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PHOTOCHEMICAL REDUCTION OF COPPER AND SILVER IONS ON CELLULOSE-CONTAINING FABRICS

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ABSTRACT

The article presents the research results on obtaining thin films of copper (II) chloride or silver nitrate on the surface of cotton fabrics. It has been demonstrated that end links contained in cellulose in the amount of a few percent are exposed to photooxidation. Photooxidation of the end links is associated with the presence of aldehyde groups, therein providing a reducing ability to cellulose. This leads to the reduction of silver nitrate and the formation of elemental silver; thus, copper (II) chloride is reduced to copper monochloride with a partial content of elemental copper. Copper monochloride is a binary semiconductor; this allows producing a surface film containing elemental copper only using additional photochemical treatment with ascorbic acid. The experiments showed that the proportion of final cellulose molecules involved in photochemical reactions was 0.98 % for the production of copper-containing films and 0.47 % for silver-containing films. From SEM images, the films contain uniformly distributed globular particles 100-600 nm in diameter.

Keywords: Cotton Fabric, End Links of Cellulose, Copper (II) Chloride, Silver Nitrate, Elemental Copper, Elemental Silver.

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INTRODUCTION

The antibacterial properties of silver have been known for a long time. Less pronounced antiseptic properties characterize copper compared to silver; however, it enhances the effect of silver preparations.[1] In addition, recent studies have shown that highly effective antiviral properties also characterize copper.[2, 3] This has become very important due to the recent global outbreak of COVID-19.

Current research in creating more effective technological methods for obtaining resistant materials against bacteria and viruses makes them necessary. The proof of this can be the constant expansion of their scope of application.[4-16]

It is proposed to use such fabrics for the production of medical products, various military uniform, sportswear, underwear, and weapon covers protecting it from various microorganisms. The use of fabrics that contain metal coatings for protection against electromagnetic radiation is also relevant. A higher protective capacity of chemically deposited copper has been noted as well.[17]There are many physical and chemical methods used to produce fabrics with a layer of metal particles.

Gas-phase, magnetron, plasma, or laser deposition of metal particles is a physical metallization method. These methods can be used to apply metal films to textile materials to produce bactericidal and antiviral properties. It should be reminded that the films must not worsen the consumer properties of fabric products and retain these properties after washing and creasing. Given these requirements, the following methods are suitable.

Recall that the films should not worsen the consumer properties of the fabric product and retain these properties after washing and folding. Considering these requirements, the following methods based on gas, plasma, or magnetron deposition of metal particles are proposed.[18-20] These methods are multi-stage and require special equipment. For example, during magnetron sputtering, metal particles are initially obtained and then applied to the material's surface in a vacuum chamber. The method is based on using an anomalous glow discharge in an inert gas, where positively charged ions are generated in the discharge bombardment. The cathode surface is in the erosion zone and metal particles are knocked out of it,

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deposited in a thin layer on the surface of the processed material. The metal coating is applied without the use of any chemicals that are dangerous to the environment. In addition, the high kinetic energy of the particles leaving the cathode surface ensures good adhesion of the formed film to the substrate.

The physical methods may also include the technology to produce medical dressings, in which silver nanoparticles deposited as a result of a chemical reaction are physically dispersed between fibrous tissues.[21]

It is proposed to use γ-radiation to produce antimicrobial silk fibers modified with silver nanoparticles[22]. The fine silk fibers, which showed antimicrobial activity of more than 96%, were previously treated with a solution of silver nitrate and subsequently exposed to γ-radiation. It also confirmed its effectiveness even after 10 washing cycles.

Non-equilibrium or cold plasma is used to modify the physical and chemical properties of textile materials.[23-25] The use of cold plasma leads to chemically active particles at low gas temperatures. Therefore, thermal degradation of the textile substrate in the course of plasma treatment will be minimal.

Disadvantages of the physical methods include the use of specialized equipment, the need for preliminary production of metal nanoparticles, the difficulty of the metallization of inner surfaces of porous materials, and the difficulty related to the regulation of coating thickness.

Reductants in the gas phase or compounds dissolved in an electrolyte solution are used for the chemical deposition of metal coatings.[26-29]

The chemical gas-phase metallization is carried out by pumping metal carbonyl vapors through a woven or non-woven material in a low vacuum. The initial material is heated to the temperature of the onset of vapor decomposition. In this case, the metal coating is applied over the entire thickness of the bulk material.[26] Disadvantage of the process includes the difficulty of obtaining carbonyl and running the process in the required mode. Relatively high process temperature and high cost of metal carbonyls prevent this process from being widespread.

