INFLUENCE OF STRUCTURAL CHANGES INDUCED BY OXIDATION AND ADDITION OF SILVER IONS ON ELECTRICAL PROPERTIES OF COTTON YARN

ANA KRAMAR,[*] JOVANA MILANOVIĆ,[*] MATEA KORICA,[*] TANJA NIKOLIĆ,[*,**]
KOVILJKA ASANOVIĆ[*] and MIRJANA KOSTIĆ[*]

[*]*University of Belgrade, Faculty of Technology and Metallurgy, Department of Textile Engineering, 4,Karnegijeva, 11000 Belgrade, Serbia*
[**]*College of Textile Leskovac, 17, Vilema Pušmana, 16000 Leskovac, Serbia*

This paper is focused on investigating the electrical behavior of cotton yarn oxidized with nonselective oxidation agent, hydrogen peroxide, through measurement of structural changes in cotton, and elucidating the influence of these changes on electrical resistance. Significant connection between the nature of the introduced polar groups, crystallinity index, water retention ability, silver sorption and electrical resistance was found. The measurement and possible control of electrical resistance could help anticipate and control the textile materials' tendency to generate static electricity, since these two parameters are closely connected and mutually dependent.

Keywords: cotton, oxidation, silver, electrical resistance, structure–property relations

INTRODUCTION

Textile materials are good insulators with very high electrical resistance, therefore they are prone to generation of static electricity on their surface. Static electricity can cause serious problems during manufacturing, as well as commercial use. Textile materials tend to exhibit a sticking effect on other materials and human bodies, they have a tendency to peel and exhibit cleaning difficulty etc., all because of the generated static electricity, which is a consequence of high resistance.[1-5] Also, static electricity generated on textile material can cause an unpleasant sensation to human body and some physiological disturbances connected to pathological reactions of the nervous and circulatory systems, although the mechanism of this phenomenon has not yet been elucidated.[3,4] The generation of static electricity and its difficult dissipation is connected to the high electrical resistance of materials. Therefore, the easiest way to estimate the tendency of materials to generate static electricity is through measuring electrical resistance.[1,3-5]

The generation of static electricity on textile material surface and of electrical resistance is closely connected to fiber type, molecular and supramolecular structure, i.e. polarity of surface groups and their distribution as well as crystallinity, with regard to content of amorphous and crystalline areas in the material. Air humidity and fiber moisture are also important factors, contributing to electrical properties of textile materials, i.e. in a more humid environment and with higher content of moisture in fibers, their electrical resistance is lower, which leads to lower generation of static electricity. All the mentioned characteristics make the nature of electrical properties of materials more complex and harder to predict and control.[1,4-7]

The oxidation of cellulose materials is one of the most used ways of cellulose modification, which is intended to introduce different functionalities in cellulose and improve certain properties. The oxidation of cellulose fibers with various oxidation agents leads to the introduction of different functional groups and changes in some important properties, like sorption properties.[8-10] Hydrogen peroxide is extensively used as bleaching agent in textile industry.[8,11-14] It

is a mild, nonselective oxidation agent for cellulose, which means that by changing treatment parameters, various functional groups in different quantity can be introduced into the cellulose material, without significant worsening of other important physical and mechanical properties.

In this work, oxidation of cotton yarn was performed using different concentration, pH and treatment time with hydrogen peroxide. After oxidation, ionic silver was bonded to cotton samples. The relationship between the structural changes induced by oxidation and the electrical resistance of cotton yarn was studied, as well as the effect of bonded silver.

Since there are limited resources in current literature dealing with the electrical properties of textile materials and the effect of oxidation on electrical resistance, the results of this work should provide useful additional information on the influence of oxidation on cellulose material.

EXPERIMENTAL
Material
Cotton yarn with the following characteristics: composition – 100% cotton, yarn type – combed, fineness of yarn – 20 tex with twist of 890 turns per meter, obtained from Strumicanka (Strumica, FYR of Macedonia), was used as experimental material. Raw cotton yarn was used as received, without any pretreatment prior to oxidation.

All chemicals used were p.a. grade.

