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Sustainable pre-treatment of cellulose knitwear in digital pigment printing processes

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Abstract

Purpose – In the field of research on the application of digital printing to textile materials, there are still many research issues that arise from the very demanding interaction of digital printing technology and the complex, heterogeneous surface system of textile materials. This is precisely why the area of pre-treatment of textile materials is in need of research, and the purpose of this research was to establish the level of influence of physical and chemical activation of the textile surface with plasma and the possibility of improving the quality of the print and colour reproduction.

Design/methodology/approach – The paper deals with the possibility of applying argon and oxygen cold low-pressure plasma in the processing of cellulose knitted fabrics, with the aim of improving the quality of the print and colour reproduction in digital pigment inkjet printing. The selected raw material samples were 100% raw cotton and lyocell. After plasma treatment, the samples were printed by digital ink jet printing with water-based pigment printing ink. An analysis of the micromorphological structure of untreated and plasma-treated samples before and after printing was carried out, and a comparative analysis of the colour of the printed elements was carried out depending on the pre-treatment.

Findings – The conducted research showed a positive influence of plasma pre-treatment on the coverage of the fibre surface with pigments, the uniformity of pigment distribution along the fibre surface and the uniformity of the distribution of the polymeric binder layer. This has a positive effect on colour reproduction. Also, certain improvements in colourfastness to washing were obtained.

Research limitations/implications – Considering the complexity of the topic, although exhaustive, this research is not sufficient in itself, but opens up new questions and gives ideas for further research that must be carried out in this area.

Practical implications – Also, this kind of research contributes to the possibility of adopting the idea of industrial plasma transformation, as an ecologically sustainable functionalisation of textiles, which has not yet been established.

Originality/value – This research is certainly a contribution to the establishment of acceptable textile pre-treatment methods in the field of digital printing, as one of the key quality factors in digital textile printing (DTP). Considering the still large number of obstacles and unanswered questions encountered in the field of digital printing on textiles, this kind of research is a strong contribution to the understanding of the fundamental mechanisms of the complex interaction between printing ink and textile.

Keywords Plasma pre-treatments, Digital ink jet printing, Cotton, Lyocell, Wash colour fastness

Paper type Research paper

Introduction

The imperative of sustainability is the absolute paradigm of the future development of the textile industry. In modern times of excessive production and consumption of resources,

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where the textile industry is one of the biggest polluters of the environment, the printing industry attaches great importance to environmental protection and eco-design (Hoque, 2021; Tyler, 2011). High consumption of chemicals used in the process of printing, such as dyes, binders, solvents, surfactants, suspended solids and some other has, been found to be environmentally hazardous and, therefore, responsible for environmental pollution. Moreover, water and energy consumption are high in textile printing. As a result, a large amount of effluent containing harmful chemicals is released from the print production floor (Hoque, 2021; Tyler, 2011; Chen *et al.*, 2015). With the entry of digital inkjet printing technology into the field of textile printing, a completely new direction of development opens, which enables the shift of textile printing technology from the "notorious" and one of the main polluters, towards green, eco-friendly and sustainable technology. This printing process is considered a new eco-friendly, green and environmentally friendly method of textile printing, which was first applied in the textile industry and has unique advantages such as low cost, high precision and speed compared to traditional printing, which was limited in its ability to produce high-quality and personalised products (Hoque, 2021; Shi *et al.*, 2021; Kan and Yuen, 2012). Digital textile printing (DTP) is recognised as an environmentally friendly technology that consumes less water and energy compared to screen printing (Chen *et al.*, 2015). As a result, less wastewater is produced, which is very beneficial for the environment. Graphix Supply World found that the DTP process enables high savings in environmental components (carbon dioxide emissions, waste generation, water and energy consumption) compared to the conventional process [1]. Notermans (2019) mentioned that the consumption of water, electricity and chemicals can be reduced by 55–60% with DTP (Notermans, 2019; Tkalec *et al.*, 2022). In the face of growing environmental concerns, manufacturers are looking for sustainable production processes.

These advantages of DTP justify considerable research and developmental efforts that are continuously invested in finding optimal solutions for obstacles and problems that, despite the great advantages and recognition of digital printing, still prevent its full commercialisation. Currently, the most important directions of research in the field of DTP are innovative approaches to printing ink formulation, modifications and pre-treatments of textile surfaces. In the application of pigments in digital printing ink formulation, strict requests are to pigment particle size, restricted content of binders and cross-linking agents in printing inks, as well as low viscosity with higher surface tension. This opens an extensive platform for researching innovative formulations of binders as well as innovative methods of textile surface pre-treatment (Ding *et al.*, 2021; Ujiie, 2006; Tawiah *et al.*, 2016; Lim and Parillo Chapman, 2022).

In the context of research on the improvement of surface treatment techniques in a more economical and ecological way, research on the application of cold plasma technology in the treatment of textiles has markedly developed during the last two decades. In the application of cold plasma technology, modifications take place in the interaction of plasma and the textile surface in order to achieve the necessary functional properties of textile products. Those are targeted modifications of various properties, occurring due to different physical-chemical processes happening between active particles created in the plasma and active groups in the textile material (Shishoo, 2007; Ercegovic Razic *et al.*, 2017).

An interesting study was conducted by Aileni *et al.*, in which the possibility of using radio frequency (RF) plasma in the hydrophobization methodology of cellulosic textile materials was investigated. The RF plasma technology of pre-treatment was compared with low-pressure plasma, amongst others. It was found that unlike RF plasma, which would negatively affect the environment through heating generated by gases and electricity consumption, there would be little or no impact from organic respiratory substances, radiation, land use and ecotoxicity as a result of plasma technology, since low-pressure plasma technology does not generate organic vapour emissions, heat or wastewater (Aileni *et al.*, 2019).

Intensive research is also being carried out into the application of plasma technology in the processes of antibacterial pre-treatment of textile materials in order to achieve improved properties of the antibacterial activators used, whereby the positive effect of plasma pre-treatment has been proven (Haji and Bahtiyari, 2021).

