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Chemical Copper Plating of Cotton Fabrics by Photochemical Activation of the Surface

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Abstract: *Activation of the surface of cotton fabrics before chemical copper plating is proposed to be carried out by applying dispersed copper particles. For this purpose, physical and chemical processes that occur in thin layers of copper chloride solutions under the influence of electromagnetic solar rays of the visible spectrum are used. Initially, copper chlorides interact with cellulose, which is the main component of the tissue, and form copper monochloride. It is shown that this interaction is stimulated by solar rays. After that, the fabric is moistened with a solution of ascorbic acid and again exposed to sunlight. Under the action of photons of solar radiation, electrons in a semiconductor acquire additional energy and restore copper to the elemental state, and the vacancies formed are filled with electrons due to the oxidation of ascorbic acid. As a result of these processes, a film is formed on the surface of the tissue containing copper particles that can catalyze chemical copper plating.*

Keywords*: cotton fabric, photochemical process, copper chloride, copper monochloride, activation*

1. Introduction

In recent years, the use of copper as a measure to prevent the spread of bacteria has been widely recognized. Among the antimicrobial and antiviral properties of copper, it should be noted that it effectively inactivates methicillin-resistant strain of Staphylococcus aureus, known as" supermicrob " MRSA [1] and viruses of the SARS-Cov-1,2 type [2]. It should be noted that the SARS-Cov-2, dubbed "COVID-19", is associated with a pandemic announced this year by WHO.

Areas of application of fabrics containing copper coatings, as well as some of its compounds, are constantly expanding [3-5]. Such fabrics are proposed to be used for the manufacture of medical devices, various types of military uniforms, sports clothing, underwear, and covers for weapons that protect them from various kinds of microorganisms. In Russia, the company "Center for modern social technologies SOCTECH" is widely advertised, which offers products of more than 100 names of copper-containing yarn under the General brand "Magic of Copper" [6].

The use of dielectric materials containing copper coatings for protection against electromagnetic radiation is also relevant. There is a higher protective ability against electromagnetic radiation of the layer of chemically deposited copper compared to chemical nickel [7].

A number of physical and chemical methods have been developed for obtaining dielectric materials with a metal coating, which can also be used for applying copper particles.

In physical methods of metallization, metal particles are applied by gas-phase, magnetron, plasma vacuum or laser deposition [8-11]. These processes require special equipment; in addition, additional operations are required to pre-obtain metal particles.

For chemical deposition of metal coatings, reducing agents are used in the gas phase, or dissolved in an electrolyte solution.

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Phosphine (PH_3) is proposed as a reducing agent in the gas phase [12, 13]. The use of phosphine allows the process to be carried out at low temperatures. The resulting metal-like copper phosphide has sufficient electrical conductivity and can serve as a sublayer for further metallization. But, this method has certain difficulties due to the toxicity of this gas and the need to conduct the process in sealed devices.

The most commonly used method of chemical metallization of dielectrics in engineering is that a reaction of reduction of catalytic metal ions is carried out on a surface sensitized with divalent tin. The treatment is carried out in solutions of noble metals, mainly palladium. Tin ions adsorbed on the dielectric surface restore palladium ions: compounds of germanium (II), iron (II), titanium (III), silicon halides, lead salts, and some dyes are also offered as sensitizers. In addition to palladium, Pt, Ag, Au, Ro, Ru, Os, and Ir are also mentioned as catalyst metals. The disadvantage of this method is the use of expensive salts.

Other compounds have been proposed as liquid-phase chemical reducing agents: hydrazine sulphate, sodium hypophosphite, formaldehyde, and dimethylformamide [14]. Deposition of copper nanoparticles (as well as silver and gold) on the surface of polymer microspheres in [15-17] was carried out by photochemical means. It is noted that the surfaces of polymer microspheres, acting as centers of sorption of metal nanoparticles, make it possible to obtain the latter in the form of stable dispersions. However, the possibilities of practical application of this process for obtaining metal coatings are not considered.

