

## Electroless deposition of nanodisperse metal coatings on fabrics

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Metal plated fabrics are modern composite materials characterized by a combination of the beneficial physiological and ergonomic properties of the textile substrate with those of the deposited metal coating.

A technology was developed for deposition, by chemical methods, of nanodisperse copper coatings with various types of dispersoids (graphite, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) onto two types of polyethyleneterephthalate (PET) polyester fabrics: woven and non-woven. The influence of the deposition conditions of the coatings on their thickness, electroconductivity, elemental composition and morphology was studied.

**Key words:** Electroless copper plating, Nanodisperse metal coatings, Woven fabric, Non-woven fabric, Specific electrical resistance, Electromagnetic interference shielding.

### 1. INTRODUCTION

Metal plated fabrics have valuable properties which make them suitable for various applications in everyday life and in engineering technologies.

Metal plated fabrics are electroconductive and are employed in electrical engineering and electronics as electric heating components. These materials are used for production of highly efficient plastic screens [1, 2] for protection against electromagnetic emissions within the radio wavelength range. The good heat reflecting properties of metallized fabrics make them perspective materials for green house construction elements, for manufacture of cold/heat-resistant clothing for protecting people exposed to extremely low or high temperatures for many hours.

All known methods for metal plating of dielectrics are employed in the process of metallization of fibres and textile materials of various chemical nature. The electroless deposition via reduction of metal ions in aqueous solutions has proved to be the most readily available, convenient and highly effective technique for deposition of metal coatings onto dielectric substrate. Various methods for metal plating of fibres and fabrics have been described in a number of articles and patents [1–6].

Reference [3] treats the two-step activation of a cotton fabric, whereby the object is first immersed

in a solution containing Sn<sup>2+</sup> or Ti<sup>3+</sup>, and then in a noble metal solution, preferably of PdCl<sub>2</sub>. Then the object is chemically plated with copper or other metal coating. Most often fibres or fabrics of PET are metal plated, which is the reason why their behaviour in alkaline medium has been investigated by many authors [4–7].

A detailed study into the pre-treatment of polyester fibres with potassium or sodium hydroxide has been described in reference [4]. The authors have established that as a result of the above pre-treatment the mass of the PET fibres is reduced by about 10%, the surface is roughened and its area increased. Moreover, etching leads to formation of caverns on the polymer surface thus increasing the thickness of the metal deposit and improving its adhesion to the substrate. The authors state that the reason for these changes is not clear.

The research reported in reference [5] has established that  $\text{PET} + 2\text{OH}^- \rightarrow \text{disodium terephthalate} + \text{ethylene glycol}$ .

The rate of polymer dissolution increases with time, temperature and area of the processed surface. The alkali concentration and the presence of a cationic surface active substance (SAS) also have an impact on the process rate.

The thickness of electroless nickel or copper coatings deposited on a textile made of polyethyleneterephthalate, as well as their adhesion and specific electrical resistance have been investigated with regard to their dependence on the etching conditions in alkaline medium and on the duration of the electroless metallization process [6].

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It has been found that with increase of NaOH concentration in the etching solution up to 250 g/L the thickness of the deposited nickel coating grows to 0.80  $\mu\text{m}$ , the adhesion determined by the metal loss in dry friction being relatively low (1.0 mg/dm). At higher alkali concentrations the investigated parameters substantially decline. The thickness, adhesion and specific electrical resistance of the coating are most significantly affected by the duration of the electroless metallization process. With an increase of the nickel layer thickness up to 3.2  $\mu\text{m}$  the metal loss rises up to 18.4 mg/dm, the specific resistance being  $0.69 \times 10^{-2} \Omega\text{m}$ .

Lately, the so called disperse coatings have been used in engineering technology. A basic characteristic of these coatings is that solid dispersoids are incorporated into the base deposition material (called matrix), thus forming a second phase. The preferred metals for matrix deposition are nickel, cobalt, copper, etc. The physical and chemical properties of dispersoids affect the properties of the deposited disperse coating. Possible dispersoids may be micropowders of nanoparticles of high-melting-point oxides, carbides, silicides, borides, nitrides, diamonds, etc.