Haji and Kan give a comprehensive overview of the application of low-pressure plasma and point out that plasma treatment is one of the emerging technologies for the environmentally friendly and sustainable functionalisation of textiles. They summarise the main results of extensive and heterogeneous research confirming that low-pressure plasma improves the dyeability of various textile fibres in dyeing processes with synthetic and natural dyes. It also improves the efficiency of washing and desizing processes as well as the improved coating and deposition of antimicrobial compounds, flame-retardants, hydrophobic monomers and electrically conductive polymers. The improvement of self-cleaning and ultraviolet (UV) protection finishing processes is also confirmed as well as the benefits of plasma pre-treatment related to the reduction of pollution, energy and chemical consumption, without deterioration of the properties of textile fibres at lower costs compared to conventional wet processes (Haji and Kan, 2021).

A considerable amount of research is focussed on the application of chitosan in cotton printing processes with reactive and direct dyes, as it is a biopolymer that introduces functional amino groups into the cotton fibre, improving dyeing properties and printability with anionic dyes due to the ionic attraction between the dye's anion and cationized amino groups. The advantage of pre-treating cotton material with plasma is particularly valuable in printing processes with direct dyes, where reduced fastness is one of the main shortcomings. Both the plasma treatment and the subsequent chitosan coating improved the colour strength of the cotton fabrics printed with direct dyes, whilst the plasma treatment improved the fastness properties of the printed samples against rubbing (wet) and washing (Haji and Hashemi, 2021). Plasma treatment of cotton fabric can reduce the problems of dyeing cotton with natural dyes, such as limited attraction to the cellulosic fibres, the use of mordants, fixatives and other chemicals and lower colour yield and colour fastness, which have limited the potential industrial applications of natural dyes (Haji and Naebe, 2020; Enawgaw, 2022).

As opposed to conventional, energetically demanding and most often environmentally non-sustainable methods of textile pre-treatment in printing processes, plasma has proven to be effective for improving printability of textile being environmentally and economically sustainable as well (DeGeyter *et al.*, 2008; Zhang and Fang, 2009; Man *et al.*, 2015; Cunko and Ercegovic Razic, 2011; Ercegovic Razic and Cunko, 2009; Chi-wai, 2015). Already, Yan and Guo, as well as Knittel and Scholmeyer, researched and confirmed that plasma treatment would modify the outermost thin layer from 10 nanometres up to several micrometres of the fabric surface whilst the fabric mechanical, physicochemical and electro-physical properties would be kept unchanged, which is one of the key advantages of plasma pre-treatment (Yan and Guo, 1989; Knittel and Schollmeyer, 2000). Morent *et al.* (2008) confirmed that plasma treatments provide improvements in surface hydrophilicity, adhesion, dyeing ability, spinning properties and printability (Zhang and Fang, 2009; Morent *et al.*, 2008).

In pigment digital printing processes, pre-treatment of the textile material is necessary because it ensures proper cross-linking by applying appropriate chemical agents to the material, controls the penetration of the dye and improves the quality of the resulting image (Ding *et al.*, 2018).

It is very well known that pigment printing is the oldest and simplest printing technology that meets the standards of environmental sustainability in today's production, as there is no fixation phase with high water consumption and the colourfastness is optimal, whilst the economic viability is reflected in the applicability on all textile substrates regardless of the fibre composition. It is also a well-known fact that pigments do not have their own affinity for the fibre and do not bind to the fibre by chemical bonds. It is necessary to use binders that are usually based on styrene-butadiene, styrene-acrylate or vinyl acetate-acrylate copolymers. When fixing with hot air, the binder forms a three-dimensional polymer shape in cooperation with the cross-linkers, which tends to change its pH value under hot air conditions. This is because the type and quantity of chemically polar groups in the textile fabric influence the fixation and adhesive strength of the polymer binder film in pigment printing. It is precisely in this area that the applicability and positive effects of the ecological pre-treatment of textile fabrics with atmospheric plasma, which improves the printability of the fabrics with pigments, are reflected (Ahmed *et al.*, 2020; Glogar *et al.*, 2022).

In the literature, when studying the influence of plasma pre-treatment of cotton or wool in digital printing with natural dyes, the positive influence of plasma on the quality of the print was confirmed. This allows a lower consumption of binder, which ensures the quality of the print, but on the other hand, highly affects the natural quality and physical-mechanical properties of the textile material (Doaa *et al.*, 2022; Thakker *et al.*, 2022).

However, a certain research gap was identified in the study of the influence of pre-treatment of cellulosic materials with plasma in digital printing processes with synthetic pigments. A comprehensive study was conducted on the influence of pre-treatment of cotton and lyocell with atmospheric oxygen and argon plasma on the formation of a polymeric binder film and the consumption of binders in pigment printing, as well as on the quality and durability of the print and the characteristics of colour reproduction. This paper presents a small part of the extensive research carried out on the application of the process of pre-treatment of cellulosic knitted fabrics with cold, low-pressure plasma. The aim was to find acceptance of the textile surface with the best possible binding of the pigment print and better quality of the print (whilst at the same time avoiding the use of conventional water preparations).

Materials and methods

Material characterisation

The research was performed on weft knitwear samples of a raw material composition of 100% cotton and lyocell. The construction and mechanical characteristics of the cotton knitwear are shown in Table 1.

Non-thermal low-pressure plasma

A low-pressure plasma system type NanoLF-40 kHz, tt. Diener Electronic GmbH was used for cellulose-knitted fabric pre-treatment, with further characteristics: low-frequency generator operating frequency 40 kHz, maximum device power 300 W, operating pressure range from 0.1 to 10 mbar, gas flow adjustable with a maximum value of 400 cm^3/min.

Oxygen and argon were used as working gases, with process parameters set as follows: for oxygen gas power 500 and 900W with time 2 and 5 min; for argon gas power 500W and time 2 min; pressure 0.34 mbar, gas flow 50–200 cm^3/min. Before plasma treatment, the samples were pre-dried at a temperature of 50 °C for 24 h. Pre-treatment with O2 (oxygen) plasma was carried out for the purpose of chemical activation of the surface of cellulose knits, and pre-treatment with Ar (argon) plasma was carried out for the purpose of physical activation of the surface of cellulose knits. The conditions of the samples pre-treatment are shown in Table 2.