In [18-19], the technological parameters of photochemical production of films of metals of the copper subgroup on textile materials are given. In these studies, their bactericidal properties were revealed, and other functional characteristics of the films were not considered. The resulting films consist of separate dispersed particles and do not have electrical conductivity, but such particles can be catalysts for chemical metallization. It follows that obtaining metal coatings of copper using photochemical methods is technologically feasible, but requires additional development.

2. Materials and methods

Cotton gauze cloth (article No. AA010278), widely used for medical purposes, was used for research. These fabrics are 97-98% cellulose. Each elementary link of the cellulose macromolecule - anhydroglucose-contains three alcohol hydroxyl, which makes it very sensitive to the action of oxidants. As a result of oxidation of alcohol hydroxyl groups, new carbonyl and carboxyl functional groups are formed in cellulose macromolecules. Oxidation begins at the surface of the fiber, and then gradually moves to deeper layers, with the amorphous part first oxidized, and then the crystalline sections [20].

To obtain metal coatings, it is proposed to use the technology of physical and chemical processes occurring in thin layers of electrolyte solutions under the influence of sunlight. Sunlight is often referred to as visible solar rays that have a wavelength of 400 to 700 nm. The energy flux density of solar radiation reaching the earth's surface reaches up to 1.4 kW/m^2. Light waves can also penetrate solid bodies, but their intensity decreases [21]. In this case, an important characteristic of the rays is the density of the solar radiation flux. To determine this value, the SM-206-SOLAR solar radiation meter was used. This meter is an accurate instrument for measuring light intensity. It is used in solar radiation measurements, solar research, physical and optical experiments, meteorology, and agriculture.

In general, the density of the solar radiation flux is affected by climatic conditions, the time of year and day, in addition to the drying process of the fabric is affected by the ambient temperature. Therefore, the main studies of the process were carried out in a laboratory room, where the temperature was maintained at 25-30^{0}C. The sun's rays penetrating through the window panes had a flux density of 1200-1300 W/m^2. Electromagnetic sun rays can penetrate through the thin solid body and the liquid medium. This promotes photochemical reactions on the inner surfaces of porous materials (e.g., fabrics) and on etched surfaces of dielectrics, increasing the adhesive properties of the applied films (Table 1).

Table 1. Permeability of certain materials when passing electromagnetic solar rays of the visible spectrum

No.	Name of the material	Thickness, mm	W, W/m^2	n, %
1	In the absence of material	-	1305	100
2	Laboratory glass	1	1214	93
3	Window glass	4	1156	88
4	Transparent polyethylene film	0.1	1184	90
5	Black polyethylene film	0.05	23	1.7
6	Red polyethylene film	0.05	1056	81
7	Green polyethylene film	0.1	493	37
8	Blue plastic film	0.1	920	70
9	White cotton fabric	0.3	351	27
10	Plexiglass plate transparent	2	1227	91
11	Plexiglass plate black	2	0	0
12	Copper plate	0,2	0	0
Designation: W- density of solar radiation energy flow after passing through the specified material, W/m^2; n - degree of permeability when the energy flow passes through the material %.				

To determine the electrical conductivity of the resulting films, a DT-830B resistance tester was used. In this case, the tester's probes were placed at a distance of 1 cm from each other and an average of 5 measurements was found. Measuring the electrical conductivity of pure copper under similar conditions, we evaluated the suitability of the resulting films for building up galvanic coatings.

The structure and composition of films and coatings were studied using the ISM-6490-LV scanning electron microscope (JEOL, Japan). The device allows you to get an electronic image of particles in the size of tens of nanometers, the elemental composition and the percentage of elements in the surface layers of the film.

When a photochemical reaction occurs on the surface of the tissue, a black film is formed, which characteristic of fine metal particles is obtained by chemical reduction.

It is known that most monovalent compounds of the copper subgroup easily disintegrate when heated slightly and under the action of light. It is also known that metal halides of the copper subgroup belong to binary semiconductors. Therefore, there is a relationship between semiconductor properties and light sensitivity. Therefore, to obtain a film with light sensitivity, it is sufficient to create a layer of monovalent halides of these elements on the surface of the dielectric.

The most common, as well as cheaper, halides of these metals are chlorides. Therefore, most of the experiments are conducted with copper chlorides, although some experiments have shown the possibility of using copper bromide for this purpose.