The influence of the particle size of diamond and tungsten carbide (150, 1000, 2000 nm) dispersed in cobalt and nickel coatings on their adhesion, hardness and tribological behavior is discussed in ref. [8, 9]. It has been established that these coatings could be an alternative to chromium coatings obtained via reduction of hexavalent chromium.

The literature survey evidences that nanodisperse coatings are mostly deposited on solid metal or dielectric substrates.

The aim of the present work is to produce nanodisperse coatings on textile materials (fabrics), which can find wide application in engineering technology (industry).

## 2. EXPERIMENTAL

Electroless deposition of disperse copper coatings on substrates of woven and non-woven textile ("Yambolen", Bulgaria) was carried out employing the following technological scheme: degreasing in alkaline solution for 15 min at 65°C; activation in colloidal activator A-75-12 (product of the Technical University-Sofia) for 5 min; alkaline treatment by a commercial X-75-4 accelerator (product of the Technical University-Sofia) for 5 min; chemical plating in copper containing electrolyte.

The basic components of the base electrolyte (BE) (working electrolyte, WE) were copper sulfate, formaldehyde,  $\text{Na}_2\text{-EDTA}$  complexing agent and stabilizer2 (a commercial product of the Technical University-Sofia). The working electrolyte had a pH within the range 12.5÷12.8.

It is a must to use non-stationary electrolytes for the deposition of disperse coatings in order to avoid sedimentation of the dispersoid. That is why air agitation was employed in the present experiments. The dispersoids used were graphite,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  in the form of powders with particle size between 30 and 60 nm for  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and between 7 – 10  $\mu\text{m}$  for graphite particles (Institut für Baustoff- und Umweltschutz-Technologie GmbH Weimar, Germany).

The deposition rate was determined by gravimetric analysis. The obtained thickness was called by us "conditional thickness of the coating".

Energy dispersive X-ray microanalysis (EDX) was used to determine the content of the dispersion particles in the coating. The coating morphology and the particle size distribution on its surface were examined by scanning electron microscopy (SEM) on the JEOL JSM 733 (Japan) microscope.

The electric conductivity of the metallized specimens was measured on a stand specially designed to that end, using a method similar to the four-point probe for measuring the conductivity of semiconductor materials.

The phases contained in the deposits were identified by X-ray diffraction analysis (XRD). An automated vertical powder diffractometer Philips PW 1050 equipped with a secondary monochromator (Cu  $K\alpha$  radiation) was used for the purpose. The XRD patterns were recorded within the angle range from 10 to 80 degrees  $2\theta$  at an angle step of 0.04° and 1s exposition time.

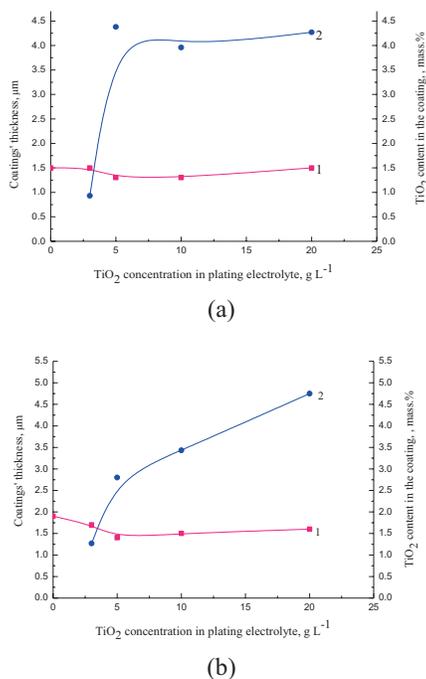
Adhesion tests of the coatings were carried out at the Technical University-Sofia and the samples were subjected to burnishing in dry and wet conditions (according to Bulgarian Standard 4680-87).

## 3. RESULTS AND DISCUSSION

### 3.1. Influence of dispersoid concentration on the conditional thickness of the coating and on its incorporation in the coating

It was established in our previous investigations [10] that the conditional thickness of the coatings increases with increasing deposition time and temperature. The best incorporation in the chemically obtained disperse coatings was observed

for TiO<sub>2</sub> as compared with the other dispersoids. Therefore, TiO<sub>2</sub> was selected for the present experiments aimed at determining the optimum dispersoid concentration in the electrolytic bath for deposition of composite copper coatings onto textile fabrics.