Methods
Oxidation
Oxidation was performed at room temperature using hydrogen peroxide of different concentrations, 3% v/v and 6% v/v with material to liquid ratio of 1:50. The pH was adjusted to different values (7 and 9), using sodium hydroxide. Oxidation was performed during 10, 20 and 30 minutes. After oxidation, the samples were rinsed with distilled water and left to dry at room temperature.

Moisture sorption
Moisture sorption of the samples was determined according to standard ASTM D, 2654-76.The samples were exposed to standard atmosphere: 20 ± 2 °C, 65 ± 2% relative air humidity, for 24 h (ASTM D, 1776-74). Moisture sorption was calculated as weight percentage of absolute dry material. For each sample, moisture was determined in duplicate.

Carboxyl and carbonyl group content
The quantity of carboxyl groups was determined, using the calcium acetate method.[15] The carboxyl groups of cellulose react with the salts of weaker acids,

such as calcium acetate, forming a salt of cellulose and releasing an equivalent amount of the weaker acid. On this basis, for determination of carboxyl content in the cellulose samples, the following method was applied. Cotton yarn samples (0.5 g) were treated with 0.01M HCl during 1 h and washed thoroughly with water. In the next step, 50 ml of distilled water and 30 ml of 0.25M calcium acetate solution were added to the samples. The samples were kept in a solution for 2 h in order to facilitate completion of the interchange. After 2 hours, 30 ml portions of the liquid were titrated with 0.01M sodium hydroxide, using phenolphthalein indicator. The carboxyl group content was calculated, using the following formula:

$$ COOH = \frac{\frac{80}{30} \times 0.01M \times V(NaOH)}{m \times \left(1 - \frac{w}{100}\right)}, mmol \cdot g^{-1} \qquad (1) $$

where 0.01M – concentration of NaOH; $V(NaOH)$ – volume of NaOH solution used for titration, (ml); m – weight of treated fibers, (g); and w – moisture content, (%). For each sample, two tests were conducted, and for each test two titrations were done, and the average volume of NaOH solution spent for titrations was used for calculation of carboxyl group content in each sample.

The carbonyl content was measured according to the method described in literature.[16,17] The samples were further oxidized with sodium chlorite at pH 4-5 for selective conversion of the carbonyl groups to carboxyl ones and carboxyl content was determined by the above mentioned calcium-acetate method. The carboxyl groups formed by $NaClO_2$ oxidation were regarded as carbonyl groups present in the original samples.

Iodine sorption value/Crystallinity index
The Schwertassek method was used for evaluating the sorption properties of the cellulose fibers.[18] The sample of cotton yarn (0.3 g) was treated with 2 ml iodine solution KI_3 (5 g I_2 + 40 g KI + 50 ml H_2O) for 3 min, then 100 ml saturated sodium sulphate (200 g/l) was added and the sample was shaken for 1 h. The iodine concentration of the sample and blank was determined by titration with 0.02 M sodium thiosulphate. The iodine sorption value (ISV) in mg of I_2 per g of sample was calculated as follows:

$$ ISV = \frac{(b-t) \times 2.04 \times 2.54}{m_a}, mg \cdot g^{-1} \qquad (2) $$

Where b is the volume (ml) of $Na_2S_2O_3$ solution for blank titration, t is the volume (ml) of $Na_2S_2O_3$ solution for the titration of sample solution and m_a is the weight of the absolute dry cotton sample(g).

According to Schwertassek, the absorption of iodine takes place in the amorphous phase. The ratio of ISV (per 1g cellulose) to 412 (mg iodine absorbed per

1g of methyl cellulose) determines the amorphous fraction.

The crystallinity index (*CrI*) was calculated using equation 3:[19]

$$CrI = 100 - \left(\frac{ISV}{412} \times 100 \right), \% \qquad (3)$$

Water retention value

Water retention value of cotton samples was determined in triplicate by the standard centrifuge method (ASTM D, 2402-78). This method is based on the determination of the quantity of water that samples can absorb and retain under strictly controlled conditions. Water retention value is expressed as the ratio between the mass of water retained in the sample after soaking and centrifuging and the mass of the absolute dry sample. The presented results are mean values of three WRV measurements obtained for each sample.

