(REFEREED RESEARCH)

EFFECTS OF ATMOSPHERIC PLASMA ON THE PRINTABILITY OF WOOL FABRICS

ATMOSFERİK PLAZMANIN YÜN LİFLERİNİN BASILABİLİRLİĞİNE ETKİSİ

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ABSTRACT

This study is about environmentally safe pre-treatment for wool fabrics to improve their printability with acid dyes. Knitted wool fabrics treated with argon and air atmospheric plasma were evaluated in terms of printability. Printing was carried out with two different receipts under different steaming conditions. The surfaces of untreated and plasma treated wool fabrics were analyzed by SEM to compare the morphological changes. Hairiness of the fabric was investigated under light microscope. The results showed that atmospheric plasma treatment improved the hydrophility of the fiber and enhanced the adhesion and penetration of printing paste to the surface with decreasing hairiness. Increased penetration of printing paste and reduced hairiness caused higher color yield even at lower steaming durations without wetting agent. Air and argon plasma treated fabrics, especially at higher exposure durations, showed higher light fastnesses. Adversely, same samples showed a decrease in wet and dry rubbing fastnesses which were probably caused from the deeper shade of the fabric.

Key Words: Atmospheric plasma, Air plasma, Argon plasma, Surface modification, Wool.

ÖZET

Bu çalışmada, yünlü kumaşların asit boyarmaddeleri ile basılabilirliğini sağlamak için çevre açısından güvenli bir işlem olan plazma ile ön işlem yapılmıştır. Örme yünlü kumaşlar, argon ve hava atmosferik plazma ile işlem görmüş ve basılabilirliği açısından değerlendirilmiştir. Baskı işlemi iki farklı reçete ile farklı buharlama koşullarında değerlendirilmiştir. İşlemsiz ve plazma işlemli yünlü kumaşlar, morfolojik değişimleri kıyaslamak için SEM ile analiz edilmiştir. Sonuçlar, atmosferik plazma işleminin lifin hidrofilitesini geliştirdiği, baskı patının daha az tüylü yüzeye adhezyonu ve penetrasyonunu kuvvetlendirdiğini göstermiştir. Baskı patının artan penetrasyonu ve azalan tüylülüğü, daha düşük buharlama sürelerinde dahi ıslatıcı olmaksızın daha yüksek renk verimine yol açmıştır. Hava ve argon plazma işlemli kumaşlar özellikle uzun süreli işlem koşullarında daha yüksek ışık haslığı değerleri vermiştir.

Anahtar Kelimeler: Atmosferik plazma, Hava plazma, Argon plazma, Yüzey modifikasyonu, Yün.

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1. INTRODUCTION

The surface morphology of wool plays an important role in wool processing. Morphologically, wool fiber consists of cuticle and cortical cells linked to one another by the cell membrane complex (CMC). The cuticle cells are located on the outermost part of the fiber surrounding the cortical cells forming a layer of flat scales overlapping one another. They are formed by epicuticle and exocuticle (A- and B- layers). The epicuticle surrounds each cuticle cell of the wool fiber. It consists of an outermost fatty acid monolayer (F-layer) (~25% by mass) and a protein matrix (~75% by mass) (1). The wool fiber exhibits hydrophobic properties due to the presence of F-layer (2). The presence of scales on a wool fiber surface also introduces a number of problems such as felting and a surface barrier to dyestuffs in dyeing and printing of wool.

In wool dyeing, this problem can be solved by using suitable dyeing auxiliaries and dyestuffs. On the other hand, there are few topics that take interest for the preparation in wool printing. Indeed, a good pre-treatment of wool fabric is absolutely essential prior to printing to obtain full color yields, levelness and brightness. However, that kind of processes can generate a number of polluting agents (acidic or alkaline wastewaters and high content of AOX, etc.). With the increasing importance of ecological and economical restrictions imposed on the textile industry, development of environmentally friendly and economical processes has become important. In this view, plasma treatment offers a solution as an alternative method for the textile industry (3).