**Fig. 1:** Influence of TiO<sub>2</sub> concentration in the plating electrolyte on the conditional thickness of the coating (curve 1) and on dispersoid incorporation in the coating (curve 2) deposited on: (a) woven fabric; (b) non-woven fabric. Deposition time 30 min at 30°C.

The experiments were conducted with TiO<sub>2</sub> concentrations in the plating electrolyte of 3, 5, 10 and 20 g/L. As is evident from the data in Fig. 1a, at TiO<sub>2</sub> concentrations from 0 to 5 g/L, a certain degree of dispersoid incorporation into the coating deposited onto a woven substrate is reached, after which the percent incorporation does not substantially change with further increase in dispersoid concentration (curve 2). At plating on a non-woven substrate, the increase in TiO<sub>2</sub> concentration (from 3 to 20 g/L) in the working electrolyte leads to a proportional increase in the percent content of TiO<sub>2</sub> in the coating (Fig. 1b, curve 2). The conditional thickness of the coating remains almost the same at different TiO<sub>2</sub> concentrations (curve 1). The composite copper coating with dispersed TiO<sub>2</sub> is a high quality coating with good adhesion and high percentage of dispersoid incorporation.

The surface structure of the disperse coatings prepared at 3, 5, 10 and 20 g/L concentrations of

TiO<sub>2</sub> in the plating electrolyte was studied. It was established that with increase in TiO<sub>2</sub> concentration in the plating electrolyte (up to 10 g/L), thickening of the individual fibres was observed, leading to a denser structure of the deposit.

### 3.2. Influence of the nature of various dispersoids on the properties of the obtained disperse coatings

These investigations were performed using a base electrolyte containing various dispersoids (graphite, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>) at a concentration of 5 g/L, 30°C and 30 min deposition time. The obtained experimental results summarized in Table 1 evidence that, on both types of fabrics, coatings with the highest conditional thickness and degree of dispersoid incorporation are obtained from solutions containing graphite. Some adhesion problems of this coating to the substrate were, however, noticed.

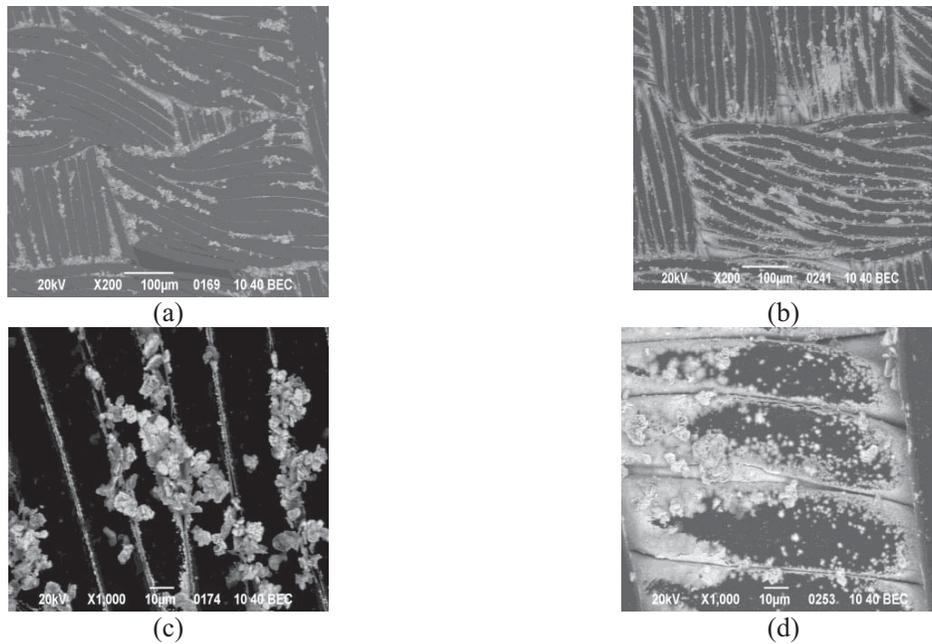
**Table 1**

Type of disperse particles	Woven textile substrate		Non-woven textile substrate	
	Condition al coating thickness, μm	Dispersoid content in coating, wt.%	Condition al coating thickness, μm	Dispersoid content in coating, wt.%
Base electrolyte (BE)	1.5	-	1.9	-
BE + 5 g/L graphite	1.8	18.7	2.5	28.3
BE + 5 g/L SiO <sub>2</sub>	1.5	1.7	1.8	1.4
BE + 5 g/L Al <sub>2</sub> O <sub>3</sub>	1.5	1.4	1.8	1.2
BE + 5 g/L TiO <sub>2</sub>	1.3	4.4	1.4	2.8