Sorption of silver ions

Sorption of Ag^+ ions was done from aqueous $AgNO_3$ solution under previously optimized conditions.[15] Briefly, the samples were treated with silver nitrate solution during 4 hours in the shaker in the dark, to avoid the possibility of photoreduction during treatment. After sorption, the change of silver ions quantity in the solution was determined using Vollhardt's method.[20]
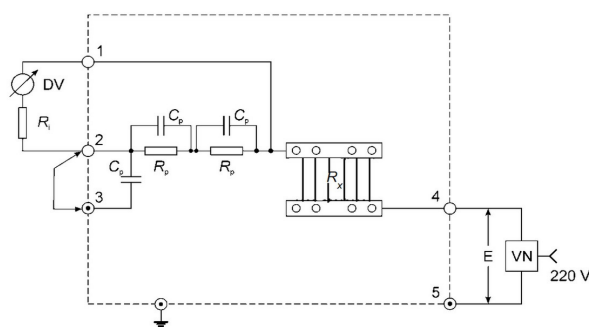
Electrical resistance

The volume electrical resistance was determined with the device developed at the Department of Textile Engineering, Faculty of Technology and Metallurgy, Belgrade University. For a detailed description of the device see reference.[3] The measurement of the electrical resistance of yarn was performed using the voltage method (detailed description is given in reference[5]), according to the electrical scheme presented in Figure 1.

The unknown electrical resistance of the cotton yarn (*Rx*) was determined using equation (4):

$$R_x = \frac{2R_p R_i}{2R_p + R_i} \times \frac{E}{U_m} \qquad (4)$$

where R_x (MΩ) is the resistance of the sample, E is applied voltage, which was 1200 V, $2R_p = 1.64$ MΩ and R_i is the resistance of the digital multimeter, which was 10 MΩ.

For each sample, three measurements were conducted, during each measurement, five threads of yarn were connected to electrodes (Figure2). In this way, total resistance is lower, more threads of sample can be included in measurement at once, the sensitivity of the method increases and the results are more accurate, compared to measuring each string separately.[5] Given that electrical resistance of textile materials strongly depends on relative humidity of the ambient air, i.e. the ability of the material to bind molecules of water from the environment and therefore become more conductive,[1,3-7] the resistance was measured under different air humidity conditions.

Figure 1: Electrical scheme of the voltage method used for measurement of electrical resistance of cotton yarns
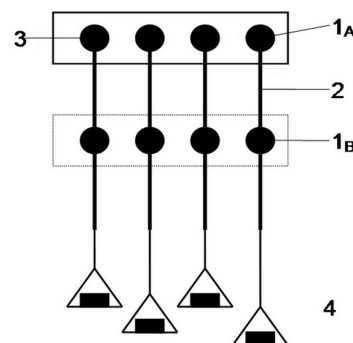

Figure 2: 1A and 1B-electrodes, 2-yarn sample, 3-screws for tightening electrode plates, 4-weights for equal tension during placement of samples between electrodes

RESULTS AND DISCUSSION
Structural changes induced by oxidation and influence on silver sorption

Hydrogen peroxide is usually used for oxidation of low molecular impurities on natural fiber surfaces, thus providing surface cleaning and oxidation of available functional groups of fibers.[8,13,14] Since hydrogen peroxide behaves as a non-selective oxidation agent, the course of oxidation could be altered and different oxidation products of cellulose could be obtained.[21]

Oxidation with hydrogen peroxide did not have any influence on the moisture content of the samples (data not shown). Therefore, in calculating the quantity of functional groups

according to eq. (1), the same value for moisture content was used for all samples. This also indicates the mild nature of the oxidation process. On the other hand, oxidation with hydrogen peroxide leads to a change in the quantity of functional groups in cotton (Figure 3). While the change in carboxyl groups is not very pronounced, a significant increase in the quantity of carbonyl groups was found. This is in good agreement with the results of previous works by other authors.[11,13,14]

