Cotton screen-printing with flavonoid natural dyes – Part II. The influence of cationization and plasma pre-treatment

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The modern textile finishing industry faces the challenge of breaking new ground and making radical changes. Since the textile industry is one of the biggest polluters, it is necessary to develop new ecologically and economically sensible methods of finishing, dyeing, textile care, etc. The studies presented here were carried out to achieve colour effects on textiles by using natural dyes of plant origin extracted from onion skins in the screen-printing process. Flavonoid dyes extracted from onion skins were used, which belong to the group of mordant dyes due to their dyeing properties and require the addition of metal salts. For this reason, the possibility of pre-treating cotton material by cationisation and argon plasma as well as a combination of these methods was investigated. It has been shown that these methods of cotton treatment prior to screen printing can replace the use of aluminum salts in the printing paste when it comes to achieving colour parameters and satisfactory fastness properties.

Keywords: *natural dyes; flavonoids; argon plasma pre-treatment; cationization; screen-printing; metal salts.*

Izvorni znanstveni rad

Suvremena industrija dorade tekstila suočava se s izazovom uvođenja radikalnih promjena. Budući da je tekstilna industrija jedan od najvećih zagađivača, potrebno je razviti nove ekološki i ekonomski održive metode dorade, bojadisanja, njege tekstila itd. Navedena istraživanja provedena su kako bi se postigli koloristički efekti na tekstilu koristeći prirodna bojila biljnog podrijetla ekstrahirana iz ljuski luka u procesu sito-tiska. Korištena bojila pripadaju skupini metalokompleksnih bojila koja zbog svojih svojstava zahtijevaju dodatak metalnih soli u procesu bojadisanja. Radi toga, istraživana je mogućnost predobrade pamučnog materijala kationiziranjem i argonovom plazmom, kao i kombinacija ovih metoda. Pokazalo se da ove metode obrade pamuka prije sito-tiska mogu zamijeniti upotrebu aluminijevih soli u tiskarskoj pasti kada je riječ o postizanju kolorističkih parametara i zadovoljavajuće postojanosti.

Ključne riječi: *prirodna bojila; flavonoidi; predobrada argonovom plazmom; kationiziranje; sito-tisak; metalne soli.*

1. Introduction

Modern industry is confronted with increasingly complex requirements that encompass ecological, economic and sociological aspects. As these aspects are particularly prominent in the textile finishing industry, the realisation of radical changes is expected. In the field of textile dyeing, the Society of Dyers and Colourists highlights the bold advances in the industrial application of natural dyes [1]. The modern view of "ecological" dyeing with natural plant dyes is based on the use of waste, easily renewable or invasive plant sources for the extraction of dyes, the use of bio-mordants, i.e. the optimization of all parameters of dye extraction, pre-treatment of the textile material and textile dyeing with the aim of obtaining products with multifunctional properties while protecting textile quality, human health and the environment [2-10]. The properties of textiles treated with natural plant dyes are based on the fact that their chemical structure mainly belongs to flavonoids [11-14]. The importance of the physico-chemical structure of the cotton material in dyeing processes with flavonoid dyes justifies the significant research in the field of fibre modification and pre-treatment in general [14-16]. The influence of the degree of pre-treatment on the supramolecular structure (arrangement of crystalline and amorphous regions, microfibrils, nanofibrils) of the cotton fibre plays an important role in the dyeing process [17, 18]. Considering that the focus of modern pre-treatments is on achieving favourable effects by modifying the surface of textiles, which ultimately contribute to the overall quality of the textile material and are more energy efficient compared to conventional finishing methods. Given the environmental and economic benefits, the interest in cationisation and plasma treatment is understandable.

The first conventional stage of cotton pre-treatment is the scouring and oxidative bleaching of natural cotton, resulting in a fibre with a cellulose I crystal lattice. Modification of the cellulose crystal lattice occurs in the mercerisation process and results in cellulose II, which increases the number of available groups in the amorphous region and increases dye absorption from 15 to 40 % [15, 17, 20, 21]. Cationisation, a modification with amines and quaternary ammonium compounds, improves the adsorption of dyes and anionic auxiliaries and leads to an even higher adsorption rate. Since cationisation reduces or even eliminates the electrolyte in the dyeing process, many authors speak of salt-free or low-salt dyeing. The disadvantage of cationisation is that uneven dyeing is achieved due to the high dye adsorption in the first phase of the dyeing process. This problem was innovatively solved by the scientists Grancarić, Tarbuk and Dekanić by performing cationisation during the mercerisation of yarn without tension [21, 22]. When cationisation is carried out with an epihalohydrin during the mercerisation process, new cellulose is formed in which the cationic compound is evenly distributed and trapped between the cellulose chains, resulting in uniform dyeing after the dyeing process [20-23]. In addition, it should be noted that cotton fabric cationised with the cationic reactive polyammonium compound Rewin OS during mercerisation has been shown to have a positive surface charge and zeta potential, suggesting similar binding to cellulose as epihalohydrins [24].