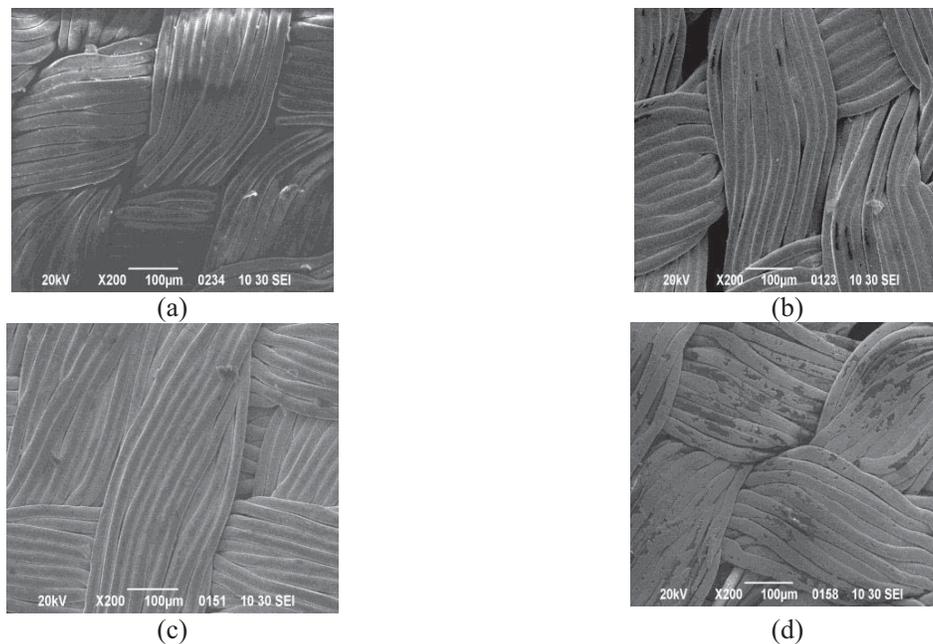
The difference in the percentage of included TiO<sub>2</sub> in the coating (4.4% in the woven fabrics and 2.8% in the non-woven fabrics), is probably due to the fact that the non-woven one consists of pressed polymer fabrics which hamper the diffusion of the electrolyte in the depth of the sample, while the woven fabrics are of porous structure.

No substantial difference in the deposition kinetics of the other dispersoids (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>) was observed, and the highest degree of incorporation was registered for TiO<sub>2</sub>.

In an attempt to resolve the adhesion problem with graphite disperse coatings we used two types of surface active substances (SAS): Veranol (nonylphenol polyglycol ether), which is a non-ionogenic surfactant, and sodium lauryl sulfate, an anionic surfactant. The following disperse coatings were deposited on the woven fabric: BE + 5 g/L graphite + SAS Veranol (0.5 g/L), and BE + 5 g/L graphite + SAS sodium lauryl sulfate (0.5 g/L). First, a pure copper coating was deposited onto the fabric for 5 min under air agitation and then