For antimicrobial treatment of cotton fabric, it is proposed to use copper nanoparticles obtained based on a composition that contains copper compounds and polyvinyl alcohol. Optimal conditions for the treatment of cellulose materials have been developed.[27]

Tannin-based and ethylene glycol-based tanning substances were used to obtain bactericidal fabrics by reducing silver nitrate.[28, 29] These technologies require additional operations to increase the adhesion of bactericidal films to the fabric surface.

Photochemical methods were also used to produce bactericidal films of metals of the copper subgroup particles. There is a method that includes photochemical reduction of transition metal compounds on the surface of polymer microspheres. The functions of sorption centers for metal nanoparticles allow their obtaining in the form of stable dispersions. This work includes photochemical synthesis of copper, silver and gold nanoparticles on the surface of polymer microspheres.[30,31] It is characterized by a better purity of formed nanoparticles due to the absence of by-products produced as the result of the use of chemical-reducing agents. However, the mechanism of the photochemical reaction of the formation of metal nanoparticles and the influence of the dielectric structure is unclear from the material used. The disadvantage of this method includes the occurrence of photochemical reaction with the formation of silver only under a specific structure of latexes, which significantly narrows the scope of method application.

EXPERIMENTAL

White cotton gauze fabric (article AA010278), widely used for medical purposes, was used for research purposes. This sort of fabric includes 97-98% of cellulose.

Pretreatment of fabric sample was carried out by holding in hot (40°C) distilled water for 30 minutes. Samples were then cut after washing and drying.

The key scope of researches was carried out in a laboratory under 25-30°C. Solar rays penetrating the window had a flux density W = 1000-1100 W/m^2. Solar radiation meter SM 206-SOLAR was used to determine this value.

Electromagnetic solar rays can penetrate through thin solid-phase bodies and liquid media. This promotes the occurrence of photochemical reactions on internal areas of fabrics.

To create a sorption layer on the surface, a sample was dipped into $CuCl_2$ or $AgNO_3$ solution for a few minutes. After that, the sample was placed on a glass surface and smoothed with a glass rod. The samples were then dried under Sunlight.

Dispersed particles of copper or silver are formed on the surface of fabric giving the film a black color. The samples were then washed to remove by-products and excessive amounts of starting salts. After washing, the black film produced due to photochemical reaction using silver nitrate remains unchanged. However, the black film produced due to photochemical reactions using copper chlorides disappears. This demonstrates the reverse oxidation of elemental copper (the transformation mechanism is given below).

Therefore, an additional photochemical reaction using ascorbic acid was carried out to produce copper-containing films. The sample was wetted with a solution of ascorbic acid and exposed to sunlight until completely dry. The black copper-containing film thus obtained is wash-resistant.

The intensity of black color of film depends on the concentration of initial solutions of metal salts. Therefore, the degree of film blackening can be used as an indicator characterizing the content of reduced metal particles in the film. The quantitative characteristics of the intensity of black films of samples can be determined using a computer. In this case, photographs of the samples are placed in a Microsoft Office Word file, brightness in the image window is changed until its complete disappearance. The added brightness characterizes the degree of blackness.

The structure and composition of films were studied using an ISM-6490-LV scanning electron microscope (JEOL, Japan). Using this device, we can obtain an electron image of particles tens of nanometers in size, elemental composition and percentage of elements in the surface layers of the film.

Resistance to washing powder was determined by changing the degree of blackness of the sample after 1 h stirring of the sample placed in a hot (40°C) solution containing 20 g/l of ARIEL washing powder in a magnetic stirrer.

RESULTS AND DISCUSSION

Photochemical processes using $CuCl_2$.Changes in intensity of black color on samples of fabric wetted in $CuCl_2$ solutions of different concentrations and dried in the sun are shown in Fig.-1. In this case, two processes occur an increase in chloride concentration in the surface film and a decrease in its thickness. Both of these factors influence photochemical processes.

In this case, no changes are observed in the surface film during the initial 30 minutes. Then, a decrease in the film's thickness makes the film permeable to electromagnetic waves of Sunlight and photochemical reactions begin to proceed.