Plasma treatment is a physical method used for surface modification, as it affects the surface both physically and chemically which is generated when a gas at low or atmospheric pressure and near ambient temperature is exposed to an electromagnetic field. The chemistry of the plasma takes place in non-equilibrium conditions (4). Temperature of the plasma is relatively low so the activating species in plasma will easily lose their energy once they have reacted with the polymer material. As a result, the penetration of the plasma into the polymer materials is on the surface that the interior of the material is only slightly affected. Plasma treatment can be used as an effective technique for modifying the surface properties of wool fabric without altering the interior part of the fiber, as the plasma species can penetrate only to a depth of about 1000 A° (5-7).

According to the applied pressure, plasmas can be classified as low pressure and atmospheric pressure plasmas. Both plasmas can be used for surface cleaning, surface activation, surface etching, crosslinking, chain scission, oxidation, grafting, and depositing materials. Generally similar effects are obtained with them but atmospheric plasma has many advantages when compared with vacuum plasma. Vacuum systems are time, place and energy consuming processes, and material properties (thickness, size) are highly dependent on size of device and process is not continuous. On the other hand, atmospheric pressure plasma can be generated under atmospheric conditions and requires no vacuum systems with continuous and open perimeter fabric flow (8).

In general, the main advantages of plasma technology are the extremely short treatment time and low application temperature along with the fact that plasma is regarded as an environmentally friendly process (6-9).

Plasma treatment of wool modifies only the cuticle surface of the fibers, without altering the material bulk properties. New hydrophilic groups such as –OH, -C=O, and -COOH are formed on the surface as a result of the hydrocarbon chain oxidation. Besides these, the fatty acid chain length is reduced, surface wettability, dyeability, fiber cohesion, and shrink resistance improve. The oxidation process also promotes cystine oxidation in the exocuticle, converting it into cysteic acid and thus reducing the number of crosslinkages in the fiber surface (5-8, 10-12). As a result, plasma treatment modifies the endocuticle and the interscale cell membrane complex, removes the layer of covalently bound fatty acids and partially destroys the epicuticle.

In this study, wool knitted fabrics were treated with air and argon atmospheric plasma and printed with two different receipts. Color yields, color fastness values, and surface topographies were investigated.

2. EXPERIMENTAL

100 % Wool knitted fabrics with an area weight of 251 g/m^2 were used. The interlock fabric was made of 22 Ne yarns. The knitting density was =11 courses/cm and = 12 wales/cm.

2.1 Atmospheric plasma treatment

In this study, uniform glow discharge plasma system operating under atmospheric condition was used (13). The distance between the electrodes was 0.2 cm. The samples were placed between the electrodes. In all treatments, air and argon were used as process gas under the power of 50, 100, 130 Watts; with different time intervals of 20, 40 and 60 seconds.

One of the most important points of wool plasma processing is the speed. When argon is used as process gas, the speed can be low like 0,5 m/min but if air is used, wool fabric starts to carbonize especially at higher powers. We assume that this can be due to the highly oxidizing effect of oxygen in the air. On the other hand, argon does not cause such kind of tendency because of the nature of noble gasses.

2.2 Printing

After the treatment with atmospheric plasma, the fabric was printed with an acid dyestuff named Lanaset Blue 2RA according to receipt given by Huntsman. The fabrics divided into two groups. In the first group wetting agent was not used.

Table 1. The receipt of printing paste

Dye	10 g
Urea	50 g
Lyoprint AP (wetting agent)	3 g
Glyecin A	50 g
Amonium tartarate	60 g
Thickener (Guar)	550 g
Water	277 g
Total	1000 g

Printing paste was applied to wool fabrics using the flat-screen printing technique with Johannes Zimmer MDK printing desk. Drying was carried out by Rapid Laboratory Type Dryer at 100° C for 2 minutes. Fixation was performed by steaming for different time intervals such as 20, 25 and 30 minutes at 102° C in a high-temperature steamer (Mathis, Switzerland). The printed fabrics were washed to remove the thickener and any unfixed dye as follows: 5 minutes rinsing with cold water, 3 minutes at 30° C in 2 g/l of soap solution, 5 minutes at 50° C in 2 g/l of soap solution, 5 minutes rinsing with cold water. Then the fabric was squeezed and dried at room temperature.