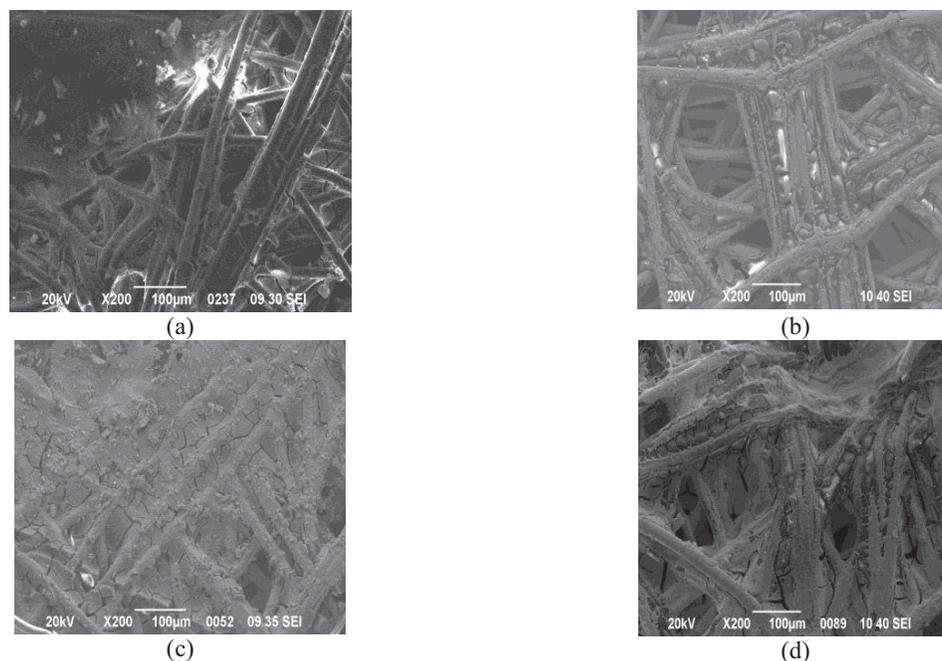
**Fig. 2:** SEM images of woven fabric: (a) and (c) with 2.5 g/L graphite; (b) and (d) with 10 g/L graphite. Deposition time 30 min at 30°C.



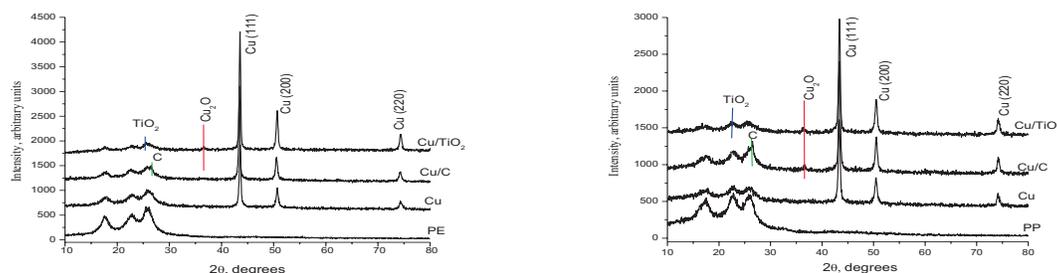
**Fig. 3:** SEM images of disperse coatings on woven fabric deposited from electrolytes containing various dispersoids: (a) non-treated woven fabric; (b) copper coating; (c) with 5 g/L Al<sub>2</sub>O<sub>3</sub>; (d) with 5 g/L SiO<sub>2</sub>; (e) with 5 g/L graphite; (f) with 5 g/L TiO<sub>2</sub>. Deposition time 30 min at 30°C.

graphite was added to the bath. Both surface active substances proved equally effective in solving the adhesion problem. The influence of graphite concentration in the deposition electrolyte on the degree of incorporation in the disperse coating was investigated by conducting deposition experiments with 1 h

deposition time and 2.5, 5 or 10 g/L graphite concentration using Veranol (0.5 ml/L) as SAS. The SEM images of the obtained coatings (Fig. 2) clearly indicate that the increased graphite concentration in the electrolyte leads to an increase in the percent incorporation in the coating.



**Fig. 4.** SEM images of disperse coatings on non-woven fabric deposited from electrolytes containing various dispersoids: (a) non-treated non-woven fabric; (b) copper coating; (c) with 5 g/L graphite; (d) with 5 g/L TiO<sub>2</sub>. Deposition time 30 min at 30°C.



**Fig. 5.** XRD patterns of disperse copper coating deposited from electrolyte containing 5 g/L TiO<sub>2</sub> (a) of woven fabric and (b) of non-woven fabric. Deposition time 30 min at 30°C.

The conditional thickness of the disperse coatings in the presence of nanoparticles remains almost unchanged upon varying the graphite concentration, except for the graphite containing disperse coating as compared to the one obtained from base electrolyte. Analogous results were obtained in previous experiments with ABS substrates [11].