Low-temperature plasma treatment, both low-pressure and atmospheric plasma, is also suitable technique for the textile surface pre-treatment. Low-pressure plasma is generated in diluted gas at a pressure well below atmospheric pressure, while atmospheric plasma is generated at normal atmospheric pressure. This type of plasma treatment is particularly suitable for treating thermally sensitive materials [19] which can be combined with other textile wet processes, such as dyeing or cationisation, or other finishing processes [25]. Plasma affects the textile surface chemically and physically, with the reactions between the plasma and the surface depending on the type of gas used and its chemical properties. Textile materials exposed to such treatments undergo chemical and physical transformations related to chemical changes in the surface layer, changes in the structure of the surface layer and changes in the physical properties of the surface layer, depending primarily on the type of gases used. The plasma generates a high density of free radicals in the dissociation of molecules during the collision of electrons and photochemical processes. This leads to the destruction of chemical bonds in the polymer surface of the fibre structure and thus to the formation of new chemical species. The effect of the plasma on the fibre surface leads to the formation of new functional groups such as hydroxyl, carbonyl and carboxyl, which influence the hydrophilicity of substances. Plasma is therefore primarily used for the surface treatment of materials, as its effect only changes the surface properties and leaves the bulk properties of the material unchanged [19, 26, 27].

Both methods, cationisation and plasma treatment, are successfully used as pre-treatment techniques for the application of natural dyes on cotton material [24, 28-31]. The selection and optimisation of pre-treatments has a considerable influence on the reproducetion of the dye [15, 16, 28, 31], metal salts are not used [16, 30] and the colour fastness is improved [16, 31-33]. However, a review of the recent literature reveals a gap in the research on the combination of these two methods, cationisation and plasma. Patino et al. achieved an increase in the hydrophilicity of cotton and an exhaustion of the reactive dye of over 90 % with the corona treatment of cotton and additional cationisation [25]. Correia et al. tested the effective-ness of combining these pre-treatments by dyeing with reactive dyes bound to cationised cotton by ionic bonds, dyeing without the addition of salt and additionally with an acid dye. Although they did not achieve satisfactory colour fastness, they were able to successfully analyse and demonstrate the effect of the plasma on the surface morphology of the cotton using Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) [29].

The research presented includes two modern methods for modifying cotton fabrics: cationisation during mercerisation [20-23], which affect the change in the charge of the cotton, and optimised argon plasma pre-treatment [27], which activates the surface of the textile material (Fig.1). It covers part of the gap in the area of combining these methods for cotton screen printing and opens up further research.

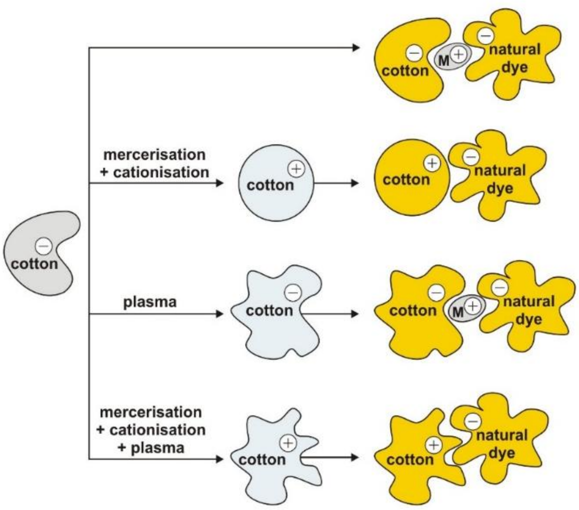

Fig.1 Schematic representation of the influence of pre-treatment with cationisation or/and plasma on the morphological and chemical properties of cotton

2. Material and methods

The experiment was carried out in steps A-E, which are shown in the diagram in Fig.2. This research is a sequel of the research by Sutlović et al. of cotton screen printing with flavonoid natural dyes [14], in which all work phases were optimised and explained, with the exception of the pre-treatment of the cotton (B). Screen-printing with natural flavonoid dye was carried out on plain weave chemically bleached cotton fabric (Čateks d.o.o., Čakovec) without pre-treatment, with argon plasma pre-treatment, cationisation during mercerisation, and a combination of cationisation and plasma (Fig.2).