2.3 Characterization of samples

Color intensities of the dyed fabrics were measured by using a HunterLab ColorQuest II spectrophotometer over the wavelength range of 390–700 nm. In a typical test, reflectance values (R) were measured and relative color strength (K/S) values were then established according to the following Kubelka–Munk equation: $K/S = [(1-R)^2/2R]$, where K and S are the absorption and scattering coefficients, respectively.

Hairiness of the atmospheric plasma treated and printed fabrics was pictured by using a Motic light microscope.

The washing, light and rubbing fastness properties were evaluated using standard methods (15-17).

For surface observation, the changes in the fabric surface were evaluated by using scanning electron microscopy (SEM). SEM observations were made with Phillips XL-30S FEG scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1 Printing

Printing was carried out with two different receipts less than three different steaming times. In Figure 1 and 2, the K/S values of plasma treated and untreated fabrics printed with and without wetting agents.

It can be seen from the K/S values that, atmospheric plasma treatment has positive effect on the printability of wool fabrics.

We assume that there are mainly two reasons for this; firstly, atmospheric plasma treatment increases wettability of wool fabric which increases penetration of any material like printing paste (11, 18, 19, 22) . Secondly, it decreased the fiber fuzziness as could be seen from Figure 3.

As known, fabric fuzziness refers to the severity of hairiness of a fabric caused by untangled fiber ends protruding from the surface. After atmospheric plasma treatment, height and density of protruding fiber ends decrease and surface became more compact which is desirable for the fabrics to be printed. This is probably caused from the etching action of the atmospheric plasma treatment which makes surface fibers more fragile and increases surface friction coefficient from 0,3056 to 0,3697 (14, 20) These increments also affect the fiber-fiber interaction and make fibers more difficult to protrude from the fabric surface. In other words, increased inter-fiber friction reduces fuzziness of the fabric. With the decreased fabric fuzziness, multi-directional scattering of light decreases. In other words, the color of the fabric seems deeper (Figure 4).

As could be seen from K/S values that higher K/S values could be obtained even at lowest plasma exposure time with the lowest steaming time, regardless of the plasma type. K/S values increased gradually with the increasing steaming time which can be seen clearly from the results. On the other hand, both air and argon plasma caused higher K/S values with the intensifying exposure time.

As we stated in our previous study, atmospheric plasma activated the surface by forming new hydrophilic groups (11). If the exposure time increased, plasma etching effect and partial degradation of fatty layer became more dominant which increased the dye penetration during printing.