The morphology of the obtained disperse coatings was examined by scanning electron microscopy (SEM). The SEM pictures are presented in Figs. 3 and 4. The SEM images in Figs. 3e and 4c support the data in Table 1 evidencing higher percent incorporation of graphite in the coatings as compared to other dispersoids. The most compact structure is observed when TiO<sub>2</sub> is present in the electrolyte (Figs. 3f and 4d). It can be presumed that the coating is initially deposited

in the caverns formed on the polymer surface as a result of etching [3], and then grows to cover the whole fibre surface.

**Table 2.**

Type of disperse particles	Specific electrical resistance, Ωm	
	Woven textile (as substrate)	Non-woven textile (as substrate)
Base electrolyte(BE)	6.0×10 <sup>-3</sup>	7.2×10 <sup>-3</sup>
BE + 5g/l graphite	6.1×10 <sup>-3</sup>	7.4×10 <sup>-3</sup>
BE + 5g/l SiO <sub>2</sub>	6.5×10 <sup>-3</sup>	7.6×10 <sup>-3</sup>
BE + 5g/l Al <sub>2</sub> O <sub>3</sub>	6.5×10 <sup>-3</sup>	7.6×10 <sup>-3</sup>
BE + 5g/l TiO <sub>2</sub>	6.8×10 <sup>-3</sup>	8.1×10 <sup>-3</sup>

For better characterization of the disperse coatings under investigation their specific resistance was determined (Table 2). The obtained experimental data evidence that the specific

electrical resistance of disperse copper coatings is of the same order (a little higher) as that of pure copper deposits.

The phases contained in the deposits were identified by X-ray diffraction analysis (Figs. 5a and 5b). For the purpose, first the diffractograms of the primary substrates were recorded and the characteristic peaks for woven and for non-woven textile were identified. This approach allowed for better distinction between the substrate peaks and the peaks identifying the different phases in the thin layers deposited onto it. The obtained diffractograms feature well pronounced peaks of Cu identified using the PDF #04–0836 entry of the database provided by the International Centre for Diffraction Data (ICDD). These experimental data indicate that the obtained coatings are of desired thickness and of adequate crystallinity. The intensity distribution is typical for randomly oriented powder samples and indicates that there are no visible texture effects in the deposits.

No signs of same influence of the dispersoids on the deposition of Cu were observed (*e.g.*, changes in parameters, crystallinity size or texture).

For the coatings containing disperse particles, only the strongest peaks of TiO<sub>2</sub> (anatase) or C (graphite) could be identified on the diffractograms due to their small amount. Their strongest peaks overlay the strongest peaks of the woven and non-woven textile phases, but still the changes in curve profile and in peak position can be distinguished fairly well to confirm the presence of minimum quantities of C (PDF #75–2078) and TiO<sub>2</sub> (PDF #89–4203) in the coatings.

As a result of Cu reactivity, slight oxidation of the sample surface is observed, which exhibits a minimum content of a Cu<sub>2</sub>O phase (PDF #65–3288).

#### 4. CONCLUSIONS

The optimum conditions of a previously developed technology for electroless metallization

of fabrics were determined. Pure copper, as well as dispersed copper coatings containing various types of dispersoids (graphite, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) were chemically deposited onto two types of polyester fabrics: woven textile and non-woven textile. Semi-bright coatings of uniform thickness were obtained which give the textiles aesthetic appearance. The specific electrical resistance of the coatings was determined.

The obtained experimental data indicate that these coatings can be used as protective screens against electromagnetic interference (*i.e.* for EMI shielding) and find application in industry, agriculture and everyday life.

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## БЕЗ-ЕЛЕКТРОДНО ОТЛАГАНЕ НА НАНОДИСПЕРСНИ МЕТАЛНИ ПОКРИТИЯ ВЪРХУ ТЪКАНИ

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Метализираните тъкани са съвременни композитни материали, характеризиращи се с съчетаването на благоприятни физиологични и ергономични свойства на текстилния носител и металното покритие. Разработена е технология за химическо отлагане на нанодисперсно медно покритие с различни диспергиращи агенти (графит, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> и TiO<sub>2</sub>) върху два вида текстил от полиетилен-терефталат (PET): тъкан и нетъкан. Изследвано е влиянието на условията на отлагане върху дебелината на покритията, електропроводимостта, елементния състав и морфологията им.