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CHEMICAL NICKEL PLATING OF COTTON FABRICS WITH THE USE OF COPPER-CONTAINING REDUCING AGENTS*

ХИМИЧЕСКОЕ НИКЕЛИРОВАНИЕ ХЛОПЧАТОБУМАЖНЫХ ТКАНЕЙ С ПРИМЕНЕНИЕМ МЕДЬСОДЕРЖАЩИХ ВОССТАНОВИТЕЛЕЙ

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To activate the surface of cotton fabrics before chemical nickel plating, it is proposed to use physical and chemical processes occurring in thin layers of solutions of copper (II) chloride under the influence of electromagnetic solar rays of the visible spectrum. It is shown that cellulose, which is the main component of the fabric, undergoes photo-oxidation in the presence of copper (II) chloride. As a result of this interaction, well-bonded copper monochloride is formed. When further processing of the fabric with phosphine gas, copper monochloride is transformed into copper and copper phosphide. Copper phosphide is a catalyst for the chemical nickel plating process. This makes it possible to obtain an electrically conductive nickel-phosphorus coating on the surface of the fabric in conventional electrolytes of chemical nickel plating. It is also found that when screening individual sections, the processes leading to the formation of copper monochloride do not occur. This allows selective metallization of the fabric.

Для активирования поверхности хлопчатобумажных тканей перед химическим никелированием предлагается использовать физико-химические процессы, протекающие в тонких слоях растворов хлорида меди(II) под воздействием электромагнитных солнечных лучей видимого спектра. Показано, что целлюлоза, являющаяся основным компонентом ткани, в присутствии хлорида меди(II) подвергается фотоокислению. В результате этого взаимодействия образуется хорошо сцепленная с тканью однохлористая медь. При дальнейшей обработке ткани газообразным фосфином однохлористая медь трансформируется в медь и фосфид меди. Фосфид меди является катализатором для процесса химического никелирования. Это позволяет получить на поверхности ткани электропроводное никель-фосфорное покрытие в обычных электролитах химического никелирования. Также установлено, что при экранировании отдельных участков процессы, приводящие к образованию однохлористой меди, не происходят. Это позволяет провести избирательную металлизацию ткани.

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Keywords: cotton fabric, copper (II) chloride, cellulose photo-oxidation, copper monochloride, activation, copper phosphide, chemical nickel plating.

Ключевые слова: хлопчатобумажная ткань, хлорид меди (II), фотоокисление целлюлозы, монохлорид меди, активация, фосфид меди, химическое никелирование.

Introduction

The acceleration of technological progress poses new challenges to the industry within the field of cloth production. One among them is that the creation of metalized fabrics that perform a particular function. A prominent place among them is occupied by nickel-plated fabrics. Nickel may be a relatively inexpensive metal with high chemical resistance and good appearance.

Nickel coating gives fabrics the subsequent functions that allow the utilization of textiles within the relevant industries:

- decorative appearance, electrical conductivity, which provides fabrics antistatic properties [1];
- creation of a lively catalytic layer on the material surface of the required layer necessary for chemical current sources and devices for producing hydrogen [2], 3];
- giving fabrics a particular electric resistance allows them to be used as flexible conductive elements, clothing with heating elements [4];
- shielding of electromagnetic wave and use in various protective devices [5…7];
- radio-absorbing properties that are widely utilized in modern industry and, especially, in products of the vested interest [8].

Depending on the aim of cloth materials, the subsequent methods of applying nickel films are used.

To obtain thin surface nickel films on synthetic fabrics, ion-plasma sputtering [1] or vacuum sputtering [9] of the nickel layer is employed. Processes are administered on special installations. Such fabrics have good decorative properties and high electrical conductivity, which allows them to be used as flexible conductive elements and when creating smart textiles [4].

By combining the most threads of the material with nickel or nickel-containing polymer threads, a textile material is obtained which will function a shield of electromagnetic wave [5…7]. it's obvious that during this case the difficulties related to the creation of additional threads.

To obtain special-purpose textile materials, chemical metallization methods also are used. Thus, chemical gas-phase metallization is performed by pumping nickel tetracarbonyl metal vapors through a woven or non-woven material during a shallow vacuum. The source material is heated to the temperature of the start of vapor decomposition, and a metal coating is applied over the whole thickness of the majority material [5]. The disadvantage of the method is that the difficulty in obtaining nickel tetracarbonyl and implementing the method.