Analysis of the micromorphology of the knitting surface using FE-SEM microscopy

The examination of the surface micromorphology and changes after the treatments on the knitting samples was carried out with a scanning electron microscope FE-SEM Tescan

Knitwear parameters	Cotton	Lyocell
Stich density in a course, [stich/cm]	11.1 ± 0.2	10.8 ± 0.2
Stich density in a wale, [stich/cm]	11.4 ± 0.2	11.8 ± 0.2
The height of the stich course, [mm]	0.88 ± 0.01	0.93 ± 0.01
Coefficient of stich density, *C*	0.97	0.85 ± 0.01
Knitwear width, [cm]	19.5 × 2 ± 0.5	0.92
X`Knitwear shrinkage after removing from knitting machine, [%]	39	20 × 2 ± 0.5
Surface mass, [g/m^2]	157 ± 3	37
The mass of running meter, [g/m]	62 ± 2	152 ± 3
Thread consumption in stich [mm]	3.15 ± 0.01	61 ± 2
Thickness of the knitwear [mm]	0.64 ± 0.01	3.13 ± 0.01
Volume mass of knitwear [g/m^3]	0.246	0.63 ± 0.01
Porosity of knitwear [%]	83	0.241
Breaking force of knitwear in wale direction [N]	472 ± 33	84
Breaking elongation of knitwear in wale direction [%]	51 ± 3	492 ± 4
Elasticity of knitwear in wale direction [%]	12 ± 2	49 ± 4
Breaking force of knitwear course direction [N]	88 ± 6	12 ± 2
Breaking elongation of knitwear in course direction [%]	364 ± 12	104 ± 6
Elasticity of knitwear in course direction [%]	200 ± 10	328 ± 14

Source(s): Table created by authors

Table 1. Constructional and mechanical knitwear characteristics

Sample	Pre-treatment conditions	Sample designation
Cotton	Untreated	CO-0
	Ar, 500 W, 2 min, flow 50%, 0.25–0.46 mbar	CO-1
	O_2, 500 W, 2 min, flow 50%, 0.25–0.46 mbar	CO-2
	O_2, 900 W, 5 min, flow 50%, 0.25–0.46 mbar	CO-3
Lyocell	Untreated	LY-0
	Ar, 500 W, 2 min, flow 50%, 0.25–0.46 mbar	LY-1
	O_2, 500 W, 2 min, flow 50%, 0.25–0.46 mbar	LY-2

Source(s): Table created by authors

Table 2. The condition of plasma pre-treatment of cotton and lyocell samples

MIRA\LMU. Changes caused by the influence of plasma were observed by microscopic imaging, and the spreading of the printing ink layer after the digital ink-jet printing process on untreated and plasma-treated samples was observed. The magnifications used for microscopic imaging were from 1000x to 4000x.

Hydrophilicity of samples - drop test

The hydrophilicity of untreated and plasma-treated knitting samples was tested using the drop-test method, according to the AATCC 79–2000 Absorbency of Textiles standard.

Digital InkJet printing

Pre-treated samples, along with the untreated ones were further digitally printed with pigment-based printing inks, using a micro piezo head DTP machine, type Azon Tex Pro, for direct printing of materials. The multi-coloured scheme with which the samples were printed is shown on Figure 1. After printing, the samples were hot-air fixed on temperature of 150 °C, for 3 min.

Colouristic comparative analysis

In order to evaluate the influence of the pre-treatment of the textile surface with plasma on the quality and colour reproduction, a comparative analysis of the colour parameters of the printed elements was carried out using a spectrophotometric measurement and an objective evaluation of the spectral and colour parameters. The colour measurement was carried out with a DataColor 850 reflectance spectrophotometer, whereby the measurement geometry (d/8°), the diameter of the measurement aperture (measurement aperture L - 2.5 cm) and the standard light (D65) were kept constant. The results are analysed in terms of colour coordinates (a*/b*), main colour parameters (L*, C, h°) and colour strength (K/S), calculated according to the CIELAB system. The colour differences were also calculated using Color Measurement Committee (CMC) standard (l:c) formula, in order to compare the colour reproduction values between untreated and plasma-treated surfaces. This formula for expressing colour differences is accepted for textiles by the International Organisation for Standardisation (ISO) standard Textiles – Tests for colour fastness – Part J03: Calculation of colour differences (ISO 105-J03:2009; EN ISO 105-J03:2009).

Wash fastness test

A wash fastness test was performed in order to evaluate the colourfastness of printed colours on the knitwear in dependence on plasma pre-treatment. The test was performed according to the standard ISO 105-C06:2010 Textiles-Tests for colourfastness-Part C06: Colourfastness to domestic and commercial laundering at a temperature of 40 °C for a duration of 30 min, with three-repeated washing, using standard detergent. The change in colour was evaluated by colour difference calculation, using CMC (l:c) formula, comparing the colour of untreated and plasma-treated samples, before and after the washing.

Results and discussion

One of the fundamental parameters of print quality in pigment digital printing is the relationship between the surface structure and the pigment layer. This is particularly evident in digital printing. The requirements for the rheological and pigment dispersion properties in digital printing require a printing ink with very low viscosity, a high water column (printing ink is water-based) and a pigment size of up to 200 nm. Due to the very small size of the pigment particles, digital printing enables a lower consumption of binders, which ensures the formation of a thinner and more flexible polymer layer that optimally follows the structure of the textile surface. In addition, due to the effect of the capillary forces of the textile, the water-based printing pigment ink is drawn deeper into the yarn structure and the tactile and appearance properties of the printed surface are more acceptable. This is where the importance of pre-treatment lies, aiming to achieve more uniform polymer layer and optimum ink coverage with minimal impact on the haptic and physical-mechanical properties of the fabric.

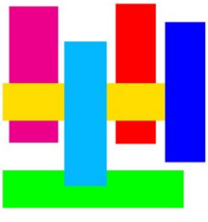


Figure 1.
Multi-coloured scheme for printing

Source(s): Image created by authors

In relation to these properties of the interaction between the printing ink and the textile substrate, it was important to assess the level of water absorption capacity of the samples. It should be emphasised that the absorptivity test was performed only on cotton because it is hydrophobic in its raw form, and it is necessary to achieve a certain level of hydrophilicity through pre-treatment, in order for the sample to be printable. A drop test was not performed on knitwear samples made of artificial cellulose fibres (lyocell) because the surface of these knitwear samples is hydrophilic itself, regardless the plasma treatment.

The results of drop-test performed on cotton-untreated and plasma-treated samples are shown in Table 3.

Results show that the hydrophilicity of the cotton samples was achieved in a time of 5 min, at a power of 900 W and a flow rate of 200 cm^3/min.

