fingerprint smudging 3 - noticeable fingerprint smudging 4 - significant fingerprint smudging 5 - very pronounced fingerprint smudging

3. RESULTS AND DISCUSSION

The number of double folds for unprinted satin paper (MS0) ranges from 65 to 281, with an average of 151 and a standard deviation of 79 (Figure 2). Exposing unprinted satin papers (MS) to 70°C for 10 minutes shows no significant change, maintaining an average of 156 and a standard deviation of 43. In contrast, printed satin paper (MSP) exposed to the same conditions shows a significant drop in double folds, with values between 8 and 32, averaging 16 and a standard deviation of 9. This indicates much lower resistance to double folds compared to unprinted satin paper. Unprinted coated paper (MG0) ranges from 270 to 543 double folds, averaging 410 with a standard deviation of 91, making it more resistant than satin paper. After exposure to 70°C for 10 minutes, coated paper (MG) shows values between 147 and 364, with an average of 273 and a standard deviation of 77, which is lower than unexposed coated paper. After printing and exposure, double folds range from 10 to 84, averaging 42 with a standard deviation of 26. Graph 1 illustrates that printed papers (MSP, MGP) have significantly lower mechanical resistance to double folds than unprinted papers (MS0, MS, MG0, MG). The mechanical resistance of satin papers changes little after exposure, while coated papers show substantial differences, affirming that coated papers are more resistant due to filler additions. The standard deviation for sample types is extremely high, which suggests a significant level of variability in the data collected. This variability can undermine the reliability of the results and may lead to inaccurate conclusions. Therefore, increasing the number of measurements is essential to enhance the statistical robustness of the findings. A larger sample size will help to reduce the impact of outliers and random errors, ultimately providing a clearer picture of the true trends and patterns. By obtaining more measurements, a more accurate assessment can be achieved and ensured that the results are applicable to broader contexts.

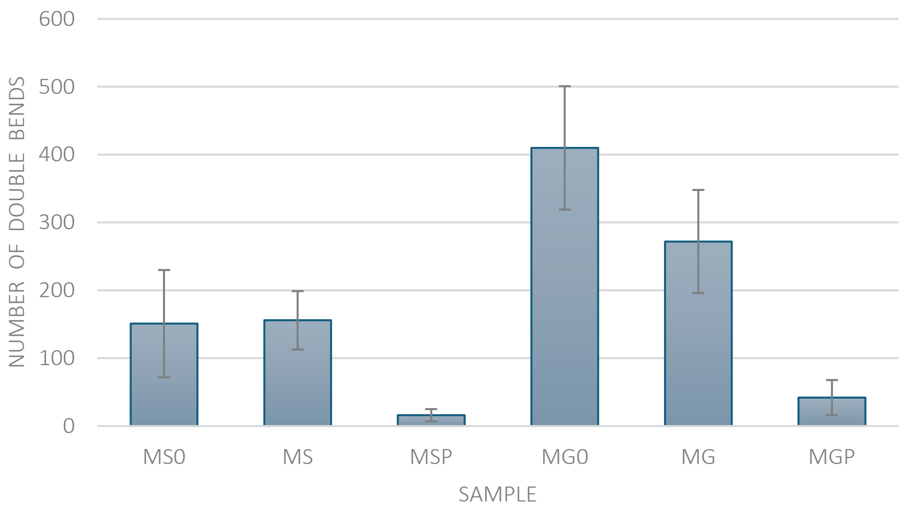

Figure 2: Comparison of the results of double folds for coated papers (MG0 - original paper, MG - paper exposed in the oven, MGP - printed thin film exposed in the oven) and satin papers (MS0 - original paper, MS - paper exposed in the oven, MSP - printed thin film exposed in the oven)

As for rub resistance tests, in Figure 3, the initial print before rub resistance test (MG_0) is shown alongside prints after rub resistance tests with no weights applied at 10 (MG_1) and 20 rotations (MG_2). Here, the rub resistance is not excessively visible, and the print largely retains its original appearance.