In general, an increase in carbonyl group content is more pronounced when higher concentration of hydrogen peroxide is used, when the pH of the solution is higher and when treatment time is longer. Considering the mild conditions of oxidation, it was expected that

hydrogen peroxide would oxidize hydroxyl groups in cellulose mostly to carbonyl, while the change in carboxylic group content could be attributed to the change in low molecular fractions on fiber surfaces. This can be supported by the appearance of nonspecific alteration in the amount of COOH groups (Figure 3 left), where it was found that the quantity of carboxyl groups decreased compared to the control sample. Low molecular fractions, which could contain some amount of COOH groups, could be further oxidized to water soluble products and be removed by prolonged time of treatment, which is probably the case here (samples oxidized for 30 min in a solution containing 3% H_2O_2 at pH 7 and 6% H_2O_2 at pH 9).
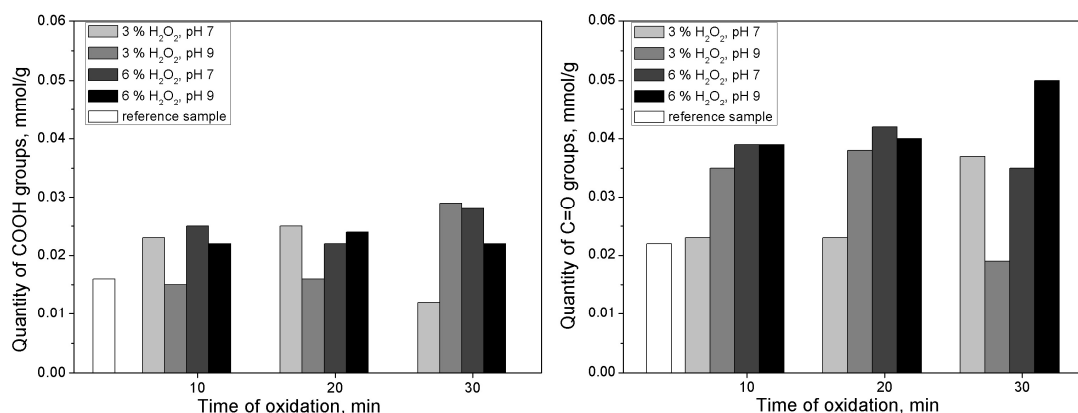

Figure 3: Quantity of carboxyl (COOH) and carbonyl (C=O) groups in samples oxidized under different conditions
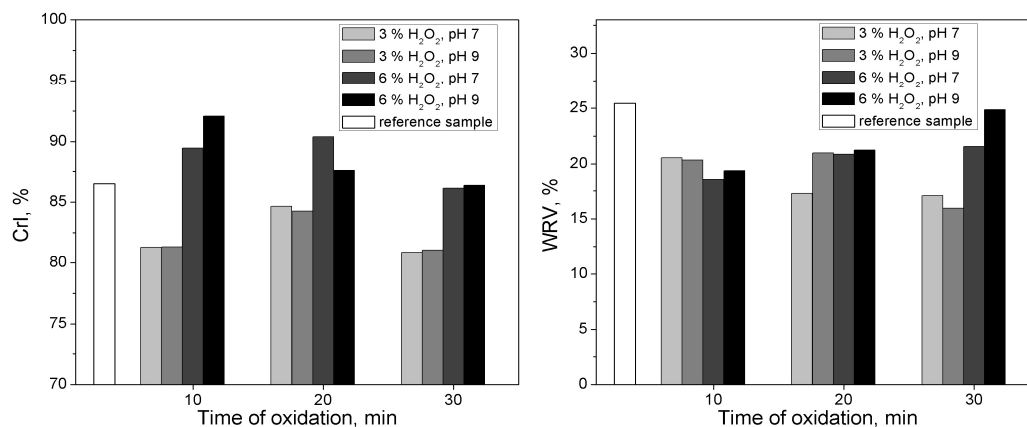

Figure 4: Crystallinity index (CrI) and water retention value (WRV) of samples oxidized under different conditions

In Figure 4, the influence of oxidation on crystallinity index (CrI) and water retention value (WRV) is presented. Oxidation with 3% hydrogen

peroxide leads to a decrease of crystallinity index in the first 10 minutes, followed by a slight increase and a repeated decrease in the case of the