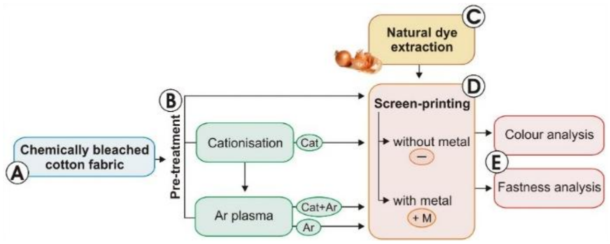

Fig.2 Schematic representation of the experiment

2.1. Cotton pre-treatment

2.1.1. Argon plasma pre-treatment

Argon gas (purity 99.998 %, Messer) was used for plasma pre-treatment at a gas flow of 200 cm^3/min and a frequency of 40 kHz in a low-pressure plasma system (NANO LF, Diener Electronic GmbH). The cotton samples were treated for 5 minutes at 300 W with an initial pressure of 0.22 mbar and a working pressure of 0.32 mbar. To remove moisture and thus accelerate vacuum generation, the samples were dried at 60 °C for 24 hours before plasma pre-treatment.

2.1.2. Cationisation

Cotton fabric was cationised during the mercerisation process with the cationic reactive polyammonium compound Rewin OS (CHT-Bezema, Montlingen, Switzerland) on a jigger in a two-stage process at room temperature. Firstly, mercerisation was carried out in a bath containing 24 % NaOH and 8 g/l Subitol MLF (CHT-Bezema, Switzerland) for 5 passages. Secondly, the alkaline cotton fabric was cationised in a bath containing 50 g/l Rewin OS dissolution in water (5 passages) before fixation in hot water, then sealed and left for 1 hour at room temperature. The cotton fabric was then fixed in hot water, neutralised in 5 % acetic acid and rinsed to neutral. The fabric was air dried.

2.2. Cotton screen-printing

For screen printing, a natural flavonoid dye obtained from onion skins was added to the printing paste. Printing was carried out using the thickener Prisulon DCA 90 (CHT, Montlingen, Switzerland) with a dry matter content of 9 % at three different pH values: acid (pH 5), neutral (pH 7) and alkaline (pH 10). The printing paste formulations were as follows: 100 g thickener, 2 g natural dye, 0.5 g urea, 0.2 g glycerol, 0.1 g $KAl(SO_4)_2 \cdot 12H_2O$. Fixation was carried out using a hot press at 120 °C for 5 minutes. After fixing, the samples were rinsed in warm and cold water [14].

2.3. Colour Analysis

Colour characteristics were measured using a remission spectrophotometer, Datacolor 850, measuring geometry d/8°, D65, measuring aperture of 9 mm. The coordinates used to determine colour values are L* for lightness, a* for redness (positive value) and greenness (negative value), b* for yellowness (positive value) and blueness (negative value), C* for chroma and h° for hue angle in the range of 0° to 360° of undyed and dyed cotton yarns were determined according to the standard ISO 105-J01:2003 *Textiles—Tests for colour fastness—Part J01: General principles for measurement of surface colour*. The colour measurements were carried out using the Datacolor Tools computer programme and "Measuring until tolerance" command. This means that at least 10 measurements must be taken at random points and the results are only accepted if the total colour difference between the individual measurements is less than 0.1 (dE* < 0.1).

2.4. Colour fastness to laundering and light

The fastness to laundering test was performed in laboratory apparatus for wet processes (Polycolor, Mathis) according to standard ISO 105-C06:2010 *Textiles—Tests for colour fastness—Part C06: Colour fastness to domestic and commercial laundering*, using 2 g/l of standard detergent (James Heal ECE A, without optical brighteners and without phosphates), with a bath ratio of 1:20, for 30 minutes, at temperature of 40 °C [14].

Colour fastness to artificial light were performed on Xenotest 440 (SDL Atlas, Rock Hill, SC, USA). Xenotest 440 is used for laboratory simulation of external weather influences on the stability and durability of textile and other materials. Analysis was evaluated according to the modified ISO 105-B02 and 13 B04 test methods using Xenotest 440. Test conditions simulated in this research were: Total light time: 41:10 h, Radiant exposure: 6226 kJ/m^2, Irradiance control: 300–400 nm, Filter system: B04, E: 42 W/m^2 (± 2 W/m^2), CHT: 32 °C (± 3 °C), BST: 47 °C (± 8 °C), RH: 40 % (± 8 %), no spray, fan speed: 2000 rpm [14].