The most commonly used method of chemical metallization of dielectrics in engineering is that a reaction of formation of catalytic metal ions is administered on a surface sensitized with divalent tin. Treatment is administered in solutions of precious metals, mainly palladium. Adsorbed on the surface of the dielectric ions are tin ions restore the palladium. Compounds of germanium (II), iron (II), titanium (III), silicon halides, lead salts, and a few dyes also are offered as sensitizers. additionally to palladium, silver, gold, rhodium, ruthenium also are mentioned as catalyst metals [10]. The disadvantage of this method is that the use of pricy salts of those metals.

A number of works are dedicated to palladium-free activation of the dielectric surface with the assembly of dispersed copper particles using chemical reducing agents [11…13]. The resulting films don't have sufficient electrical conductivity for the electroplating process, and aren't catalysts for chemical nickel plating. this needs the next application of a layer of chemical copper, on which the electroplated nickel is then deposited.

It should be noted that photochemical methods also can be wont to activate the dielectric surface. Thus, treatment with solar rays results in the reduction of silver from its halides [14], [15].

These data show that there are still unsolved problems in existing methods of nickel plating of materials, therefore the creation of latest alternative technologies has relevancy.

Materials and Methods

Cotton gauze cloth (article No. AA010278), widely used for medical purposes, was used for research. So as to get rid of industrial contamination, the material was prepared by holding it for half-hour in hot (70ºC) water. Then, after washing and drying, the samples were cut out. The obtained samples were wetted by dipping for a couple of minutes in $CuCl_2$ solution. Then, the sample was placed on a glass or polymer surface and smoothed with a glass stick. The quantity of $CuCl_2$ solution introduced into the material was about 0.5 ml/dm^2. Then, the samples were dried under the influence of sunlight. Sunlight is an electromagnetic ray that features a wavelength from 400 to 700 nm. Light waves also can undergo solid bodies, but their intensity decreases. A crucial characteristic of the rays is that the density of the radiation flux [16]. To work out this value, the SM206-SOLAR radiation meter was used. Studies of the method were administered during a laboratory room, where the temperature was maintained at 25-30ºC.

To conduct experiments, the samples were placed perpendicular to the sun's rays and exposed until completely dry. The colour of the sample changed from green (the color of $CuCl_2$ solutions) to black. Black color is typical for fine metal particles formed during chemical reduction.

Moreover, the intensity of the black color of the film depends on the concentration of the first $CuCl_2$ solution during which the material was wetted. Therefore, the degree of blackening of the film is often used as an indicator of the content of reduced metal particles within the resulting film. Quantitative characteristics of the intensity of black film samples are often determined employing a computer by finding the degree of brightness of the drawing within the work with drawing window. To try to this, photos of samples obtained at various stages of the method were placed on white book and brightness was added for every sample until the image of the drawing disappeared completely. This added brightness was the degree of blackness (as a percentage) of the film on the sample. For instance, the degree of blackness within the computer's color palette was 100%.

After photochemical treatment, the samples were washed with water to get rid of the reaction byproduct (HCl) and excess $CuCl_2$, and dried at temperature for half-hour. The marginally moistened fabric contained only copper chloride (1). In some experiments, a part of the material surface was shielded with a black polymer washer with a thickness of two mm, which prevents the sun's rays from penetrating the material.

This sample was then placed during a sealed chamber for treatment with phosphine gas (PH_3). Phosphine may be a strong reducer and, when interacting with the surface film, reduces copper (I) chloride to elemental copper and copper phosphide [17]. Additionally, phosphine contributes to the formation of copper phosphide within the surface film, which provides it catalytic properties that allow it to get a chemical nickel coating of the specified thickness that's immune to atmospheric conditions [18].

The structure and composition of films at separate stages of the process were studied using a raster electron microscope ISM-6490-LV (JEOL, Japan). The device allows you to get an electronic image of particles with a size of tens of nanometers, the element composition and the percentage of elements in the surface layers of the film.

Results and Discussions

To apply nickel coatings to fabrics, the subsequent basic operations are required:

- creating an indelible layer of copper chloride (I) on the surface of the fabric;
- transformation of chloride (I) to copper phosphide;
- obtaining a metal coating by chemical nickel plating.

The creation of an indelible layer of copper monochloride on the surface of the material was administered by exposure to radiation on the surface of the material, previously moistened with an answer of $CuCl_2$. The cellulose that creates up the material contains three alcohol hydroxyl, which in certain cases are often subjected to oxidation. When drying such a cloth under the influence of sunlight, cellulose is photo-oxidized by reaction 1. During this case, the role of the oxidizer is performed by $CuCl_2$.