Plasma treatment is a physicochemical method used for surface modification because it affects the surface both physically and chemically, depending on the working gas applied, without altering the material bulk properties. An increase in the surface energy of the plasma-exposed surface improves the surface bonding properties. When cellulose textile material is oxygen plasma pre-treated, the number of carboxyl groups increases in the molecular chain of cellulose, resulting in improved hydrophilicity of the fabric, as well as the characteristics of wettability, printability and adhesion.

On the other hand, the argon plasma treatment physically changes the textile surface. The discharge of high-energy electrons can act on the fabric surface and cause an etching effect (ablation), which contributes directly to an increase in surface roughness.

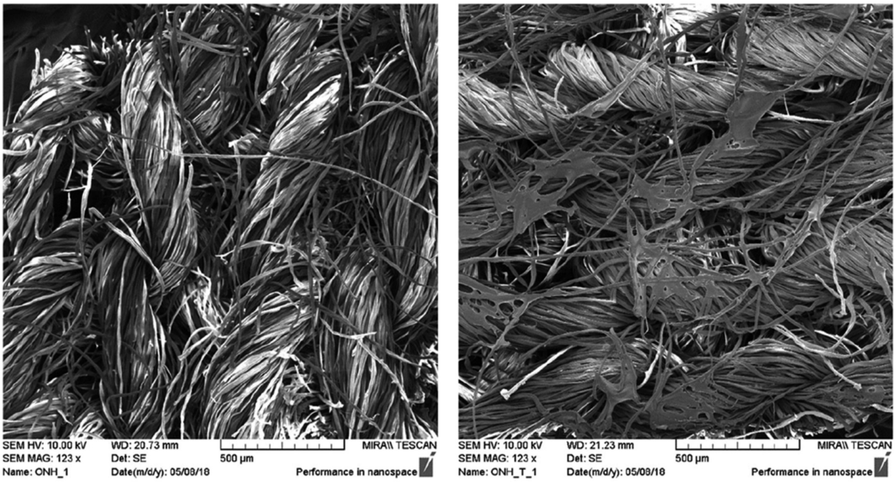
Both influences are important in achieving the improvement effect in digital printing processes, in the context of improved adhesion of the polymer binder layer and a more even distribution of pigment within the layer. So, in the next step, scanning microscope imaging was performed aiming at micromorphological analysis of the surface of untreated and plasma-treated samples (before and after printing) indicates the influence of plasma pre-treatment on the micromorphological structure of the fibre itself and thus on the adhesion and distribution of printing ink on the surface of the fibre. The scanning electron microscope (SEM) images of cotton fibres before and after plasma treatment and ink jet printing are shown on Figure 2.

The micrographs of the cotton fibres (Figure 2) show the characteristic micromorphological structure with visible twists and fibrils aligned along the fibre axis. Untreated samples printed with digital inkjet pigment show the presence of pigments distributed over the surface of the fibres. Treatment with oxygen/argon plasma has a positive effect on improving the coverage of the fibres with pigment and contributes to the overall coverage of the sample surface with a digital print. Such a reaction is particularly visible in the sample pre-treated with argon plasma. The pigment print coats almost every fibre, preserving the visible micromorphological structure of the cotton fibre surface and a sufficient amount of pigment on the fibre surface. The reason for this lies in the physical changes (etching or ablation) that take place at the level of morphology because of the plasma pre-treatment, which will certainly have an effect on the improved hydrophilic and wetting properties.

Sample	Pre-treatment	Time, t [s]
Cotton knitwear	Raw sample	/
	Ar, 500 W, 2 min, flow 50%, 0.25–0.46 mbar	>3600
	O_2, 500 W, 2 min, flow 50%, 0.25–0.46 mbar	>3600
	O_2, 500 W, 5 min, flow 50%, 0.25–0.46 mbar	600
	O_2, 900 W, 2 min, flow 50%, 0.25–0.46 mbar	>3600
	O_2, 900 W, 5 min, flow 50%, 0.25–0.46 mbar	22

Source(s): Table created by authors

Table 3.
Cotton samples absorbency test

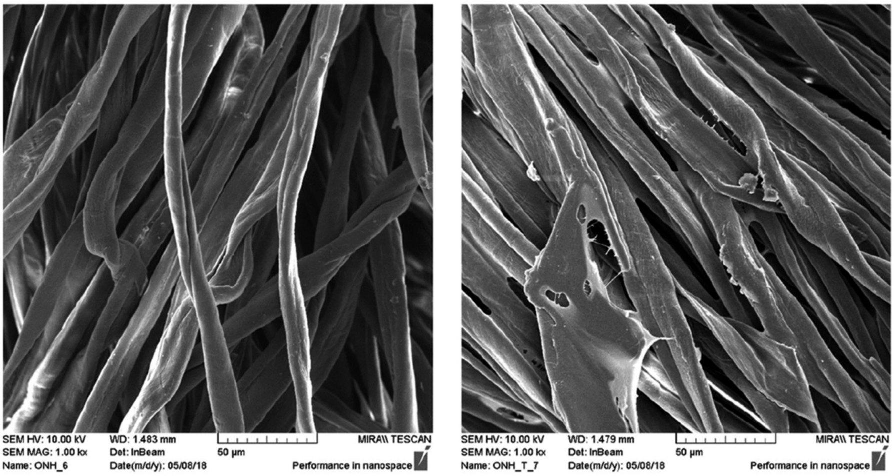


Untreated (magnification120x)

(a)

Untreated, printed (magnification 120x)

(a1)



Untreated (magnification 1000x)

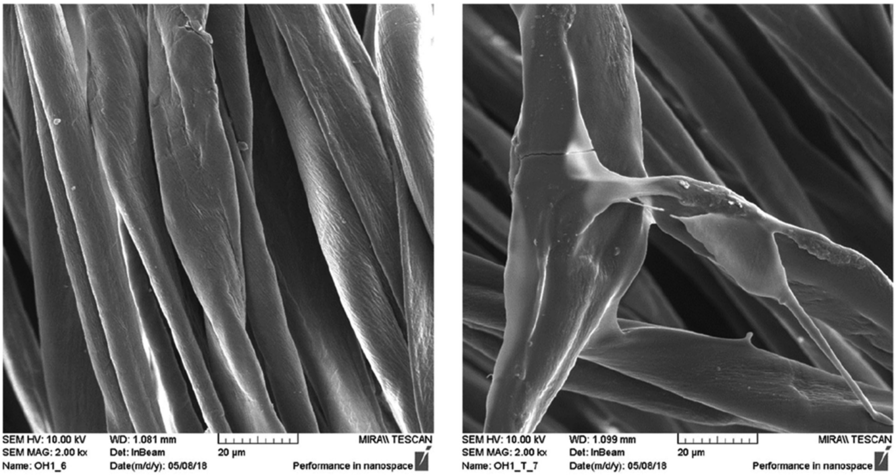
(b)

