

ABSTRACT

of the dissertation for Doctor of Philosophy PhD degree on
the specialty 6D072000- «Chemical technology of inorganic substances»

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on the theme «Development of the technology of chemical coatings with the use of
photochemical processes»

Actuality of the work. Metallization of non-conductive materials makes it possible to obtain products with completely new functional, decorative and protective properties. Traditionally, the materials subject to metallization include various polymers (plastics), glass, ceramics, fibers (cotton, synthetics), natural materials, etc. In general, metallized plastics have become a very important composite material both in everyday life and in industry. Today, chemical packaging technology is developing rapidly due to the progressive nature of science and technology. It is important to obtain multifunctional and durable coatings on surfaces from various materials. In many developed countries, work is actively underway to increase or change the properties of dielectric materials by applying coatings on their surfaces. Among such coatings, the process of coating dielectric materials with copper, silver, gold and nickel coatings is of great importance. Such films have a number of useful properties, therefore they are widely used in various fields of modern science and technology: chemistry and medicine, electronics, communications, aerospace and aviation industries, in the manufacture of decorative items, etc. The metal shell of dielectrics can be used in mechanical engineering, automotive and instrument making, as well as in the production of household appliances. The economic and environmental efficiency of obtaining metal coatings on the surface of dielectric materials is high. Palladium and its salts are traditionally used as reducing agents in the production of such films, which have several properties.

Today, it is important to obtain multifunctional useful coatings on the surface of various household, medical and special materials on a large scale. The relevance of enhancing the technology of obtaining coatings with protective, decorative and conductive properties on the surface of dielectric and fabric materials increases over time. Such packaging can be used in the production of medical products, various military uniforms, sportswear, cases for weapons, as well as products that can protect against various microorganisms.

In particular, copper and silver casings have high protective properties, i.e. bactericidal. For example, the bactericidal ability of gold is 2-3 times lower than that of silver. To improve the bactericidal properties of coatings from these metals, it is necessary to develop a technology for producing mixed coatings. By increasing the bactericidal properties of metals (copper, silver), they enhance the bactericidal ability of each other. However, due to the complexity and cost of methods for producing thin films from these metals, there is a need for the development and study of complex technological methods.

It is theoretically known that most of the monovalent metal compounds (copper and silver) in the copper subgroup are readily decomposed by light when heated slightly. In addition, the halides of these metals are binary semiconductors. That is, there is a relationship between the properties of semiconductors and the properties of light transmission.

There are many methods for incorporating metals into the copper subgroup on dielectric surfaces. But some of them require complex and expensive equipment or go through various gearboxes. The main advantage of the photochemical method is that there is no need to add a reducing agent to the reaction medium. The photochemical process is provided by photons of light. This reduces the complexity and cost of the technology. Based on the results of the work, innovative effective methods for the photochemical production of copper and its analogs using composite coatings have been developed, their bactericidal properties have been studied, and their resistance to known bacteria has been proved.

The aim and tasks of research. Development of technology for photochemical deposition of copper and silver films on various dielectric materials, development of the mechanism of photochemical decomposition and study of the physicochemical, mechanical and bactericidal properties of films obtained by the photochemical method. When analyzing membranes obtained by the photochemical method, reliable modern methods of physicochemical analysis were used. The composition and structure of shells of various models were studied using an ISM-6490-LV scanning electron microscope (JEOL, Japan) and D8 (Bruker) diffractometer.

Depending on the purpose of the work, it is planned to solve the following tasks:

- determination of optimal physico-chemical parameters of the process of obtaining copper and silver coatings;
- introduction of monovalent copper chloride with semiconducting properties (I) on the surface of solid-phase dielectric materials;
- to determine the kinetic characteristics of the photochemical process used in the production of copper and silver coatings;
- to determine the protective ability of copper and silver coatings from harmful electromagnetic rays;
- to determine the efficiency of photochemical activation by the method of chemical nickel plating with gas-phase phosphine;
- investigation of the bactericidal properties of copper and silver coatings.
- development of a technological scheme for the production of copper and silver coatings using photochemical processes;
- mathematical treatment of the copper chloride reduction process on the surface of cotton fabric.