30 minute oxidation, regardless of solution pH. At the same time, water retention value decreases, which could indicate crosslinking by forming hemiacetals between carbonyls and alkoxyl groups and consequently closing pores and capillaries.[9,22] There is no clear explanation for the crystallinity index decrease and, simultaneously, the decrease of water retention value in the case of the samples treated with 3% hydrogen peroxide, but most probably the reorganization of the amorphous areas in fibers is a possible reason for these results. In the samples oxidized with 6% hydrogen peroxide, the crystallinity index is higher compared to the control sample, which indicates the removal of low molecular amorphous parts of fibers to some extent, accompanied by further crosslinking, due to the higher amount of carbonyl groups introduced in the samples.
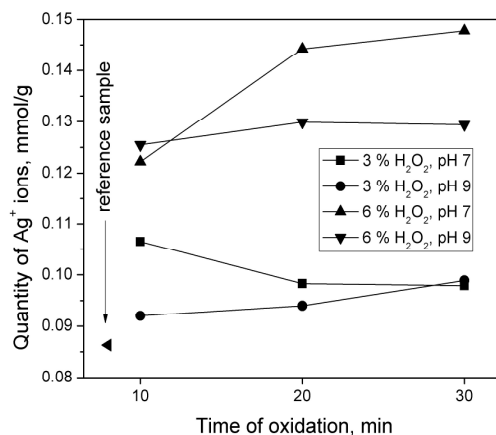

Figure 5: Silver sorption by peroxide oxidized samples

The oxidation of cotton yarn contributes to the increase of sorbed silver in the samples (Figure 5). This is particularly interesting due to the above presented data, which could lead to the presumption that silver ions would bond in a lower degree in the oxidized samples, compared to the control sample, due to obvious "closing" of the structure, at least towards water and iodine solution. However, this only confirms the complex nature of metal ion sorption in cellulose and the great affinity of silver ions towards peroxide oxidized cotton. A usual presumption is that silver ions react with carboxyl groups in cellulose.[15,23]

In this case, the amount and change in carboxyl group content is almost negligible. Therefore, we must assume that this increase in silver content is a consequence of the physical changes and removal of low molecular fractions and impurities from the fiber surface. It is very possible that, although crystallinity index is higher and WRV lower for the samples oxidized with 6% hydrogen peroxide, silver ions are able to reach the intermolecular space unavailable for water or iodine molecules, due to rearrangement of amorphous areas.

Also, the possibility of silver deposition on fiber surface should not be neglected. Although sorption of silver was performed in the dark, there is a possibility that some amount of silver ions may be deposited on the surface, especially considering the fact that after drying the samples, a slight color change was observed from pure white to very light brown.

Influence of structural changes on electrical resistance

Oxidation of cotton yarn with hydrogen peroxide, although under mild conditions, leads to significant changes in electrical resistance (Figure 6). This means that even small changes in structure can lead to big changes in the electrical properties of textile materials. The most pronounced change in electrical resistance was recorded in the samples treated with 6% hydrogen peroxide. While in the samples treated during 20 minutes using 3% hydrogen peroxide, electrical resistance was lower compared to the control sample, the biggest increase in resistance was found in the sample treated with 6% hydrogen peroxide at pH 7 during 30 minutes. The lower electrical resistance of the samples treated with 3% hydrogen peroxide could be connected to the lower amount of carbonyl groups introduced in the samples, compared to the samples treated with 6% hydrogen peroxide, as shown in Figure 3.

In Figure 7, the set of experimental data on electrical resistance measured at 65% air humidity was plotted against the quantity of functional groups measured in the oxidized samples. No significant correlation was found between the quantity of carbonyl and carboxyl groups in the cotton samples oxidized with hydrogen peroxide, but the general trend is that the increase of carbonyl groups in cellulose leads to an increase in electrical resistance.