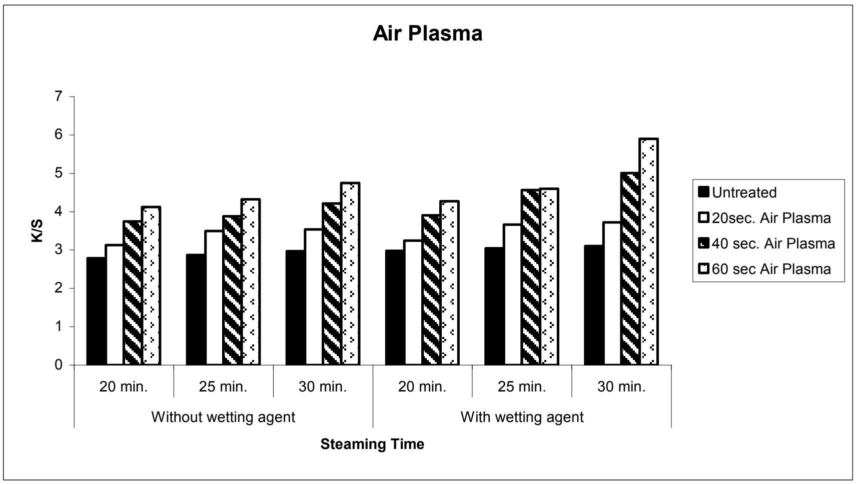


Figure 1. K/S values of untreated and air plasma treated fabrics

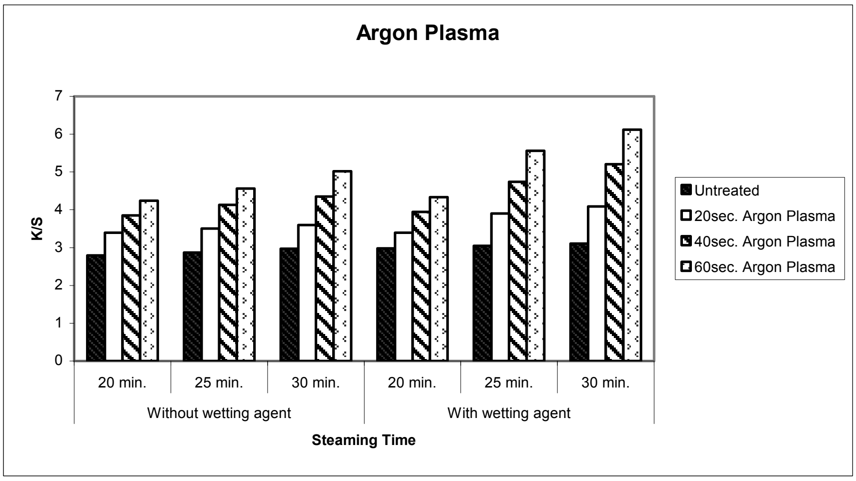
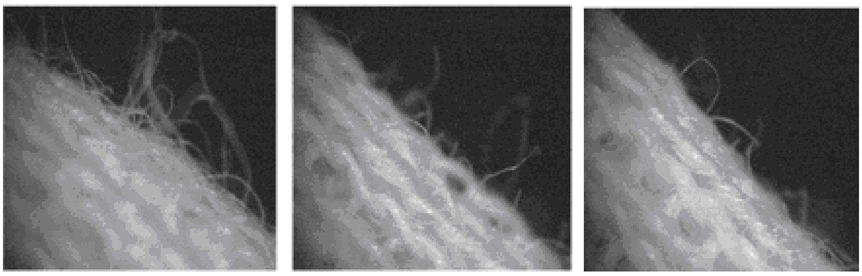
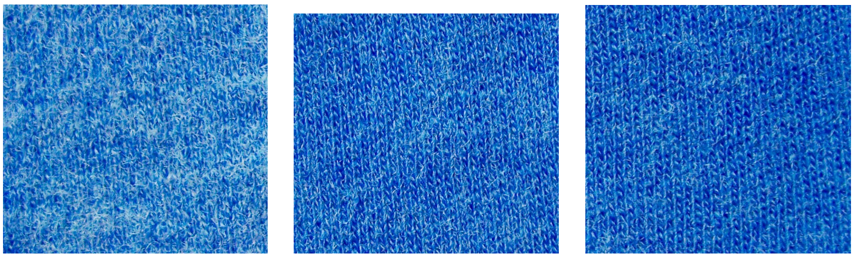


Figure 2. K/S values of untreated and argon plasma treated fabrics



a b c

Figure 3. a) Untreated **b)** 60 sec. air and **c)** 60 sec. argon plasma treated fabrics



a b c

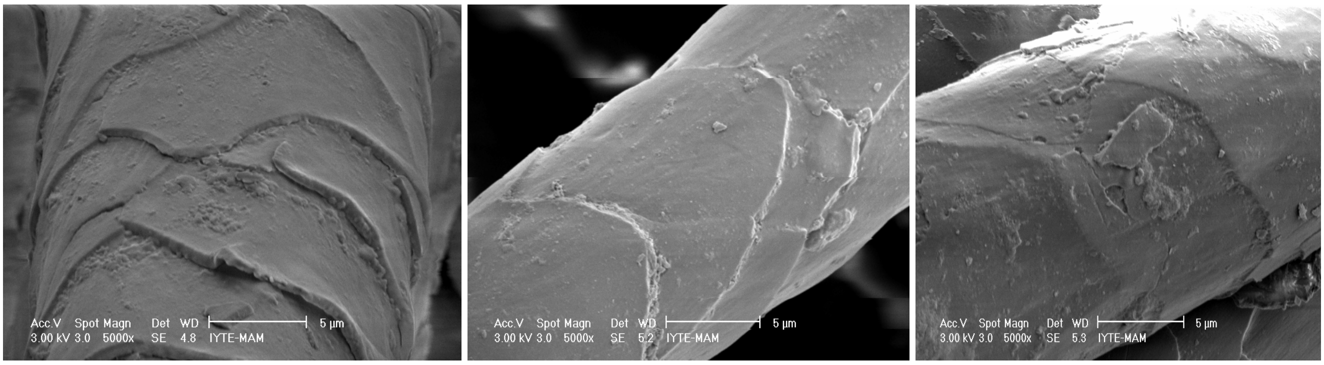
Figure 4. a) Untreated **b)** 60 sec. air and **c)** 60 sec. argon plasma treated and printed fabrics