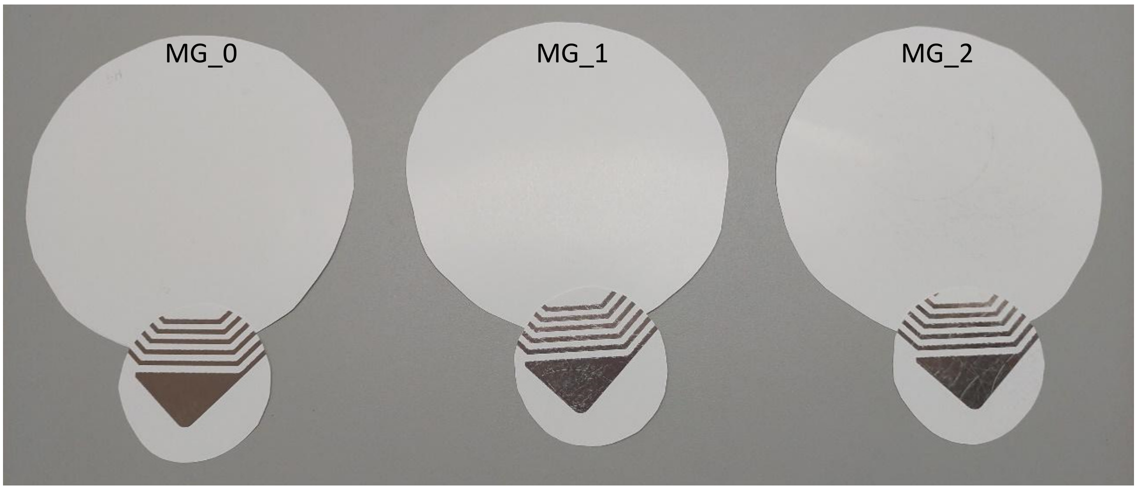

Figure 3: MG 0,1,2

In Figure 4, prints after 30 (MG_3), 40 (MG_4), and 50 rotations (MG_5) without weights are shown. Here, the abrasion on the prints is more noticeable, resulting in lower scores during visual assessment. Although little ink remains on the substrate, the prints themselves are visibly damaged.

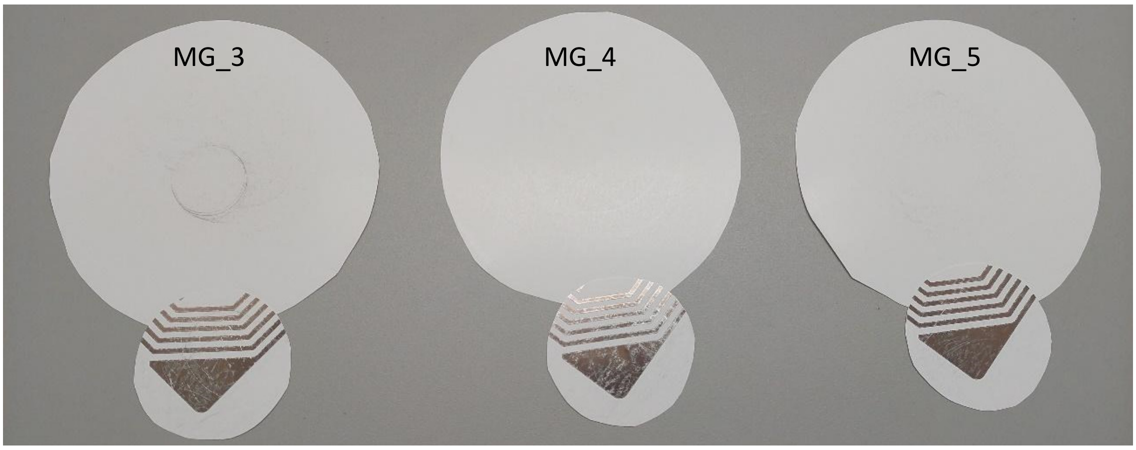

Figure 4: MG 3,4,5

In Figure 5, the initial print (MG_0) is displayed alongside prints after 10 (MG_6) and 20 rotations (MG_37) with weights. While it was anticipated that adding weights would adversely affect the abrasion, no significant differences are evident when compared to the prints tested without weights.