In Figure 8, the dependence of electrical resistance measured at 65% air humidity on crystallinity index and water retention value is presented. As can be seen, a small decrease of WRV value and a small increase of CrI lead to the increase of the samples' electrical resistance. This is a direct consequence of the nature of resistance in textiles, i.e. amorphous areas' conductivity. As Hearle stated, the conductivity of fibers strongly depends on air humidity and amorphous areas in fibers, since amorphous areas are the main sites for interaction with water and water has high conductivity.[1] Therefore, a lower crystallinity index, i.e. an increase in amorphous areas, should lead to better interaction of fibers with air humidity, thus providing better conductivity and vice versa. The obtained results, presented in Figure 8, are expected and in good agreement with the mentioned theoretical principles. Despite the fact that there is no clear correlation, the general trend of electrical resistance increase is supported by the increase of CrI values occurring during oxidation.
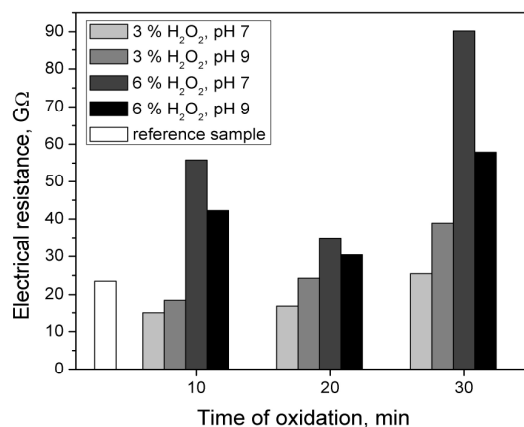

Figure 6: Influence of conditions of oxidation with hydrogen peroxide on electrical resistance of cotton samples measured at 65 % air humidity
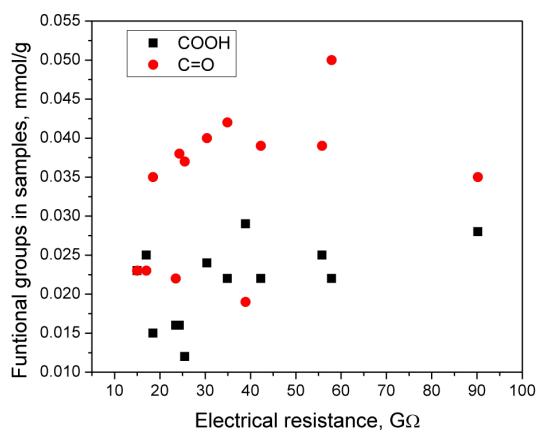

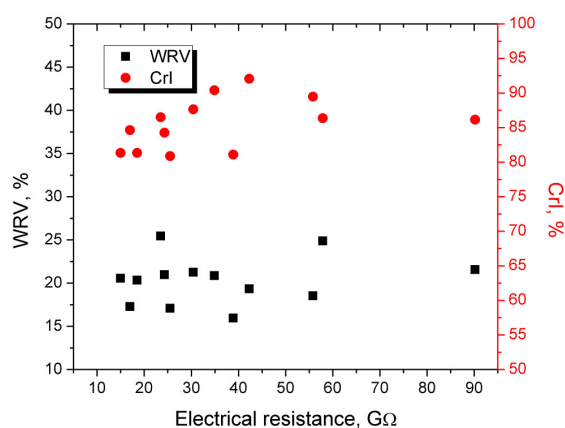Figure 7: Relationship between quantity of functional

Figure 8: Relationship between water retention value (WRV) or crystallinity index (CrI) and electrical

groups and electrical resistance of cotton samples measured at 65% air humidity
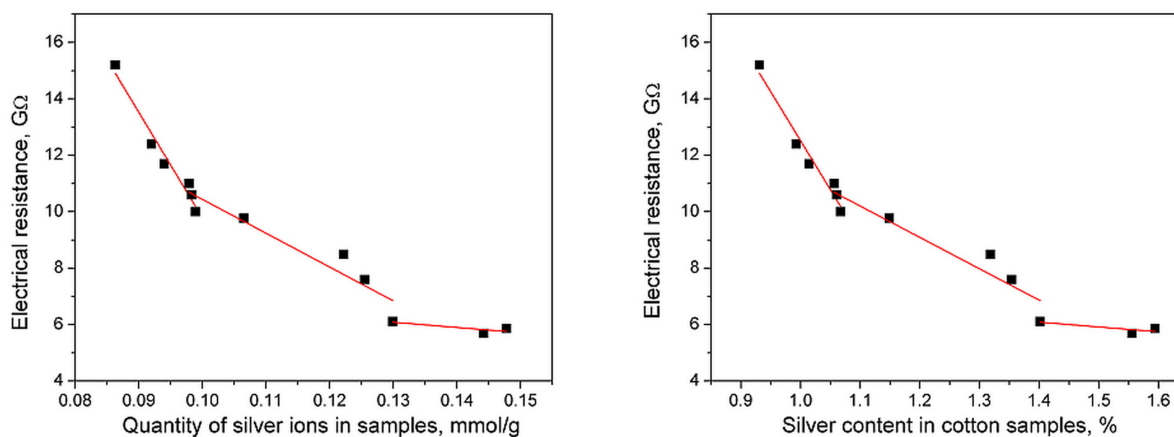
Figure 9: Correlation between quantity of silver ions in cotton samples (left) or silver content in cotton samples, given in % (right) and their electrical resistance measured at 65% air humidity
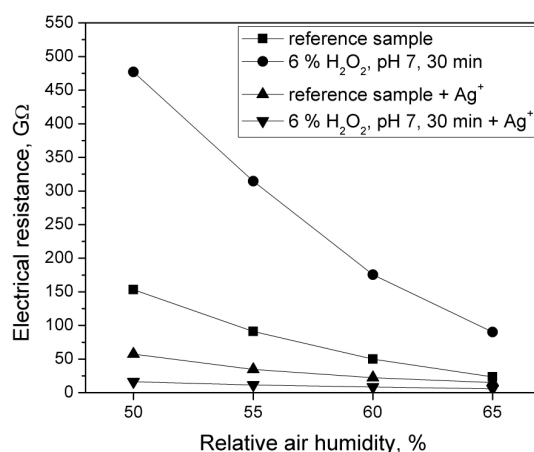