When they occur on samples with a lower $CuCl_2$ content (10 and 30 g/l), the degree of blackness decreases at the initial moment. This indicates that there is a transition of $CuCl_2$ (dark green) → CuCl (colorless). This effect is leveled at higher concentrations of $CuCl_2$ since the change in the ratio of bi- and monovalent copper becomes less noticeable. Then there is an increase in the degree of blackness to a specific value on all samples.

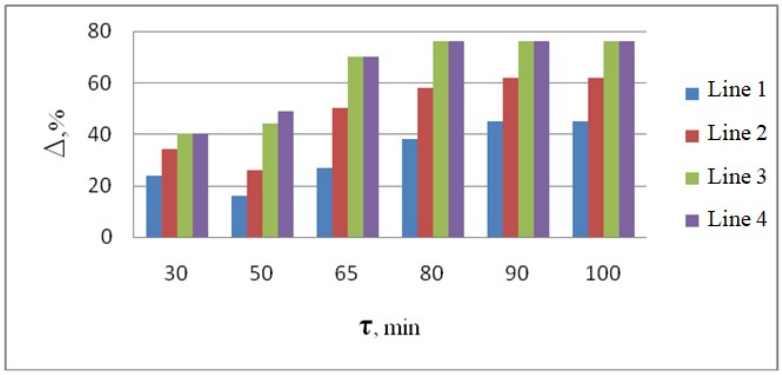

Fig.-1: Change of Blackness (Δ, %) of Samples of Fabric wetted in Solutions of Copper (II) chloride depending on the timing of exposure to Solar Rays (τ, min). Copper (II) chloride concentration, g/l: line 1-10; line 2-30; line 3-50; and line 4-60.

From the curves above, one can see that the dependence of blackness on CuCl2 concentration takes up up to 50 g/l. With a further increase in concentration, the degree of blackness remains unchanged. Hence, only a particular portion of cellulose molecules acquires reducing properties under the effect of Sunlight.
Cellulose is a natural polymer and consists of many individual chains. Ends of individual chains form links that are different from the rest of the chain links. End links of chains can exist in two tautomeric forms (Fig.-2) – cyclic (semi-acetal) and open (aldehyde).
Therefore, the following reactions occur on cotton fabric with a layer of an aqueous solution of $CuCl_2$ under the effect of Sunlight.
Reduction of bivalent copper to monovalent:

$$Cu^{2+} + Cl^- + e = CuCl, \quad E=0.566\ V \tag{1}$$

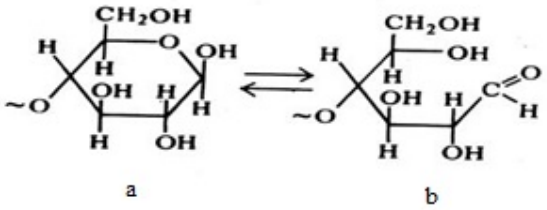

Fig.-2: Tautomeric Forms of End Molecules of Cellulose[33]: a – cyclic; b – open.

The equation describing the reaction of oxidation of aldehyde group of open tautomeric form is as follows:

$$R_cCHO + H_2O - 2e = R_cCOOH + 2H^+ \tag{2}$$

Where R_c – a part of the non-oxidized open-end cellulose molecule.
The formula of the overall reaction is as follows:

$$R_cCHO + 2CuCl_2 + H_2O = R_cCOOH + 2CuCl + 2HCl \tag{3}$$

The thermodynamic possibility of these reactions can be assessed by comparing their standard potentials. So if we assume that the potential of reaction 1 is close to the standard potential E^o=0.566 V [34], and the potential of reaction 2 does not differ much from the oxidation potential of an individual formaldehyde molecule ($HCHO+H_2O-2e = HCOOH + 2H^+$, E=-0.01 V [34]), oxidation of the end cellulose molecule by reaction 3 is thermodynamically possible.
The resulting copper monochloride is a binary semiconductor. Therefore, when exposed to photons of electromagnetic rays of Sunlight, a part of the electrons passes into the conduction zone and acquires the ability to restore monovalent copper.

$$CuCl + e \rightarrow Cu + Cl^- \qquad E^o = 0.137\ V \tag{4}$$

where E^o is a standard equilibrium potential of this system

After this, the semiconductor has vacancies that can get electrons from CuCl only:

$$CuCl + Cl^- - e \rightarrow CuCl_2 \qquad E^o = 0.538\ V \tag{5}$$

Photochemical reaction will occur in this case:

$$2CuCl \xrightarrow{h\nu} Cu + CuCl_2\ (solid) \tag{6}$$

When the surface film dries out, $CuCl_2$ crystallizes and loses its activity, which is an additional factor contributing to reaction 6.