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

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

$$CuCl + e \rightarrow Cu + Cl^-, \quad (2)$$

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 pH of less than 7 requires a potential of more than 0.8 V, then the preferred electron donors will be CuCl molecules.

$$CuCl + Cl^- - e \rightarrow CuCl_2, \quad (3)$$

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.

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

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.

Figure 1 shows photos of a fabric sample before (a) and after (b) applying a photochemical copper film. Measurements of the degree of blackness according to the above method showed that for the original fabric, this value is 22%, and after applying the film, 65%. The formation of a black film on the surface of the tissue shows the possibility of reaction 4.

a) b)

Fig. 1

During subsequent washing with water, the non-reacting 1 part of the original $CuCl_2$ is removed. In addition, this leads to the disappearance of the black color of the fabric. Therefore, the secondary $CuCl_2$ formed by reaction 4 is not removed during washing, but remains in the structure of the binary semiconductor. Under the influence of water, it is activated again and contributes to the flow of reaction 4 from right to left. This is confirmed by the fact that if the washed fabric is dried again under the sun, the black film appears again. Moreover, the degree of blackness is practically unchanged. Thus, as a result of photochemical processes, a layer of elemental copper (if the fabric is dry) or a layer of monochlorous copper (if the fabric is moistened) is formed on the surface of the fabric.

Electromagnetic rays of the sun can partially penetrate the fabric material, and the oxidation process begins at the surface of the fiber, and then gradually moves to deeper layers, while first the amorphous part is oxidized, and then the crystalline sections. This leads to the fact that the formation of CuCl occurs both in the surface and deep layers of the fabric. As a result, there is a good connection between the copper, it and the fabric. Perhaps chemosorption is taking place here.

After treatment with phosphine, the fabric acquired a stable dark color, which did not change when washed with water. The dark color is characteristic of copper phosphide Cu_3P. Elemental analysis also showed the appearance of phosphorus in the surface film. The analysis also showed the presence of chlorine in the surface film. This may be due to the partial oxidation of copper, which leads to the formation of insoluble basic copper chloride. Moreover, this compound does not affect the process of chemical nickel plating.

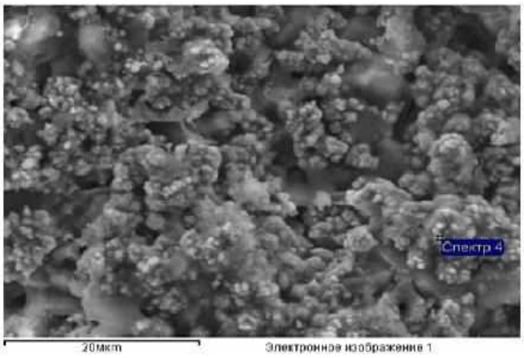

Fig. 2

Chemical nickel plating in the electrolyte usually used in practice made it possible to obtain an electrically conductive film on the fabric without much difficulty. The process was performed at room temperature for 1 hour. At a loading density of 2 dm^2/l, an electrically conductive coating ($p=7\times10^{-7}$ Om×m) was obtained (Fig. 2). Visual comparison of the diameters of the outer threads of the fabric in Figure 5 showed an increase of 1.3-1.6 microns. At the same time, high electrical conductivity was both illuminated by the sun's rays, and the reverse side of the fabric.

Spectral analysis of the surface layer showed that the film has a composition characteristic of coatings obtained by chemical nickel plating. At the same time, the fabric has a soft neck, air and moisture permeability, and retains its strength characteristics (Fig. 3, Table 1).

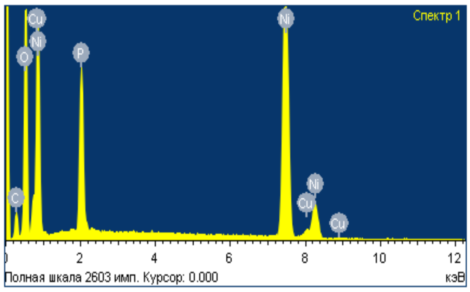

Fig. 3

Table 1

Element	Weight, %	Atomic, %
C	10.35	24.58
O	21.71	38.70
P	8.66	7.98
Ni	57.96	28.15
Cu	1.32	0.59
Total	100.00	

CONCLUSIONS

The following basic processes were used for nickel plating of cotton fabrics. Pre-soaked in a solution of dichloride of copper were dried by exposure to sunlight. At the same time, due to the influence of electromagnetic waves of solar radiation, cellulose (the main component of the fabric) was oxidized and copper monochloride was formed. The permeability of electromagnetic waves leads to the formation of copper monohydrate on both sides of the fabric. Moreover, copper monochloride is strongly bound to the fabric and can withstand numerous washings.

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