Difference in cotton-onion before and after laundering and exposure to light is evaluated through the total colour difference (dE) and colour depth (K/S) at λ_{max} = 400 nm.

3. Results and discussion

The visual evaluation of the printed cotton samples is shown in Tab.1. All samples show satisfactory surface coverage, sharp contours and the typical colour hue for flavonoid compounds [10-13], i.e. a yellowish colour. Considering the process parameters of pre-treatment of the material, addition of aluminium salts and pH of the printing paste, it can be emphatically stated that without pre-treatment of the cotton material yellow-orange samples are obtained, whereas with the addition of aluminium they are yellow. The pre-treatment of the cotton by cationisation with argon (Ar) plasma and their combination lead to dark brown samples and light brown samples with the addition of aluminium salt. Regarding the subjective evaluation of the colour tone depending on the pH

Tab.1 Printed samples cotton-onion

pH	Without pre-treatment		Cationisation		Ar plasma		Cationisation + Ar plasma	
	-	Al	-	Al	-	Al	-	Al
5								
7								
10								

Tab.2 Colour parameters of cotton-onion samples printed with acid, neutral and alkaline paste

Metal ions	pH 5					pH 7					pH 10				
	L*	***a****	***b****	***C****	***h°***	***L****	***a****	***b****	***C****	***h°***	***L****	***a****	***b****	***C****	***h°***
Without pre-treatment															
-	75.65	5.01	30.88	31.29	80.79	75.47	5.30	30.62	31.08	80.19	70.09	6.90	32.82	33.54	78.12
Al	75.93	3.69	36.29	36.48	84.20	75.22	4.15	37.94	39.16	83.92	71.33	5.34	39.66	40.02	82.34
Cationisation															
-	66.67	14.47	21.17	25.64	55.64	63.91	16.55	22.23	27.80	53.45	59.50	15.17	24.01	28.40	57.72
Al	71.96	11.48	25.25	27.74	65.54	73.72	10.99	26.11	28.33	67.17	71.67	11.49	25.65	28.11	65.86
Ar plasma															
-	70.11	11.47	14.24	18.29	51.14	70.15	12.82	14.92	19.67	49.33	60.30	13.90	17.70	22.51	51.86
Al	75.25	10.38	18.96	21.61	61.30	74.17	10.73	19.54	22.29	61.23	70.77	11.63	19.05	22.32	58.60
Cationisation + Ar plasma															
-	66.61	14.00	17.83	22.67	51.85	64.51	15.20	17.88	23.47	49.63	59.29	14.63	22.62	26.94	57.10
Al	74.69	10.30	19.73	22.25	62.43	72.22	11.33	22.35	25.05	63.12	71.34	11.17	20.92	23.71	61.89

value, it is obvious that the samples obtained with alkaline paste show a higher colour intensity and a better surface coverage.

The spectrophotometric analysis of cotton samples printed with acid, neutral and alkaline paste, with the addition of natural dyes extracted from onion skin, with and without the addition of aluminium salt is shown in Tab.2. Objective instrumental measurements confirm the subjective assessment, i.e. the samples without pre-treatment have a hue (h°) between 78.12 and 80.79, while with the addition of aluminium to the printing paste the hue shifts even more strongly into the yellow range, i.e. h° is between 82.34 and 84.20. In addition, these samples have the highest chromaticity (C*) compared to the other samples, which is between 33.54 and 40.02. This colour of the cotton fabrics is the result of the formation of ligands between the hydroxyl group of the cellulose, metal ions and hydroxyl or carbonyl groups of the reactive flavonoid compounds [14]. Flavonoid glycosides can be easily hydrolysed at high temperatures in acidic and alkaline media and under the influence of enzymes [1].