Table 3. Light fastness values

	Steaming Time	Untreated	20sec. Air Plasma	20sec. Argon Plasma	40 sec. Air Plasma	40 sec. Argon Plasma	60 sec Air Plasma	60 sec Argon Plasma
Without wetting agent	20 min.	5	5	5	5-6	5-6	6	6
	25 min.	5	5	5	5-6	5-6	6	6
	30 min.	5	5-6	5-6	5-6	5-6	6	6
With wetting agent	20 min.	5	5	5	5-6	5-6	6	6
	25 min.	5	5	5	5-6	5-6	6	6
	30 min.	5	5-6	5-6	6	6	6	6

Table 4. Rubbing fastness values

	Steaming Time	Untreated		20sec. Air Plasma		20sec. Argon Plasma		40 sec. Air Plasma		40 sec. Argon Plasma		60 sec. Air Plasma		60 sec. Argon Plasma	
		wet	dry	wet	dry	wet	dry	wet	dry			wet	dry	wet	dry
Without wetting agent	20 min.	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5
	25 min.	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5
	30 min.	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5	3-4	4	3-4	4
With Wetting agent	20 min.	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5
	25 min.	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5
	30 min.	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5	3-4	4	3-4	4



a) Untreated **b)** 130 W 60 sec. air-plasma treated **c)** 130 W 60 sec. argon-plasma treated

Figure 5. a) Untreated **b)** 130 W 60 sec. air and **c)** 130 W60 sec. argon plasma treated fabric

Wetting agent had positive effect on the printability of untreated and treated wool fabrics. Although wetting agent increased, the penetration of printing pat, atmospheric plasma treatment was more effective as could be seen from the results. In many cases wetting agent would not be required if plasma treatment was carried out.

If we take into consideration the plasma type, argon plasma seems more effective than air plasma. This is probably caused from higher etching affect of noble gases (21).

3.2 Color Fastness

In the case of colorfastness to washing, all samples showed the value of staining value between “4” and “5”. Although washing fastnesses were similar, especially 40 and 60 seconds, air and argon plasma treated fabrics had higher light fastness regardless of the wetting agent.

In Table 3 and 4, light and rubbing fastness values were given. There are no significant changes in terms of rubbing fastnesses. Light fastness showed higher values when compared with untreated one which can be due to the higher K/S values of plasma treated fabrics.

3.3 SEM Analysis

As could be seen from Figure 5, both air and argon atmospheric plasma treatments had an etching effect on the wool fiber surface. Argon plasma was more effective than air plasma this was probably caused higher etching tendency of noble gases (21).

4. CONCLUSION

In the printing process of wool fabrics, a good pretreatment is absolutely essential to obtain full color yields, levelness and brightness. However, that kind of processes can generate a number of polluting agents (acidic or alkaline wastewaters and high content of AOX, etc.). In this view, atmospheric plasma treatment offers a solution as an alternative method for the wool printing with the advantages of extremely short treatment time and low application temperature without any chemical and water consumption.

As shown in the K/S results, atmospheric plasma had a positive effect on the printability of wool fabrics. Color yield increased gradually with the exposure and steaming time. Better results could be obtained by plasma treatment without wetting agent, at lower steaming times.

Although washing fastnesses values were similar, air and argon plasma treated fabrics showed higher light fastness regardless of the wetting agent especially treated at 40 and 60 seconds.

On the whole, we can deduce that atmospheric plasma treatment is a successful pretreatment for the printability of wool fabrics. Also, the type of process gas is of significance in order to obtain better results. From our results we observed that atmospheric argon plasma had dominant etching effect in comparison to air plasma which could be seen from SEM images and K/S results clearly.