Summarizing all the reactions above, we can say that the overall process consists of two main stages. Stage one is photooxidation of end aldehyde groups of cellulose and simultaneous reduction of $CuCl_2$ to CuCl. Stage two is associated with the semiconductor properties of CuCl and it also occurs only when exposed to electromagnetic waves of Sunlight. Therefore, both of these stages can be considered photochemical.

The copper film formed as the result of reaction 6 is unstable because, when exposed to water, $CuCl_2$ is again activated and thermodynamic reaction becomes more possible.

$$Cu + CuCl_2 \rightarrow 2CuCl \quad (7)$$

A SEM image of a fabric sample after stage one, thoroughly washed with distilled water and dried in the dark (to avoid the occurrence of reaction 6) is shown on Fig.-3. The elemental composition of such a fabric is characterized by a higher (in comparison with the stoichiometric ratio of Cu:Cl = 1:1) copper content in relation to chlorine. Therefore, the surface film contains both CuCl and elemental copper. It is possible that aldehyde groups display donor properties and reaction 5 is involved.

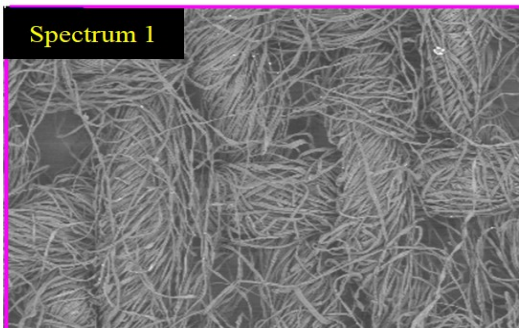

Fig.-3: SEM Image of Sample of Fabric after stage one of Photochemical Treatment and Drying in the Dark

Table-1: Elemental Composition of Spectrum 1 (Fig.-3)

Element	Wt., %	Atom, %
C	48.01	56.05
O	49.00	42.95
Si	0.87	0.43
Cl	0.50	0.20
Cu	1.62	0.36
Total	100.00	

The presence of elemental copper can also be seen on SEM images of individual regions of the sample. You can see a region of fabric (Spectrum 1) on Fig.-4 where half of the copper is a part of CuCl, and the other half is elemental. Meanwhile, the neighboring region (Spectrum 2) consists mainly of CuCl.

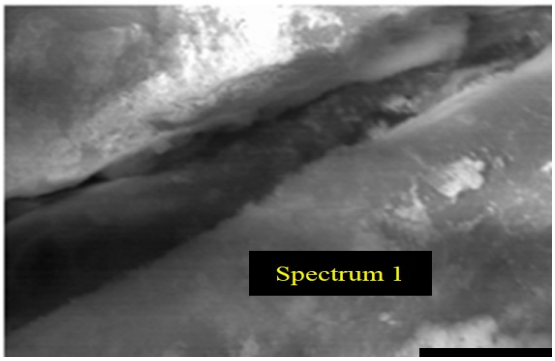

Fig.-4: SEM Images of Various Regions of Sample of Fabric after stage one of Photochemical Treatment and drying in the Dark

Table-2: Elemental Composition of Spectrum 1 and Spectrum 2 (Fig.-4)

Element	Wt., %	Atom, %
C	58.35	65.87
O	36.49	30.99
Si	4.24	1.91
Cl	0.27	0.54
Cu	0.54	0.69
Total	100.00	

In this event, using an additional treatment with ascorbic acid, it is possible to obtain a film containing copper only. The redox potential of the ascorbic acid – dehydroascorbic acid system is changing from - 0.329 V to - 0.057 V at an increase of pH 0 to 7. Therefore, it has a higher donor capacity than copper monochloride.
In this case, instead of reaction 5, the following reaction will occur:

$$A\text{-}(OH)_2 - e \rightarrow A\text{-}OOH \quad (8)$$

where A is an unchangeable part of the ascorbic acid
The total photochemical reaction looks as follows:

$$CuCl + A\text{-}(OH)_2 \xrightarrow{h\nu} Cu + HCl + A\text{-}OOH \quad (9)$$

$A\text{-}(OH)_2$ and A-OOH can be easily removed at washing. Therefore, $A\text{-}(OH)_2$ preventing the formation of $CuCl_2$ promotes the preservation of elemental copper film on the fabric surface.[33] The equivalent ratio of $CuCl:A\text{-}(OH)_2$ = 1:1.1 provided the maximum degree of blackness of the fabric surface.
As the result of these processes, a film containing elemental copper in the form of spherical particles 100-600 nm in diameter remains on the fabric's surface (Fig.-5).