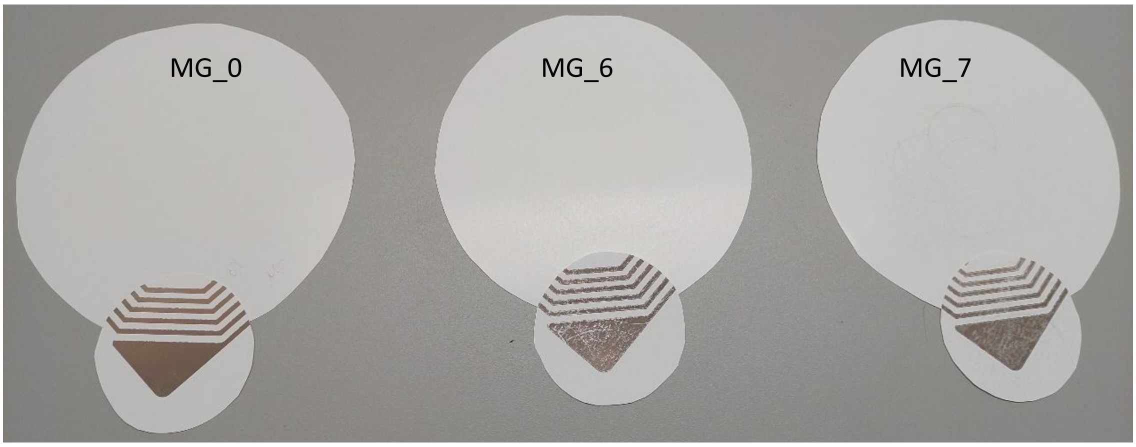

Figure 5: MG 0,5/,6

Figure 6 displays prints after 30 (MG_8), 40 (MG_9), and 50 rotations (MG_10) with weights. Here, the smudging is significantly more pronounced, evident both on the substrate and on the prints themselves, which show clear signs of damage. These observations are also corroborated by the results of the visual assessment.

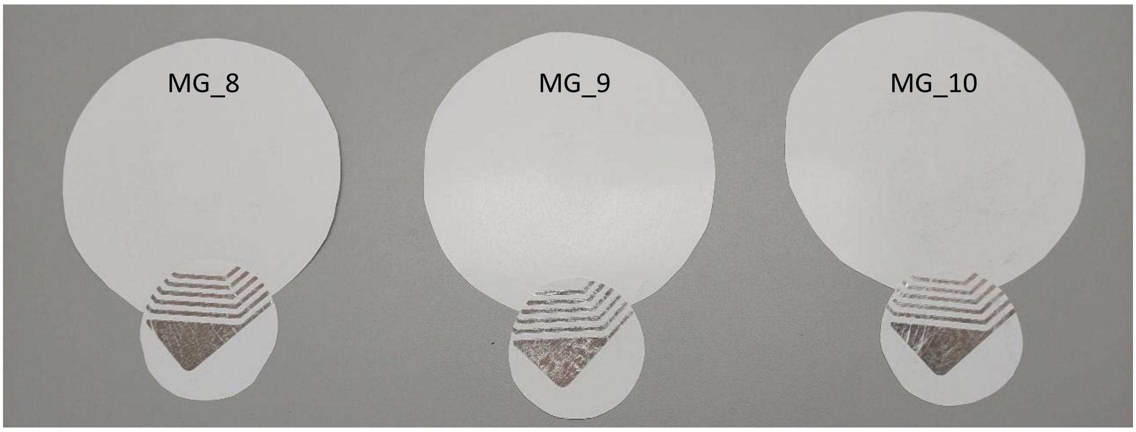

Figure 6: MG 8,9,10

The results show that prints with fewer rotations received higher ratings (Table 1), as there was minimal ink transfer to the substrate and fewer imperfections in the prints. In contrast, as the number of rotations increases, the effects of rubbing becomes much more evident. Abrasion is particularly noticeable on satin paper. The most significant negative impact is observed in the prints subjected to 50 rotations with weights. Figure 7 presents the initial print (MS_0) along with prints after 10 (MS_1) and 20 rotations (MS_2) without weights. In these samples, abrasion is minimal, and the prints have largely maintained their original appearance.