Research methods: the study used modern physical and chemical, physicochemical methods, scanning electron microscope (SEM, JSM6490 LV JEOL), scanning electron microscope (SEM, NOVA 2000 Nano-SEM), D8 (Bruker) diffractometer.

The object of research. Cotton fabric (AA011228), plastic and glass.

The main provisions submitted for defense:

1. The protective properties of fabric materials modified with films of copper and silver from the harmful effects of electromagnetic waves of household appliances (cell phones and rectifiers) measured with the SM204-SOLAR and DT-1130 detectors shows a decrease in the flux density of these waves by 96-97%.
2. The optimal conditions for activating the surface of fabric materials with copper or silver particles by the photochemical method are the concentration of CuCl_2 50-100 g/L, AgNO_3 1-10 g/L, exposure to the sun at a temperature of 25-40⁰C for 40 -60 minutes.
3. To obtain copper and silver films, the recommended sunlight flux density is 1000-1200 W/m^2 and 500-600 W/m^2 , respectively.
4. The results of studies of the antibacterial properties of modified materials show that their bactericidal ability against bacteria *St. Epidermidis* is manifested in Ag (24 mm (100%)), Cu-Ag (22 mm (91%)), Cu (19 mm (82%)).
5. Nickel-containing films were obtained by additional treatment with phosphine. SEM images shows that upon photochemical activation, a film containing 38.27% Ni is formed on the surface of the dielectric, on which nickel of the required thickness can be electroplated.

Scientific novelty of the work. In accordance with the purpose of the work, the technology of photochemical deposition of copper and silver coatings on various dielectric materials has been developed, their mechanical, physicochemical and bactericidal properties have been studied.

The following scientific results were obtained in the dissertation:

1. For the first time, a connection has been established between the content of dispersed metal particles in the surface layer of a dielectric, obtained using photochemical processes, and a change in the degree of surface emissivity. This made it possible to use this value as an indicator in photochemical studies.
2. For the first time, the process of obtaining silver particles on the basis of semiconductor silver chloride obtained by transformation of copper monochloride was carried out (a patent for a useful model No. 4342 was obtained).
3. A scientifically grounded research methodology in the field of photochemical processes has been developed (copyright certificate No. 4911).
4. For the first time, photochemical activation of a dielectric surface before applying a chemical coating was proposed (a patent for a useful model No. 5088 was obtained).
5. For the first time, the photosensitivity of the processes occurring in binary semiconductor films of metal halides of the copper subgroup has been revealed, which makes it possible to carry out selective metallization of dielectrics.
6. For the first time, the protective ability (96-97%) of coatings on the surface of dielectric materials obtained by photochemical reduction from harmful, harsh sunlight has been determined.

7. It is shown for the first time that the driving force of the photochemical reduction of metal halides of the copper subgroup on the surfaces of cotton fabrics is the photooxidation of cellulose molecules that make up the fabric.

8. In the surface layer of cotton material, the resistance of films containing copper and silver obtained by photochemical method to *S.epidermidis* bacteria (test culture ATCC 14990) (silver (24 mm (100%)), copper-silver (22 mm (91%)), copper (19 mm (82%))).

9. The process of copper phosphide formation was carried out by treating a mono-chloride copper film with gaseous phosphine.

10. An analog simple technology for obtaining copper, nickel and silver coatings using photochemical processes on the surface of dielectric materials has been developed.

11. The optimal parameters of the photochemical reduction process were determined (50-200 g/L for the concentration of CuCl_2 , AgNO_3 1-20 g/L, 40-60 minutes in time, 25-40⁰C in temperature, CuCl_2 -1000-1200 W/m^2 in the density of the sunlight flux, AgNO_3 - 500-600 W/m^2).

12. Methods of mathematical planning of the process of formation of metallic copper as a result of reduction of copper (II) chloride are applied, linear and quadratic functions are established.