When cotton is pre-treated by cationisation, plasma and their combination, the same direction of changes in the colour parameters is observed, although the changes in the colour parameters are more pronounced in acid and alkaline media, since according to Grotewold [1] hydrolysis of the glycosides takes place, i.e. their cross-linking decreases and they become more reactive [14]. The pre-treatment with cationisation and plasma as well as their combination leads to similar shifts in colour parameters, hue moves towards the orange-red range 49.33 to 57.72 (Tab.2), chroma (C*) drops below 30 and lightness (L*) below 70. Considering that subjective colour perception involves the synergy of all three parameters (hue, chroma and lightness), it is normal for these samples (Tab.1) to be dark brown. For the samples pre-treated by cationisation (Tab.2), colourations with a lower value of lightness from 59.50 to 66.70 was obtained for the pastes of all three pH values compared to the unpretreated ones, and the same applies to the chroma value. When aluminium is added to the printing paste, this influence is significantly lower, as the metal cation impairs the binding of the dye anion to the cationised cotton, as can be seen in Fig.1.

Pre-treatment with argon plasma has a smaller effect on the lightness, but in the same direction. The lightness assumes values from 60.30 to 70.11, and with the addition of aluminium above 71. However, a significant drop in the chroma value to 18.29 to 22.51 is observed with argon plasma pre-treatment and slightly less when aluminium salt is added to the printing paste. By combining the methods of pre-treatment (cationisation and argon plasma), the samples with the lowest lightness from 59.29 to 66.61, and with a chroma value of 22.67 to 29.94 were obtained. The addition of metal cations disrupts this effect as it is positively charged cotton.

When using natural dyes for textile applications, in addition to the subjective and spectrophotometric evaluation of the colour obtained, colour fastness is also important so that these materials can be used not only aesthetically but also functionally. The colour fastness of all samples to laundering is shown in Fig.3, the fastness to artificial light in Fig.4. It is important to consider the colour fastness values for all process parameters that were varied in the first part of the research [14] compared to the proposed cotton pre-treatments. Considering Fig.1, i.e. changes in the charge of the cotton due to the cationisation and changes on the surface due to the argon plasma treatment, the colour fastness values shown in Fig.3 and Fig.4 are obtained.

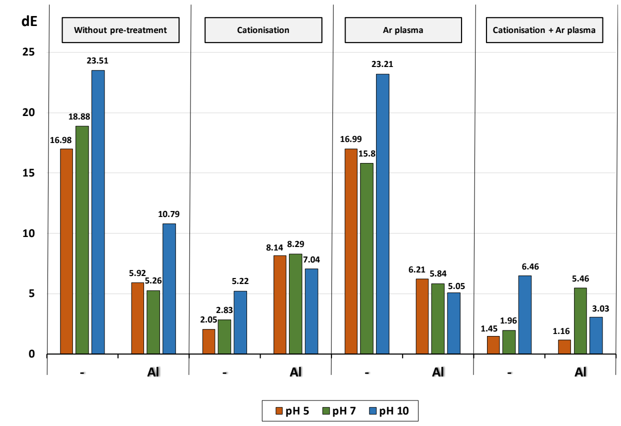

Fig.3 Fastness to laundering of cotton-onion samples printed with acid, neutral and alkaline paste

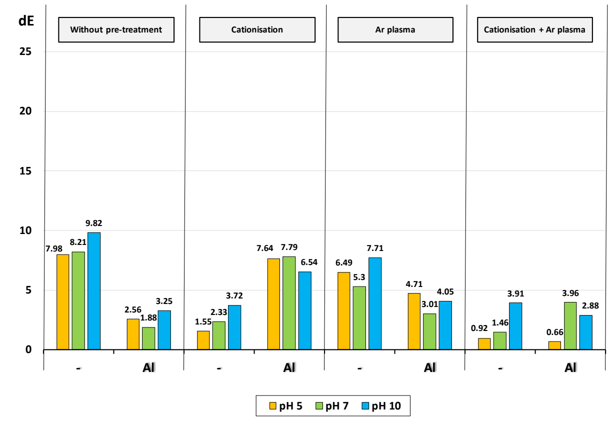

Fig.4 Fastness to artificial light of cotton-onion samples printed with acid, neutral and alkaline paste