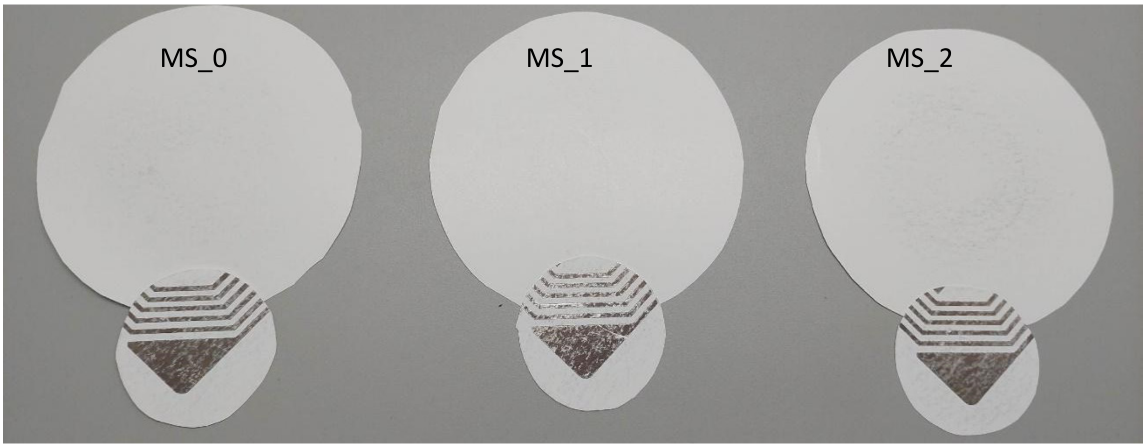

Figure 7: MS 0,1,2

The abrasion of prints after 30 (MS_3), 40 (MS_4), and 50 (MS_50) rotations without weights is illustrated in the Figure 8. The abrasion is most pronounced after 30 rotations, while it becomes less noticeable at 40 and 50 rotations, leading to prints that exhibit less overall damage. While ink transfer to the substrate is minimal, the prints exhibit visible damage, though still within acceptable limits (Figure 9). The most significant damage is observed in the print that was tested with the frequency of 40 with weights (Figure 10). The prints after 30 and 50 rotations are quite similar, with less noticeable damage.