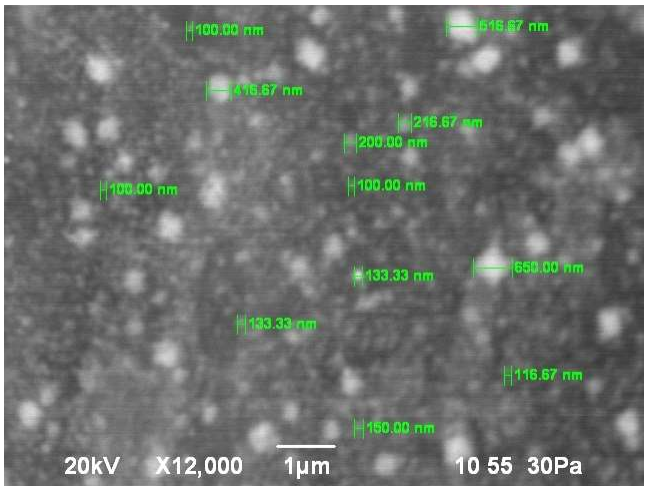

Fig.-5: Structure of Photochemically produced Copper-containing Films

This film allows using fabric to protect against bacteria. In addition, it allows, if necessary, applying a layer of electrically conductive copper to fabric by chemical copper plating.
Photographs of fabric samples after each of the above operations are shown in Fig.-6. A sample of original fabric (6a) was wetted in a $CuCl_2$ solution (50 g/l) and dried at a solar flux density of 1010 W/m^2 (6b). One sample after washing was dried in a dark place (6c), while another sample, after washing, was wetted with a solution of ascorbic acid (27.5 g/l) and again dried in the sun and washed to remove reaction by-products (6d).
The subsequent chemical coppering was carried out at room temperature for 10 minutes in a solution of the following composition, g/l: $CuSO_4$ x $6H_2O$ (20 g/l), Trilon B – 55 (g/l), NaOH - to pH=12.5, formalin-(15 g/l). In this case, a brown coating was obtained (6e) characterized by electrical conductivity typical to metals.

Fig.-6: Photographs of Samples of Fabric after Various Technological Operations
(See text for designation)

Photochemical processes using $AgNO_3$. Photooxidation of aldehyde groups of end links of cellulose using silver ions is thermodynamically more likely, assuming that the standard reaction potential is

$Ag^+ + e = Ag, \quad E^0 = 0.799$ V (10)

0.233 V is more favorable than reaction (1) using $CuCl_2$, which also anticipates a higher speed of individual process stages.

Reaction (3) of oxidation of the aldehyde group in the open tautomeric form remains unchanged, and the total reaction is as follows:

$$R_cCHO + 2AgNO_3 + H_2O = R_cCOOH + 2\,Ag + 2HNO_3 \quad (11)$$

The photochemical nature of the formation of elemental silver is confirmed by the outcomes of experiments where a fabric wetted with silver nitrate was dried in a dark place. Blackening of the fabric was not observed. Therefore, there is no chemical interaction of silver nitrate with aldehyde groups of end links of cellulose or otherwise, its rate is very slow.

Visual observations demonstrated that reaction 11 immediately follows fabric exposure to Sunlight. Consequently, the fact that the reaction product is elemental silver accelerates the process of moisture removal and the fabric dries faster (Fig.-7).

It can be seen from this figure that the maximum blackness for various concentrations of silver nitrate is reached here faster as compared to copper chloride (Fig.-1).

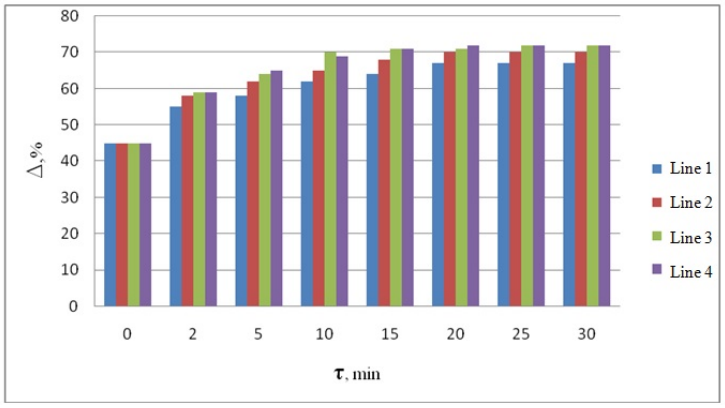

Fig.-7: Change of Blackness (Δ,%) of Samples of Fabric wetted with Silver Nitrate Solutions on the timing of exposure (τ, min) of Sunlight. Silver Nitrate Concentration, g/l: line 1-5; line 2-15; line 3-30; line 4-50.