Figure 10: Influence of air humidity on electrical resistance of cotton samples before and after silver sorption

The introduction of silver ions into oxidized cotton had a significant impact on the electrical resistance of the samples (Figure 9). The samples with silver demonstrated lower electrical resistance, which, as it was found, depends on the quantity of sorbed silver ions in cotton yarn. The decrease of the electrical resistance of silver loaded cotton yarns with an increase of the quantity of sorbed silver ions shows three different linear areas (Figure 9 left). An initial phase of up to 0.10 mmol Ag/g fibers, in which electrical resistance decreased sharply for around 5 measurement units, was followed by the second phase of up to 0.13 mmol Ag/g fibers, where the decrease of electrical resistance was slower (a decrease by around 2.5 measurement units), which means that in the second phase the decrease is almost twice slower than in the first phase. In the final third phase, a further increase in silver content, above 0.13 mmol/g, does not have almost any influence on electrical resistance.

To further elucidate this dependence, the silver content was recalculated, i.e. expressed as percentage of silver in material, and further plotted against electrical resistance measured at 65% air humidity (Figure 9 right). A sharp linear decrease of electrical resistance occurs only when the silver content in the samples is up to 1.05%;

more than 1.4% of silver in the material has no influence on resistance whatsoever. These results are very similar with O'Sullivans' findings, when he investigated the influence of electrolyte content on the electrical resistance of hygroscopic fibers and found that at high electrolyte content (above 1%), resistance was independent of the nature or amount of electrolyte in material, but below 1% resistance was proportional to electrolyte content.[1] A similar conclusion could be drawn with regard to silver, i.e. at low silver content, electrical resistance depends on silver amount.

Experimental findings indicate that silver ions attached to the material take the role of charge carriers. This becomes more obvious when we compare results of electrical resistance in samples recorded before and after silver sorption, obtained under different air humidity (Figure 10).

In the oxidized sample without silver, the resistance measured at 65% air humidity is around 5 times lower than electrical resistance recorded at 50% air humidity. For the oxidized sample treated with silver, the ratio R_{50}/R_{65} is around 3, which suggests less dependence of electrical resistance on air humidity. This means that in the fibers with silver, the sites with silver ions are the main charge carriers, whilst in the oxidized samples, the charge carriers are mostly the sites with bonded molecules of water, therefore in conditions of decreased air humidity, these oxidized samples exhibit a significant increase in electrical resistance.

CONCLUSION

In this work, the influence of oxidation with hydrogen peroxide and of changes occurring during the process on the electrical resistance of cotton yarn was studied. The results revealed that the changes, which include parameters important for the interaction of water and cellulose (polar groups, water retention value, crystallinity index) can have a significant impact on the electrical properties of cellulose. Generally speaking, the increase of carbonyl groups, decrease of water retention value and increase in crystallinity (decrease of amorphous areas) lead to an increase of electrical resistance. Sorption of silver onto cotton causes a significant decrease of electrical resistance. The samples with silver have lower resistance compared to the samples without silver, which suggests that silver ions bonded to cellulose act as main charge carriers. This was further confirmed by comparing the samples'

electrical resistance at different humidity, which revealed that the samples with silver were less sensitive to changes in air humidity than the samples without silver.