Without pre-treatment of the cotton, the greatest colour differences were obtained between untreated samples and samples after laundering (Fig.3), i.e. light-exposed samples (Fig.4), as a reaction between the negatively charged cotton and the anionic flavonoid dye occurs during screen printing at all pH values. The addition of aluminum leads to the formation of a ligand: Cotton-aluminum-Quercetin and to an increase in fastness properties, as described in the first part of the research [14]. When the cotton is cationised, excellent fastness is achieved in with acid and neutral printing paste. The use of acidic printing paste results in the dissociation of all amino groups and an increase in the number of ionic bonds, which leads to an increase in colour fastness. The total colour difference (dE) decreases to a value below 6 after laundering and below 3 after exposure to light. However, the addition of aluminium cations represents a competitive reaction (Fig.1) and the fastness decrease when metal salt is added to the printing paste (dE > 6). In this case, the metal cation was bound to the cotton and interfered with the binding of the anionic flavonoid dyes, which could be easily removed during laundering. Since the plasma only acts on the surface of the cotton and argon as a working gas reacts to the physical ablation of the fibre surface, the use of salt is necessary to achieve better fastness. Excellent results for acid and neutral printing paste dE > 2 were achieved by the combination of cationisation and argon plasma without metal addition. In general, better artificial light and fastness to laundering were obtained with acid printing paste with the combination of cationisation and plasma when comparing the samples before and after analysis in Xenotest, with dE = 0.92.

As the pre-treatments cause surface changes on the cotton, and change its charge, which in combination with the addition of aluminum salts and the pH of the printing paste considerably influence the ability to bind the anionic flavonoid dye and consequently its stability, in Tab.3 are shown the colour depth values (K/S) at λ_{max} = 400 nm of all samples.

Tab.3 *K/S* values at λ_{max} = 400 nm of cotton-onion samples printed with acid, neutral and alkaline paste before and after laundering and exposure to light

Metal ions	**pH 5**			**pH 7**			**pH 10**		
	After printing	After laundering	After Xenotest	After printing	After laundering	After Xenotest	After printing	After laundering	After Xenotest
Without pre-treatment									
-	3.125	1.239	2.158	3.107	1.072	1.938	3.534	1.153	2.202
Al	3.361	1.939	2.202	3.514	2.278	2.247	3.868	1.824	2.418
Cationisation									
-	3.598	2.412	1.753	3.233	2.745	1.871	4.048	2.839	2.433
Al	1.967	1.153	1.593	1.909	1.086	1.636	2.053	1.291	1.593
Ar plasma									
-	1.619	1.467	1.585	1.786	1.632	1.592	2.358	1.893	2.227
Al	1.971	0.964	1.256	2.030	1.004	1.451	3.364	1.094	1.732
Cationistion + Ar plasma									
-	3.854	2.728	2.874	3.323	2.962	1.762	4.486	3.095	3.674
Al	1.953	1.913	1.636	2.190	1.843	1.653	2.332	2.089	1.731

The colour depth values are between 3.107 and 3.534 after screen-printing without pre-treatment, and with the addition of metal K/S increases by 0.2 to 0.4 units. In these samples, the addition of metal has a positive effect on the colour fastness of all pastes, regardless of the pH value. For cationised samples, a greater colour depth was obtained (from 3.233 to 4.040) compared to the samples without pre-treatment. The addition of metal interferes with the binding reaction of the flavonoid dye to the cotton material, resulting in a lower colour depth. Although pre-treatment with argon plasma also has an exclusively positive effect on fastness, a lower colour depth is generally observed. When using argon plasma, the influence of the addition of metal salts is not conclusive, as in some situations salts reduce the dyeing depth and even the fastness. This may be an indication of uneven processing and a possible chemical reaction on the surface of the cotton fabric caused by the action of the plasma. By combining these pre-treatment methods, a synergistic effect is observed. Without the use of metal salt, the highest colour depths of 3.323 to 4.486 were generally obtained, decreasing with the addition of metal.

Indeed, in addition to the individual positive effects of cationisation and argon plasma pre-treatment on the effect of textile printing with anionic flavonoid dyes on cotton without the addition of metal salts, a significant synergistic benefit was observed.

4. Conclusion

The cotton pre-treatment by cationization during mercerisation, by argon plasma and their combination can be a pre-treatment for successful screen printing with natural flavonoid dye from onion skins, considering the surface coverage and the sharpness of the contours. The results obtained show that without pre-treatment of the cotton, samples with vivid yellow tones are obtained, the h° value is greater than 80, and the chroma value even reaches the value of 40. However, these samples do not show satisfactory fastness to laundry and to light (dE > 16). The synergy of the effect of cationisation and plasma on the functional properties of cotton printed with natural flavonoide dye, is confirmed by the excellent fastness obtained with acid paste without the use of metal, i.e. dE < 1.5 for fastness to laundry and dE < 1 for fastness to artificial light. These results are confirmed by the colour depth value. The excellent fastness properties indicate that when using flavonoid dyes, pre-treatment of the cotton by a combination of cationisation and argon plasma is preferable and that the width of the colour hue should be achieved by the selection of the plants.

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