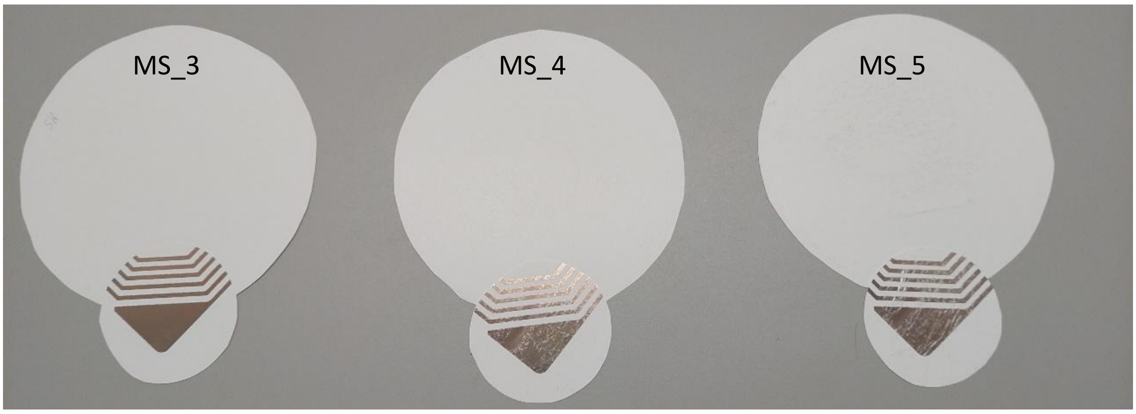

Figure 8: MS 3,4,5

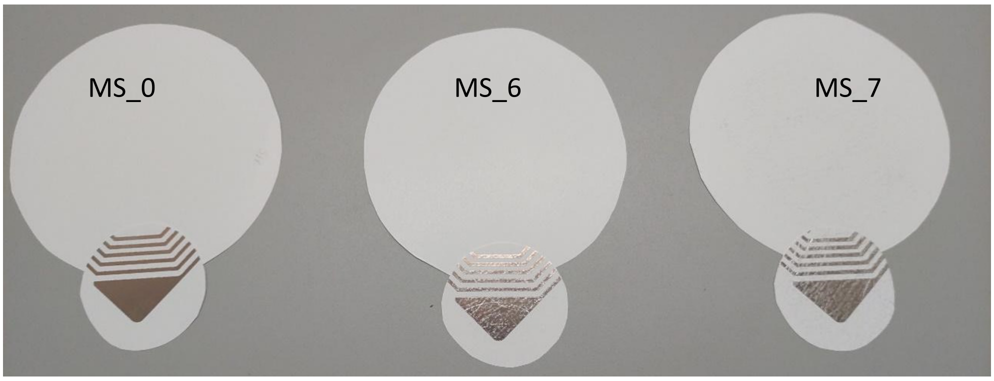

Figure 9: MS 0,6,7

Figure 10: MS 8,9,10

The visual assessment of coated paper is notably better. In comparison to satin paper, abrasion is less prominent across multiple samples (Table 1). When comparing the results for rub resistance on satin and coated paper, it is clear that less ink transfers from prints made on coated paper, making these prints more durable.

Table 1: Evaluations of the visual assessment of prints on coated papers (MG 1-10) and satin papers (MS 1-10)

Sample	Grade	Sample	Grade
MS-1	2	MG-1	2
MS-2	2	MG-2	1
MS-3	3	MG-3	4
MS-4	4	MG-4	3
MS-5	4	MG-5	2
MS-6	2	MG-6	3
MS-7	3	MG-7	4
MS-8	3	MG-8	3
MS-9	4	MG-9	4
MS-10	5	MG-10	3

The average electrical resistance of the selected line on the coated paper measures 135 ohms, in contrast to 51 ohms for the satin paper. The standard deviation is significantly greater than any individual measurement, indicating inconsistency in the obtained prints. The values obtained from measuring the resistance of lines printed on paper can be highly unbalanced due to several factors. Firstly, the inherent variability in the printing process itself can lead to inconsistent ink deposition, resulting in uneven conductivity along the printed line. Additionally, the properties of the paper substrate, such as its texture and moisture content, can affect how the ink adheres and interacts with the surface, further contributing to variations in resistance. Lastly, environmental factors, such as temperature and humidity, can also impact the electrical properties of both the ink and the paper, leading to fluctuating resistance measurements.

4. CONCLUSIONS

The research results show that conductive thin films based on silver printed using screen printing on fibrous substrates exhibit variable properties in response to various external factors, such as mechanical bending, abrasion, and exposure to high temperatures. Thin conductive films printed on coated papers demonstrated greater resistance and stability compared to those on satin papers, highlighting the importance of selecting an appropriate substrate for applications in smart packaging solutions. However, challenges such as reduced mechanical resistance after printing and heat exposure indicate a need for further research and optimization of the process. Although silver-based conductive inks provide a solid foundation for the further development of printed electronic components on paper substrates, implementing them in mass production will require additional improvements to achieve long-term durability and sustainability. These results represent a step forward in the development of sustainable smart packaging that integrates advanced technologies while preserving the environment. Future research should focus on sintering the prints at higher temperatures to enhance their conductivity, although higher-temperature sintering may cause the paper to become more brittle and less resistant to external mechanical impacts, such as double bending. Therefore, the study should be conducted on a variety of papers to identify one that is less negatively affected by exposure to high temperatures. Additionally, to ensure the results are as relevant as possible and to discount measurements with excessive deviations, future research must involve a significantly larger number of measurements to identify the best printing substrate and the optimal finishing method for the prints.

5. ACKNOWLEDGMENTS

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