Preliminary preparation of the tissue sample was carried out by degreasing in ethyl alcohol (10 minutes) and washing with distilled water. The process consisted of wetting the fabric by dipping it for a few minutes in a solution of $CuCl_2$, while a sorption layer containing 0.5 ml/dm^2 of this solution is formed on the surface of the fabric used in this work. This fabric was then dried when exposed to sunlight. In this case, the following qualitative change of the surface film occurs: $CuCl_2 \rightarrow CuCl \rightarrow Cu$. Dispersed copper particles give the film a black color. Moreover, the intensity of the black color of the film depends on the concentration of the initial solution of $CuCl_2$. Therefore, the degree of blackening of the film can be used as an indicator that characterizes the content of reduced metal particles in the film. Quantitative characteristics of the intensity of black film samples can be determined using a computer by changing the brightness in the window.

3. Results and discussions

When exposed to solar radiation, the following processes occur on the surface of the fabric previously moistened with a solution of $CuCl_2$:

- evaporation of water from the solution in the surface layer on the tissue, leading to an increase in the concentration of copper chloride;
- the interaction of dichloride of copper with cellulose with the formation of copper monochloride (binary semiconductor);
- photochemical reaction with the formation of elemental copper;
- complete drying of the surface water layer, resulting in the termination of the photochemical reaction

The formation of a semiconductor layer of monovalent copper chloride occurs due to the interaction of $CuCl_2$ with cellulose.

$$2CuCl_2 + H_2O + R\text{-}OH \rightarrow 2\ CuCl + 2\ HCl + R\text{-}OOH \qquad (1)$$

where R - the elementary unit of cellulose.

Monovalent copper chloride is a binary semiconductor, so when photons are exposed to electromagnetic rays of sunlight, some of the electrons passes into the conduction band and acquire the ability to restore monovalent copper

$$CuCl + e \rightarrow Cu + Cl^-, \qquad E^o = 0{,}137\ B \qquad (2)$$

where E^o - the standard potential of the electrochemical reaction

After that, vacancies remain in the semiconductor, for which only CuCl and a water molecule can be used as electron donors. If we consider that the oxidation of water molecules at a *p*H of less than 7 requires a potential of more than 0.8 V, then the preferred electron donors will be CuCl molecules.

$$CuCl + Cl^- - e \rightarrow CuCl_2, \qquad E^o = 0.538 \qquad (3)$$

The electromotive force of the reaction 2 and 3 is -0.401 V. Therefore, the additional energy received from the sun's rays must provide a real voltage in the system exceeding this value. In this case, a photochemical reaction will occur.

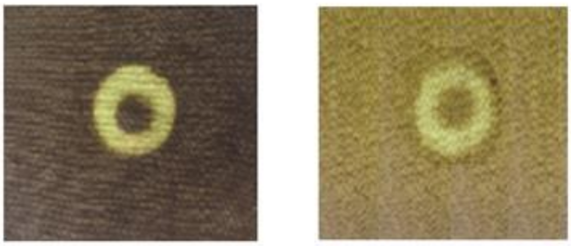
$$2CuCl \xrightarrow{h\nu} Cu + CuCl_2 \qquad (4)$$

Moreover, $CuCl_2$, when the surface film dries, crystallizes and loses its activity, which is an additional factor contributing to the reaction 4.

The resulting particles of elemental copper give the film a black color characteristic of metals obtained from salt solutions using various reducing agents.

The degree of blackening of the fabric surface depends on the intensity of solar radiation and the concentration of copper chloride in which the fabric was soaked. Moreover, not only the side facing the solar radiation turns black, but also the opposite side. While the degree of blackening of the reverse side is always lower than the front side (Figure 1). This is due to the permeability of electromagnetic solar rays through these materials. Light waves can also penetrate some solids, but their intensity decreases, and with a sufficient thickness of black materials, the permeability becomes zero.

So, if part of the fabric surface is shielded with a black washer (2 mm thick), then the color of the fabric does not change under the washer. After washing the fabric, the elemental composition of these areas corresponded to the original composition. This shows that reaction 1 is stimulated by electromagnetic solar rays and does not occur in their absence. In addition, in the absence of a semiconductor film of copper monochloride, respectively, photochemical reactions 2, 3, 4 will not occur.



a **b**

Figure 1. Photochemical films on tissue samples from the side facing the solar radiation (a) and from the opposite side (b)

The dependence of the degree of blackness of the fabric on the concentration of $CuCl_2$ in the solution used to create the sorption layer is shown in Figure 2.