An especially important finding is related to the correlation of electrical resistance with the quantity of silver ions in the sample, the measurements showed that electrical resistance decreases with an increase of the amount of silver ions in the samples and is dependent on the silver content in cotton. This could be a baseline for a future investigation regarding the control and lowering of static electricity generation on textile materials.

REFERENCES
[1] W. E. Morton and J.W.S. Hearle, in "Physical Properties of Textile Fibres", Wood head Publishing Limited in association with The Textile Institute, Cambridge, England, 2008, pp. 643-664.
[2] K. Bal, V.K. Kothari, *Indian J. Fibre Text.*, **34**, 191 (2009).
[3] K. A. Asanovic, T. A. Mihajlidi, S. V. Milosavljevic, D. D. Cerovic, J. R. Dojcilovic, *J. Electrostat.*, **65**, 162 (2007).
[4] K. A. Asanovic, PhD Thesis, University of Belgrade, Belgrade, Serbia, 2003.
[5] M. M. Kostic, B. M. Pejic, K. A. Asanovic, V. M. Aleksic, P. D. Skundric, *Ind. Crop. Prod.*, **32**, 169 (2010).
[6] K. Asanović, T.Mihailović, P. Škundrić, Lj. Simović, *Text .Res. J.*, **80**, 1665 (2010).
[7] D. D. Cerovic,K. A. Asanovic, S. B. Maletic, J. R. Dojcilovic, *Compos.Part. B-Eng.*, **49**, 65 (2013).
[8] P. J. Wakelyn, N. R. Bertoniere, A. D. French, D. P. Thibodeaux, B. A. Triplett*et al.*, in "Handbook of Fiber Chemistry", edited by M. Lewin, third edition, Taylor & Francis Group, London, 2007, pp. 521-666.
[9] T. Nikolić, M. Kostić, J. Praskalo, Ž. Petronijević, P. Škundrić, *Chem. Ind. Chem. Eng. Q.*, **17**, 367 (2011).
[10] J. Z. Milanović, M. M. Kostić, P. D. Škundrić, *Chem. Ind. Chem. Eng. Q.*, **18**, 473 (2012).
[11] U. Henninges, A. Potthast, *Restaurator*, **30**, 294 (2010).
[12] T. Topalović, PhD Thesis, University of Twente, Netherlands, 2007.
[13] M. Lewin, *Macromol.Symp.*, **118**, 715 (1997).
[14] J.F. Haskins, M. J.Hogsed, *J. Org. Chem.*, **15**, 1264 (1950).

[15] J.Z. Praskalo-Milanovic, M.M. Kostic, S.I. Dimitrijevic-Brankovic, P.D. Skundric, *J. Appl. Polym. Sci.*, **117**, 1772 (2010).

[16] T. Saito, A. Isogai, *Biomacromolecules*, **5**, 1983 (2004).

[17] E.J. Parks, R.L. Hebert, *Tappi J.*, **55**, 1510 (1972).

[18] B. Siroka, M. Noisternig, U.Griesser, T. Bechtold, *Carbohyd. Res.*, **343**, 2194 (2008).

[19] M.L. Nelson, M. Rousselle, S.J. Cangemi, P. Trouard, *Text. Res. J.*, **40**, 870 (1970).

[20] P. Patnaik, in "Handbook of Environmental Analysis", Lewis Publishers, CRC Press, Boca Raton, London, New York, 1997, pp. 39-64.

[21] M. M. Kostic, P. D. Skundric, J. Z. Praskalo, B. M. Pejic, A. H. Medovic, *Hem. Ind.*, **61**, 233(2007).

[22] A. Potthast, T.Rosenau, P. Kosma, A.-M.Saariaho, T. Vuorinen, *Cellulose*, **12**, 43 (2005).

[23] T. Saito, A. Isogai, *Carbohyd. Polym.*, **61**, 183 (2005)