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REFERENCES

1. Leeder J. D., 1986, "The cell membrane complex and its influence on the properties of the wool fiber" *Wool Science Review*, Vol. 63, pp. 3.
2. Negri A. P., H. J. Cornell, D. E. Rivett, 1993, "A model for the surface of keratin fibers", *Textile Research Journal*, Vol. 63, No.2, pp.109–115.
3. Kan C.W., K. Chan, C.W.M. Yuen, M.H. Miao, 1998, "The effect of low-temperature plasma on the chrome dyeing of wool fiber", *Journal of Materials Processing Technology*, Vol. 82, No. 1, pp. 122–126.
4. Grill A., 1993, "Cold Plasma in Materials Fabrication, From Fundamentals to Applications" IEEE Press, NY.
5. Yan H.J., W.Y. Guo, 1989, Fourth Annu. Int. Conf. Plasma Chemistry and Technology, pp. 182.
6. Kan C.W., K. Chan, C.W.M. Yuen, M.H. Miao, 1998, "Surface properties of low-temperature plasma treated wool fabrics", *Journal of Materials Processing Technology*, Vol. 83, pp. 180–184.
7. Hesse H., H. Thomas, H. Höcker, 1995, "Zero AOX shrinkproofing treatment for wool top and fabric: Part 1: Glow discharge Treatment", T*extile Research. Journal*, Vol. 65, No.6, pp. 355–361.
8. Canup, L. K., 2000, "Non aqueous treatment of fabrics utilizing plasmas", A thesis submitted to the graduate faculty of NCSU.
9. Bureau E. I., 2003, "IPPC Reference Document on Best Available Techniques for the Textile Industry, European Commission," Directorate General JRC, Seville.
10. Johan F., G. Paul, H. P. Schreiber, 1994, *Journal of Applied Polymer Science*, Vol. 51, p.285.
11. Demir A., H. A. Karahan, E. Ozdogan, T., Oktem, N. Seventekin, 2008, "Synergetic effects of alternative methods in wool finishing", *Fibres & Textiles in Eastern Europe*, Vol. 16, No. 2 (67)
12. Kang J., M. Sarmadi, 2004, "Textile Plasma Treatment-Review-Natural Polymer Based Textiles", *AATCC Review,* pp. 28-32.
13. Koçum C., H. Ayhan, 2007, "Design and construction of uniform glow discharge plasma system operating under atmospheric condition", *Review of Scientific Instruments*, 78, 063501.
14. Lima M., L. Hes, R. Vasconcelos, J Martins, 2005, "Frictorq, Accessing Fabric Friction With a Novel Fabric Surface Tester", *AUTEX Research Journal,* Vol. 5, No 4, pp. 194-201.
15. AATCC Test Method 61-1996, Color Fastness to Laundering, Home and Commercial: Accelerated, North Carolina: AATCC.
16. AATCC Test Method 16-1998, Color Fastness to Light, North Carolina: AATCC.
17. AATCC Test Method 8-1996, Color Fastness to Crocking: AATCC Crockmeter Method, North Carolina: AATCC.
18. Ryu J., T. Wakida, T. Takagishi, 1991, "Effect of Corona Discharge on the Surface of Wool and Its Application to Printing", *Textile Research Journal*, Vol. 61, No. 10, pp 595-601.
19. Radetic M., Jocic D., Trakovic R., Petrovic Z. Lj., 2000, "The effect of low-temperature plasma treatment on wool printing", *Textile Chemist and Colorist & American Dyestuff Reporter*, Vol. 32, No. 4, pp. 55-60.
20. Karahan H. A., 2007, "A Research About Changing The Surface Properties of Natural Fibers by Using Atmospheric Plasma", A Master Thesis Submitted To The Institute of Natural and Applied Sciences of Ege University.
21. Poletti G., Orsini F., Raffaele-Addamo A., Riccardi C., Selli E., 2003, "Cold Plasma Treatment of PET Fabrics:AFM Surface Morphology Characterization", *Applied Surface Science* Vol. 219, pp. 311–316.
22. Karahan H.A, Özdoğan E, Demir A, Koçum İ.C. Öktem T, Ayhan H., 2008, "Effects Of Atmospheric Ppessure Plasma Treatments On Some Physical Properties Of Wool Fibers", *Textile Research Journal*.

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