Untreated, printed (magnification 1000x)

(b1)

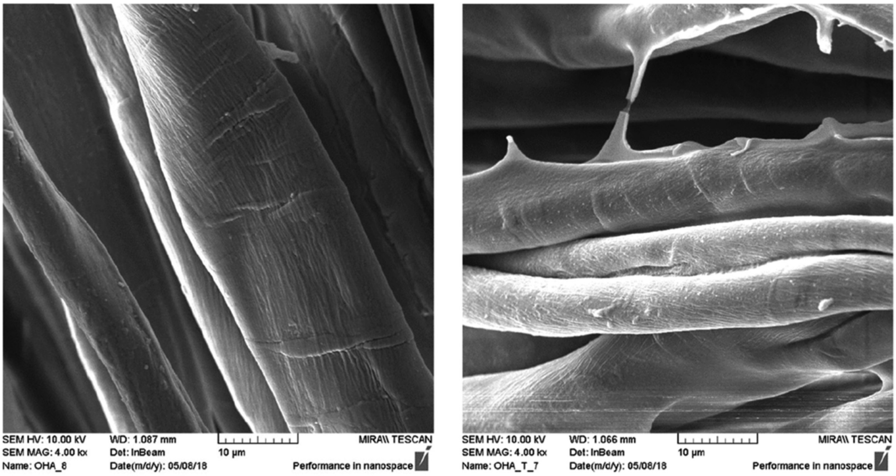
Figure 2.
Cotton samples - a, b: Untreated sample - magnification 120 and 1000x; a1, b1) raw sample + ink jet digital printing, magnification 120 and 1000x; (c) oxygen plasma, magnification 2000x and c1) oxygen plasma + ink jet printing, magnification 2000x; (d) argon plasma, magnification 4000x, d1) argon plasma + ink jet printing, magnification 4000x

(*continued*)



O_2 (magnification 2000x)
(c)

O_2 printed (magnification 2000x)
(c1)



Ar (magnification 4000x)
(d)

Ar printed (magnification 4000x)
(d1)

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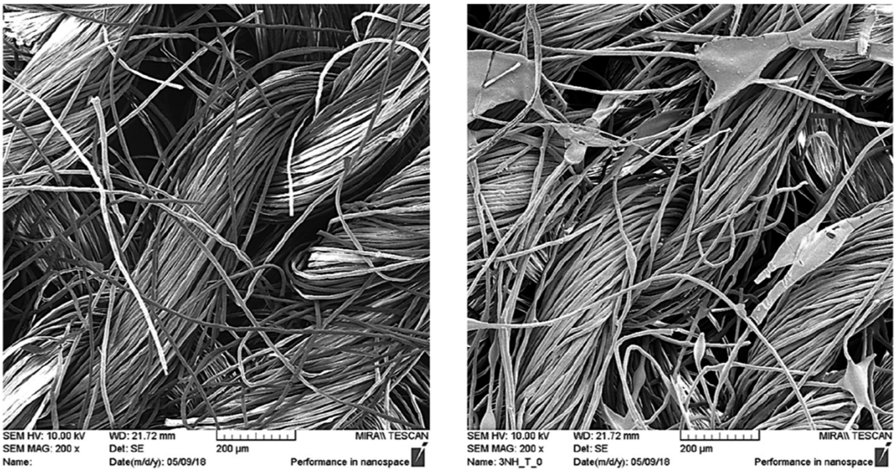
Figure 2.

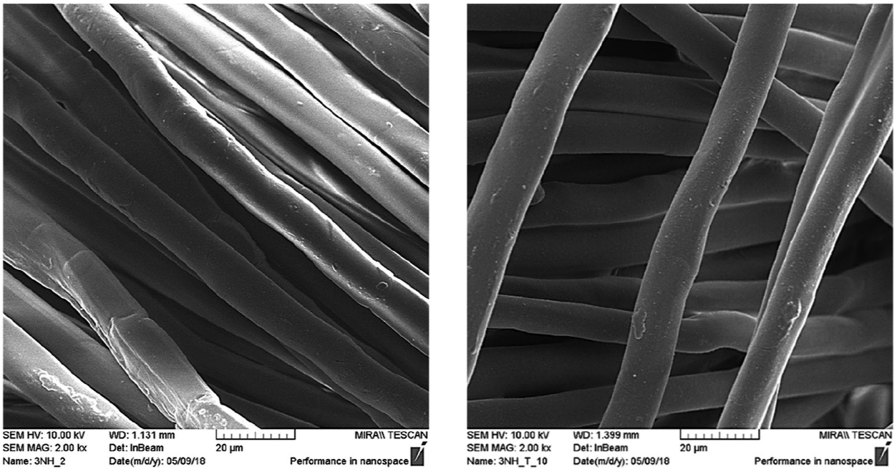
Oxygen plasma also contributes to better coverage of the pigment print around the individual fibres, but a certain amount of binder is visible compared to plasma pre-treatment with argon, where the amount of acrylic binder is less visible.