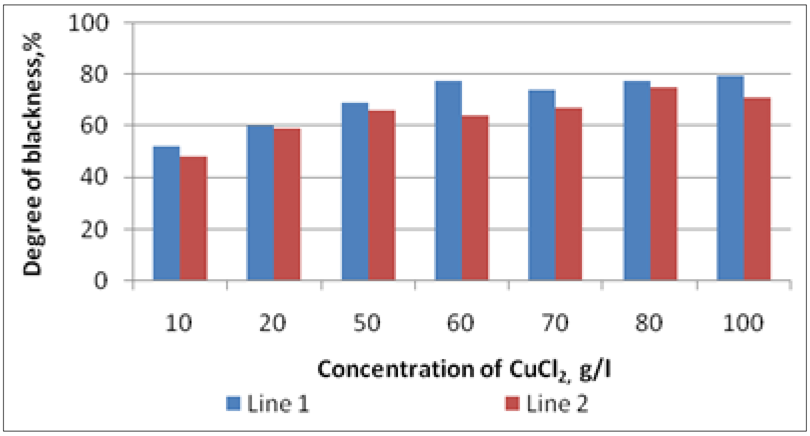


Figure 2. Effect of the concentration of $CuCl_2$ in the solution used to create the sorption layer on the degree of blackness of the tissue after photochemical processes: Line 1 is the front side of the fabric; Line 2 is the back side of the fabric

As can be seen from the figure, the degree of blackness of the front side, which was directly exposed to sunlight, at all concentrations is higher than the degree of blackness based on the change in the density of the ray flux when penetrating the thickness of the fabric. Thus, the beam flux density changed quite significantly: from 1305 to 351 W/m^2. This indicates that other factors, such as the duration of drying of the surface film, also influence the degree of transition $CuCl_2 \rightarrow CuCl \rightarrow Cu$.

In addition, the figure shows that concentrations of more than 60 g/L no longer affect the degree of blackness of the resulting film. This allows us to consider this concentration optimal for this tissue. Further increase in the concentration of $CuCl_2$ leads only to an increase in its content in washing solutions.

Thus, when exposed to sunlight on the surface layer of copper chloride, films consisting of copper particles and $CuCl_2$ are formed. This system is stable only in the absence of water, since in the presence of water, a thermodynamically more likely reverse reaction occurs.

$$CuCl_2 + Cu \rightarrow 2CuCl \quad (5)$$

This makes it impossible to further process the tissue with water solutions. The formation of $CuCl_2$ is associated with the reaction (3), so it is necessary to add a reagent to the reaction medium that would have a higher donor capacity than copper monochloride. Our experiments have shown that such a reducing agent is ascorbic acid, which is then oxidized to dehydroascorbic acid.

It is known from the literature [22] that the redox potential of the ascorbic acid-dehydroascorbic acid system changes from -0.329 V to – 0.057 V when the *p*H increases from 0 to 7. in Addition, it is noted that this system is electrochemically inert, and "electrode catalysts"must be added to display redox properties. Indeed, experiments have shown that no traces of chemical transformation are found on tissue moistened with a solution of $CuCl_2$ - 60 g/L, A-$(OH)_2$-80 g/L and dried in the dark. At the same time, these samples, dried when exposed to sunlight, are covered with a black film, characteristic of dispersed metal particles. At the same time, if individual sections are shielded from the sun's rays with polymer washers, these sections remain unchanged. Therefore, under the influence of sunlight, ascorbic acid is activated and promotes the transition from CuCl→Cu.

$$A\text{-}(OH)_2 - e \rightarrow A\text{-}OOH \quad (7)$$

where A is not a changing part of ascorbic acid

General photochemical reaction will have the form

$$CuCl + A\text{-}(OH)_2 \xrightarrow{h\nu} Cu + HCl + A\text{-}OOH \quad (8)$$

A-$(OH)_2$ and A-OOH easily removed when rinsed. Therefore, A-$(OH)_2$ prevents the formation of $CuCl_2$ and helps to preserve the film containing elemental copper particles on the surface of the tissue. The equivalent ratio of $CuCl_2$: A-$(OH)_2$ = 1:1.1 provided the maximum degree of blackness of the fabric surface.