From Fig.-7, one can see that at a silver nitrate concentration of 30 g/l, blackness is at its peak value and further increase of concentration results in no change.

The SEM image shows that many surface filaments are white, which is typical of metal films. The elemental composition shows that the silver content in the surface layer is 2.54%.

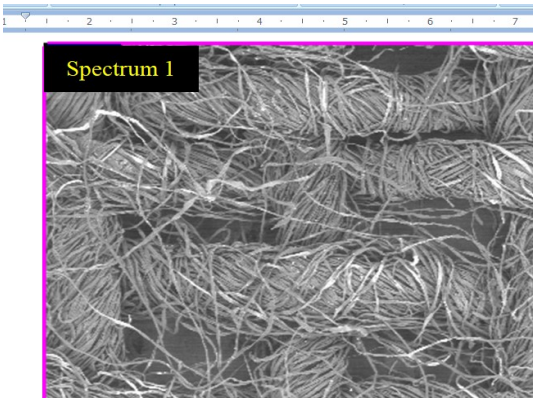

Fig.-8: SEM Image of Sample of Fabric wetted with Silver Nitrate Solution and dried in the Sunlight

Table-3: Elemental Composition of Spectrum 1 (Fig.-8)

Element	Wt., %	Atom, %
C	47.43	55.84
O	48.97	43.29
Al	0.24	0.13
Si	0.82	0.41
Ag	2.54	0.33
Total	100.00	

Photochemical processes result in the formation of film containing elemental silver in the form of spherical particles 100-600 nm in diameter on the surface (Fig.-9).

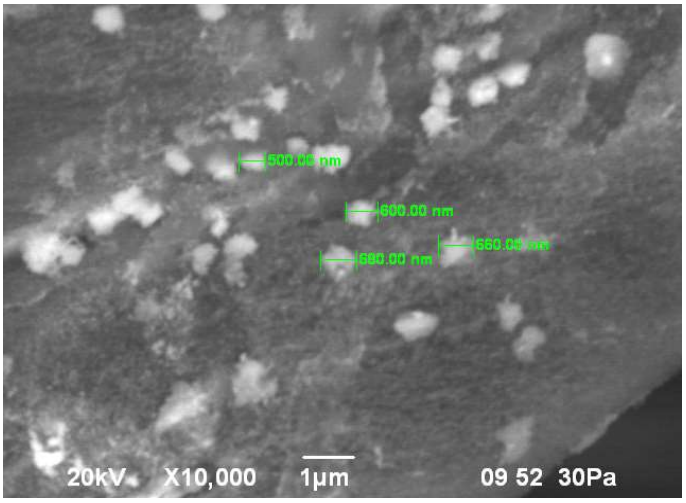

Fig.-9: SEM Image of Structure of Silver-containing Films produced by Photochemical Method

Therefore, photooxidation of cellulose-containing fabric by Sunlight in the presence of silver nitrate leads to the formation of silver-containing films. The process proceeds only due to the presence of aldehyde groups of end links of cellulose and does not require the use of other reducing agents.

It should be noted that the samples of fabrics containing films of both copper and silver demonstrated high stability in solutions containing washing powders. After one hour of stirring a sample placed in a hot (40°C) solution containing 20 g/l of washing powder in a magnetic stirrer, the blackness of the silver-containing sample decreased by 3%, and the copper-containing one by 5%.

CONCLUSION

The aldehyde groups of end links of cellulose can undergo photooxidation under the influence of electromagnetic waves of Sunlight.

This promoted the creation of a technology for producing copper- and silver-containing films on cellulose-containing fabrics. Thus, surface films containing elemental silver are formed on fabrics wetted with silver nitrate solutions and dried in the sun. A similar use of copper dichloride allows obtaining a film containing monochloride and elemental copper. Additional photochemical treatment with ascorbic acid reduces copper monochloride to elemental one.

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