A very similar trend of distribution and amount of pigment and binder on the surface of the lyocell fibres due to pre-treatment with plasmas is followed in the case of the knitting sample from lyocell fibres (Figure 3). In the case of lyocell samples, the plasma etches the smooth surface of the fibres, which then becomes more accessible for printing with pigment ink and its uniform distribution over the surface. This is evident after argon plasma pre-treatment, which has a physical effect on the ablation of the surface and stronger physical "damage" by particles in the plasma; thus, the surface becomes rougher and more accessible for a digital print. In general, it can be seen that the argon plasma pre-treatment has a more favourable effect on the distribution and coverage of the digital print in the tested samples of



Untreated (magnification120x)
(a)

Untreated, printed (magnification 120x)
(a1)

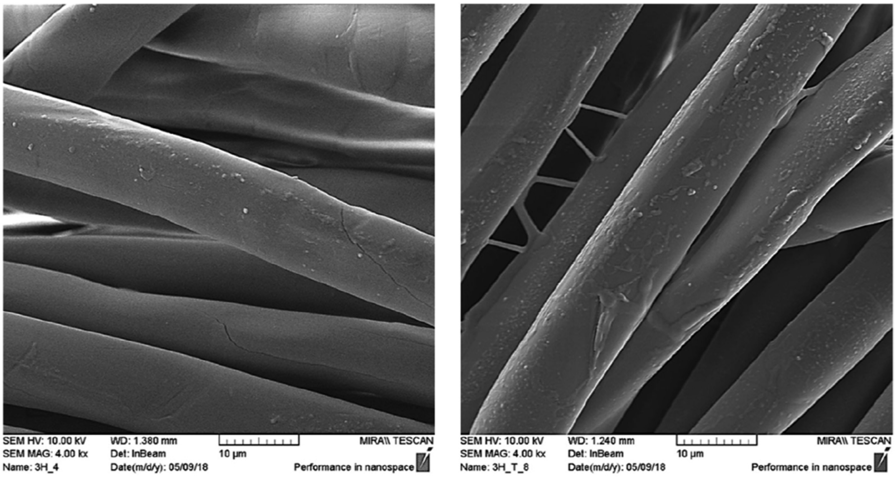


Untreated (magnification 1000x)
(b)

Untreated, printed (magnification 1000x)
(b1)

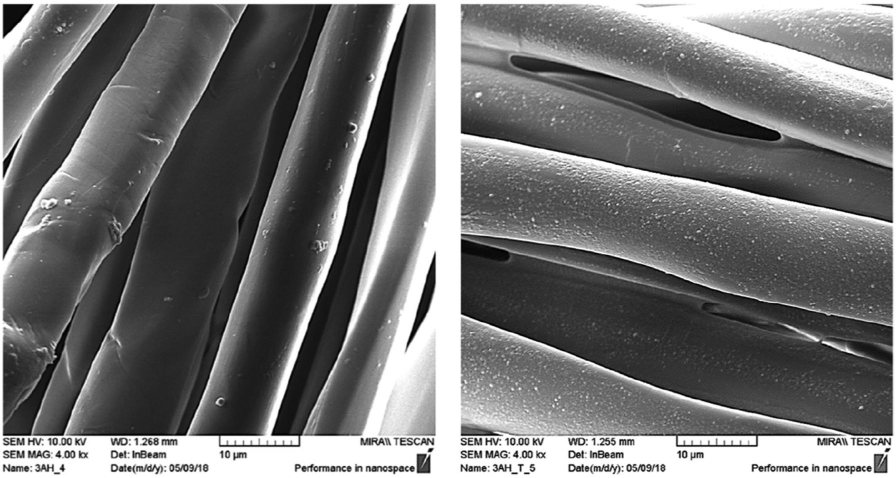
Figure 3.
Lyocell samples - (a, b): Untreated sample - magnification 120 and 1000x; a1, b1) raw sample + ink jet digital printing, magnification 120× and 1000×; (c) oxygen plasma, magnification 2000x and c1) oxygen plasma + ink jet printing, magnification 2000x; (d) argon plasma, magnification 4000x, d1) argon plasma + ink jet printing, magnification 4000x

(*continued*)



O_2 (magnification 2000x)
(c)

O_2 printed (magnification 2000x)
(c1)



Ar (magnification 4000x)
(d)

Ar printed (magnification 4000x)
(d1)

Source(s): Figure courtesy of Assist. prof. Zorana Kovacevic, Ph.D., University of Zagreb Faculty of Textile Technology (2024)

Figure 3.

cellulose fibres, which is reflected in the nature of the gas and the mechanism of its action on changes in the surface of the fibres.

In the next phase, a comparative colour analysis was carried out based on spectrophotometric measurement and objective colour evaluation. Figures 4 and 5 show a graphical comparison of the value of the colour strength (K/S).

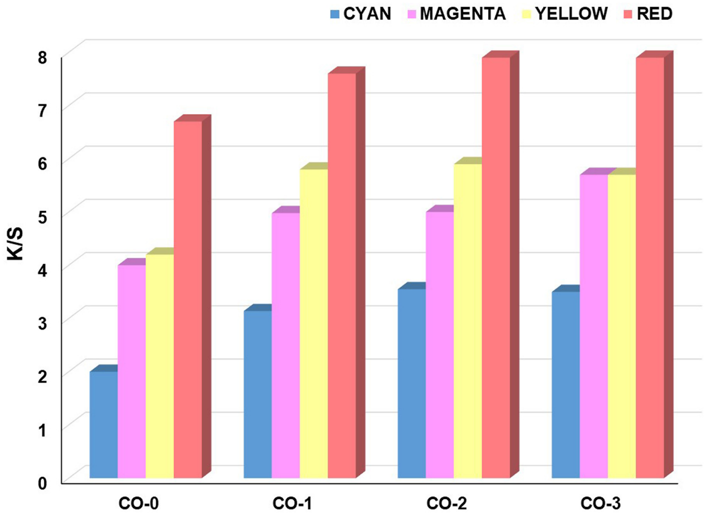


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Figure 4.
K/S values for cotton samples

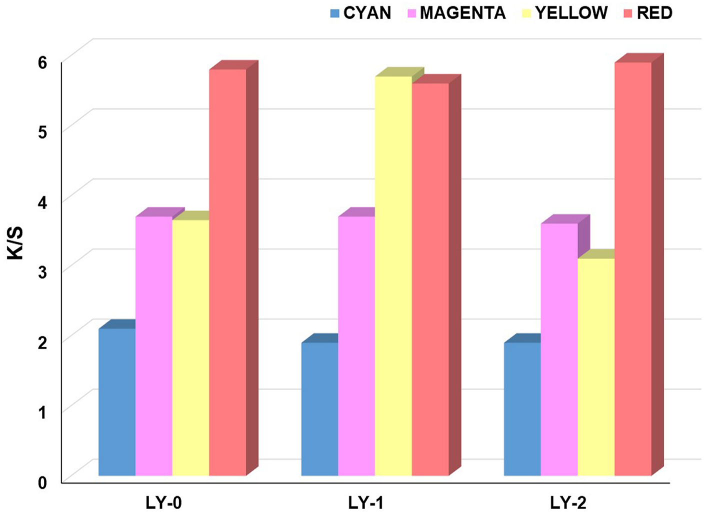

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Figure 5.
K/S values for lyocell samples

For the cotton samples, an increase in the K/S value is observed on the plasma-treated samples, which indicates a higher pigment yield and a better coverage of the surface with colour. For a clearer insight into the relationships between K/S values, it is necessary to provide a few concrete numerical results, although the relationship is shown graphically. For Cyan colour, an increase in the K/S value was obtained from two for the untreated sample to 3.5 for the sample treated with 500 W oxygen plasma. The decreases in the other samples were on average for approximately 1–1.5 units of the K/S value.