Thus, a film containing elemental copper in the form of spherical particles with a diameter of 100-200 nm remains on the surface of the dielectric (Figure 3). This film can be used as an activator of chemical copper plating.

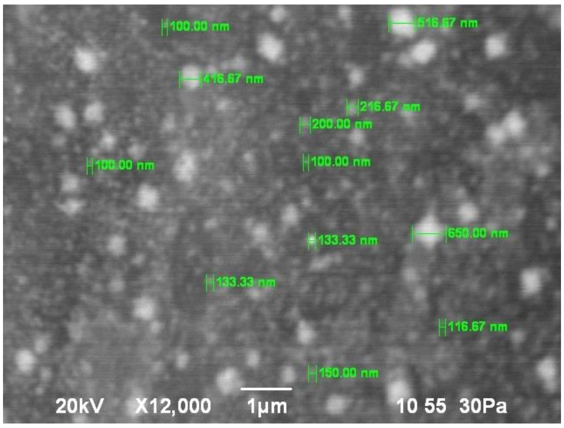
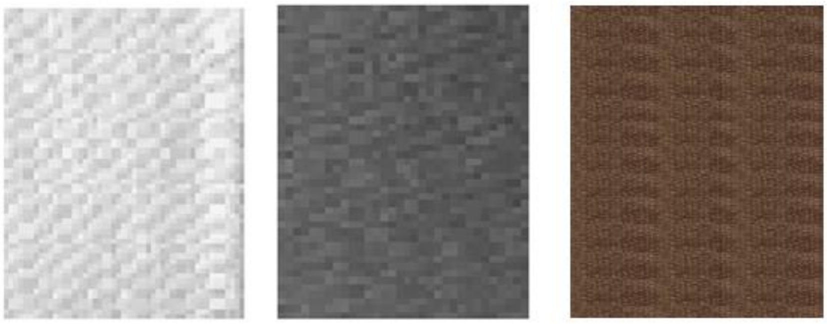


Figure 3. Structure of copper films obtained by photochemical method

Taking into account this mechanism, the process of obtaining an electrically conductive copper film was performed as follows. The original fabric (Figure 4a) was wetted in a $CuCl_2$ solution and after the fabric dried, a black film remained on its surface. The sample was then washed with distilled water. In this case, the excess $CuCl_2$ and the reaction by – product (1) - HCl were washed off. The washed cloth contained only copper monochloride. This sample was lowered into a solution of A-$(OH)_2$ (80 g/l) and subjected to repeated exposure to sunlight. In this case, a black film was formed again, which can be washed off from the compounds A-OOH and excess A-$(OH)_2$. This film contains particles of elemental copper, which are catalysts for chemical copper plating (Figure 4b). Subsequent chemical copper plating was performed in a solution of the composition: $CuSO_4 \bullet 6H_2O$-20 g/L, NaOH to *p*H=12.5, formalin-15 g/L. The process was carried out at room temperature until the gas release was stopped (about 2 h). In this case, a brown coating was obtained (Figure 3c), which has an inherent electrical conductivity for metals.



a b c

Figure 4. Changes in the appearance of a tissue sample at certain stages of chemical copper plating: a-initial sample; b-sample after applying catalytically active copper particles; c-sample after applying chemical copper

4. Conclusions

When exposed to sunlight on cotton fabric moistened with a solution of $CuCl_2$, initially due to the interaction of chloride with cellulose, which is the basis of the fabric, monovalent copper chloride is formed. This copper compound is a binary semiconductor and in the future, under the influence of sunlight, a photochemical reaction of the formation of elemental copper occurs, and to provide electrons for the vacancies formed in this case, the tissue is additionally moistened with a solution of ascorbic acid. As a result of these processes, a film containing dispersed copper particles is formed on the fabric. This film can serve as a catalyst for chemical copper plating.

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