For the lyocell sample, a more noticeable difference in the K/S value was obtained for the yellow colour and for the sample treated with Argon, where the K/S value increased from 3.6 to 5.7 for the sample treated in duration of 2 min and with power of 500 W.

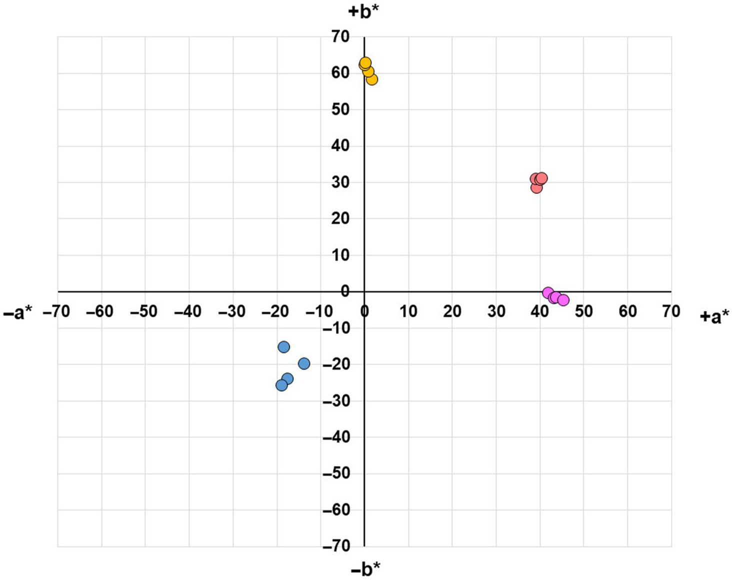
For further analysis, the placement of the samples in a*/b* colour space is shown in Figures 6 and 7.

According to the position of the samples in the a*/b* colour space, a more pronounced influence of pre-treatment can be observed on cotton samples, more emphasis for yellow and most for cyan. This further indicates changes in the colour hue and Chroma parameters. For the lyocell samples, no pronounced differences are noticeable.

A detailed analysis of the parameters lightness (L*), Chroma (C*) and hue (h°) was carried out. The obtained results are shown in Table 4 for cotton samples and in Table 5 for lyocell samples. An increase in the chroma value is observed for samples pre-treated with plasma, which is in accordance with the obtained higher K/S values for the same samples and indicates and confirms a higher yield of pigment in the polymer layer that binds the pigment to the textile substrate.

For example, for the colour cyan, an increase in chroma is observed from the value of 24.2 for untreated sample to the value of 29.7 for the sample treated with argon plasma and 31.3 and 31.8 for the samples treated with oxygen plasma. For the colours magenta and red, the increases in the chroma value are slightly smaller, whilst for the colour yellow, an increase in chroma is obtained from a value of 58.4 for the untreated sample to 62.9 for the sample treated with oxygen plasma for 5 min, with a power of 900 W.

In the colour analysis, in addition to the individual approach to colour parameters, the specific relationship between lightness and chroma, which defines the colour intensity, must also be observed. As lightness and chroma are interdependent up to a certain level, with an increase in the value of chroma (C*), a decrease in the value of lightness (L*) is observed.



Source(s): Figures created by authors

Figure 6.
a*/b* values for cotton samples

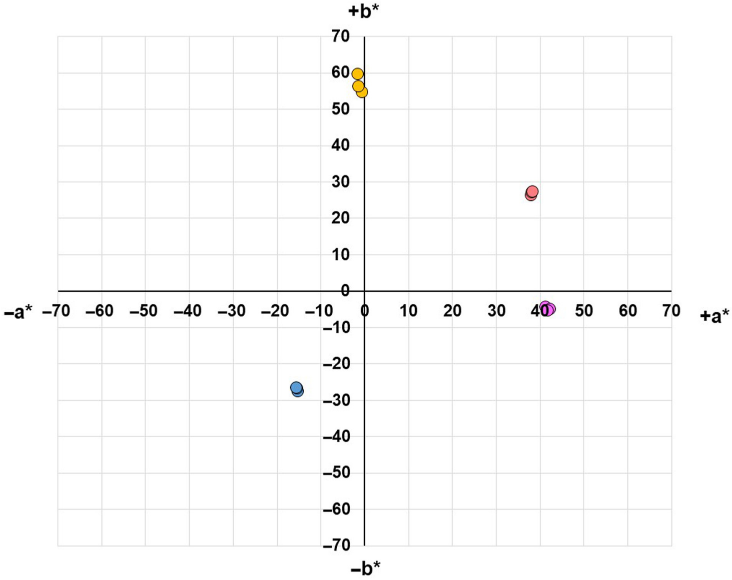


Figure 7. a*/b* values for lyocell samples

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Table 4. Colour parameters of lightness L*, chroma C* and hue h° for cotton samples

Sample		L*	C*	h°
CO-0	Cyan	58.3	24.2	234.9
	Magenta	50.3	41.8	359.5
	Red	48.8	48.5	36.1
	Yellow	75.3	58.4	88.3
CO-1	Cyan	54.9	29.7	233.6
	Magenta	48.2	43.3	357.6
	Red	49.1	49.8	38.3
	Yellow	72.5	60.5	89.1
CO-2	Cyan	54.0	31.3	233.7
	Magenta	48.3	43.6	358.0
	Red	48.3	50.5	37.5
	Yellow	73.1	62.3	89.9
CO-3	Cyan	54.6	31.8	233.6
	Magenta	47.3	45.3	357.0
	Red	48.6	50.9	37.6
	Yellow	72.2	62.9	89.9

Source(s): Table created by authors

For lyocell samples, although less emphasised, the difference also exists in relation to the untreated sample.

Changing the specific ratio of chroma (C*) and Lightness (L*) in the context of colour intensity, as already mentioned above will have a different meaning depending on the nature of the colour itself. For example, in the case of yellow, an increase in lightness and chroma indicates an increase in colour intensity. As opposed to that, in colours that are naturally

Sample		L*	C*	h*
LY-0	Cyan	61.3	31.5	241.1
	Magenta	52.1	41.5	353.3
	Red	50.2	46.2	35.0
	Yellow	78.5	59.8	91.5
LY-1	Cyan	62.2	30.9	239.8
	Magenta	51.9	42.5	353.4
	Red	50.4	46.8	35.4
LY-2	Cyan	62.3	30.7	239.4
	Magenta	52.4	41.9	352.7
	Red	50.4	47.1	35.7
	Yellow	78.6	56.3	91.5

Source(s): Table created by authors

Table 5.
Colour parameters of lightness L*, chroma C* and hue h° for lyocell samples

darker, such as blue hues, the increase in intensity will be defined by the opposite relationship between lightness and chroma.

Furthermore, total colour differences (dE) were calculated using the formula CMC (l:c) and taking the untreated sample as a reference. The obtained values are the result of comparing the plasma-treated samples with the reference, untreated sample. The obtained values of differences are shown in Table 6.

The values obtained for the total colour difference (dE) confirm the influence of the plasma treatment and indicate more pronounced colour changes in pre-treated samples. For the cotton knit samples, all total colour difference values (dE) determined were above the agreed tolerance range.

Looking at the results obtained for cotton knitted fabrics in terms of specific colour, the highest values of total colour difference (dE) were obtained for the colour cyan. In particular, for a cotton fabric sample treated with oxygen plasma for a duration of 5 min and with a power of 900 W, the values of total colour difference are the highest compared to the untreated sample and are 4.5 for cyan, 2.9 for magenta, 2.3 for yellow and 1.9 for red.

The total colour difference (dE) results obtained for the lyocell samples are lower. Actually, the total colour difference (dE) values were achieved within the agreed tolerance limits for all samples. An exception is the lyocell sample, which was treated with oxygen

Sample		dE (CMC)	Sample	dE (CMC)
CO-1	Cyan	*3.4*	LY-1	0.7
	Magenta	1.4		0.4
	Red	1.6		0.4
	Yellow	1.4		0.1
CO-2	Cyan	*4.4*	LY-2	0.8
	Magenta	1.4		0.4
	Red	1.3		0.6
	Yellow	1.9		1.3
CO-3	Cyan	*4.5*		
	Magenta	*2.3*		
	Red	1.5		
	Yellow	*2.3*		

Source(s): Table created by authors

Table 6.
Total colour total difference for cotton and lyocell samples

plasma for 2 min at a power of 500 W, where the value of the total colour difference (dE) was slightly outside the agreed tolerance ranges (dE = 1.3).

Finally, the colourfastness of the printed elements was tested during washing. It should be noted that pigment printing is not only about the possible colour release during washing, but that the entire polymer layer that binds the pigment to the textile substrate is actually damaged or even removed. Therefore, colour changes in pigment printing are usually the result of mechanical damage to the polymer layer during the washing process. The results of the wash fastness of the samples are expressed by calculating the total difference (dE_{CMC}) between the samples before and after washing. The values obtained are listed in Table 7.

The results confirm the very positive influence of plasma pre-treatment on colourfastness in cotton samples.

In the cotton samples, it is immediately noticeable that the values of the total colour difference (dE), which are determined by comparing the sample before and after washing, are highest for the untreated sample. For the treated samples, the values of the total colour difference are much lower. The best results were obtained for the colour red for a cotton sample treated with oxygen plasma for 2 min at a power of 500 W (dE = 0.8), and for the colours magenta and yellow, a cotton sample was treated with oxygen plasma for 5 min at a power of 900 W (magenta dE = 0.9; yellow dE = 0.8).

In the case of lyocell samples, generally higher colour differences were obtained (dE from 2.5 to 11.1). However, although the values are all outside the tolerance limits, the differences obtained in the pre-treated samples are smaller compared to the untreated ones. In the pre-treated samples, the decrease in the overall colour difference indicates an improvement in the fastness and durability of the pigment polymer film. It should be emphasised that lower wash fastness are otherwise characteristic and a problem in pigment printing, especially in digital pigment printing. Therefore, although these values are outside the tolerance limits, they speak in favour of the contribution of plasma pre-treatment.

Conclusion

The obtained results show the positive influence of oxygen plasma pre-treatment and argon gases on colour reproduction as well as on colour wash fastness, due to chemical and physical changes (etching and ablation of the surface) at the level of micromorphology.

Table 7.
Total colour total differences for cotton and lyocell samples after the wash fastness test

Sample		dE (CMC)	Sample	dE (CMC)
CO-0	Cyan	*3.3*	LY-0	*5.9*
	Magenta	*2.9*		*7.4*
	Red	*3.0*		*9.8*
	Yellow	*4.5*		*11.1*
CO-1	Cyan	1.6	LY-1	*4.6*
	Magenta	*2.3*		*4.3*
	Red	1.5		*4.4*
	Yellow	1.9		*4.2*
CO-2	Cyan	*3.3*	LY-2	*6.8*
	Magenta	*3.4*		*2.5*
	Red	0.8		*5.3*
	Yellow	1.4		*3.5*
CO-3	Cyan	*2.1*		
	Magenta	0.9		
	Red	1.4		
	Yellow	0.8		

Source(s): Table created by authors

The wettability and hydrophilicity of the surface are increased after pre-treatment, especially in cotton-fibre knitting samples. Pre-treatment with oxygen and argon plasma has a positive effect on digital printing, where plasma enables better adhesion of the pigment paste applied by digital ink jet printing.

Plasma certainly contributes to more uniform distribution of the pigment dispersion over the fibre itself whilst maintaining the visible specific micromorphology of the fibres, which contributes to better persistence and coverage of the pigment on the surface.

The application of plasma achieves improved adhesion of the polymer binder layer that carries pigments on the surface of the textile substrate and enables a more even distribution of the pigment and a thinner and more flexible polymer layer, as well as a more even coverage of the textile surface with paint, whilst maintaining the microstructural properties.

These conclusions are based on analyses of colour values and colour differences of untreated and treated samples as well as testing the fastness of printing and washing.

Note

1. https://www.gsw.co.za/growth-of-digital-textile-printing/

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