The theoretical and practical significance of the work. Based on the research results, a simple analogous technology was developed for obtaining coatings from copper, nickel and silver on the surface of dielectric materials using photochemical processes and a method for activating the surface of dielectric materials before metallization. The research results have shown a high theoretical and practical value of metallization of the surfaces of dielectric materials and the production of nanoscale coatings with multifunctional properties.

The results obtained were introduced into the educational process and industrial at the Department of "Chemical technology of inorganic substances" of M. Auezov University.

Relationship with scientific-research works and state programs. The dissertation work was carried out in accordance with the scientific direction of M.Auezov South Kazakhstan University, carried out within the framework of the state budget theme scientific-research work of the Department of Chemical technology of inorganic substances B-16-02-03 "Composite coatings for various functional purposes".

The personal contribution of the doctoral student. The analysis of literature data and patent research on the topic of the thesis was carried out. The author himself performed the analysis, formulation, generalization and processing of the results of experimental research based on the implementation of the intended direction of research, definition of goals and objectives and analysis of literature, presentation of materials at scientific conferences and in the form of scientific papers.

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for the publication of the article Studies of the Application of Electrically Conductive Composite Copper Films to

Cotton Fabrics in the magazine Journal of Composites Science. 2022, 6, 349. <https://doi.org/10.3390/jcs6110349>.

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for the publication of the article Chemical Copper Plating of Cotton Fabrics by Photochemical Activation of the Surface in the magazine Revista de Chimie journal (Rev. Chim., 71 (8), 2020, -P. 90-97 Bucharest Romania).

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for the publication of the article Photochemical Method of Depositing Silver Films on the Surface Cotton Fabrics in the magazine Oriental Journal of Chemistry (2018; 34(6). –P. 2755-2761, India).

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for the design of the article Method of applying silver films to the surface of cotton materials in the journal Vestnik KazNRTU (No. 1 (131) 2019. -P.571-576).

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for the preparation of the article Obtaining antibacterial copper-containing nanofilms on dielectric surfaces in the journal Vestnik KazNRTU (No. 5 (141) 2020. -P.747-753).

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for the preparation of the article Combined Method of Nickel Plating of Cotton Fabrics in the magazine Revista de Chimie journal (Rev. Chim., 71 (12), 2020, –P. 76-84. Bucharest Romania).

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for the presentation of the article Chemical copper plating of dielectric materials by photochemical activation in the collection Proceedings of III International scientific practical conference "Post-crisis development of education and science in Europe and Asia" (2020, - P. 112-118. Aachen, Germany).

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for the article Obtaining chemical copper coating of dielectric materials by photochemical activation of surface in the International conference on integrated innovative development of zarafshan region: achievements, challenges and prospects (2019. –P.322-327. Uzbekistan. Navoi).

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for the preparation of the article Use of copper bromides for photochemical silvering of tissues in the collection of the international scientific and practical conference "Auezov Readings - 16" (2018, -p. 291-294).

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for the preparation of the article Method for introducing grafite and titanium dioxide into composite coatings in the collection of the international scientific and practical conference "ICITE - 2018" (2018. Volume I. –P.272- 277).

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for the design of the article "Chemical copper plating of metallic and non-metallic materials by photochemical activation of surface in the collection of the international scientific and practical conference "ICITE - 2019" (2019. Volume II. –P.338-343).

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for the preparation of the article "Method of chemical copper plating by activating the surface of dielectric materials without palladium in the collection of the international scientific and practical conference "Kuatbekov Readings-1: Lessons of Independence" (2021, volume II, - P. 4-6).

The doctoral student prepared experimental data for the publication of the monograph "Obtaining functional films on dielectric materials" (2018. UDC 621.793. LBC 34. P 53. Printing house "Alem". Shymkent).

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for registration of a patent for a useful model No. 4133 (Publ. In bull. No. 4342 of 10.04.2019) for a Method of applying silver films to the surface of cotton materials.

The doctoral student was directly involved in obtaining experimental data, processing and interpreting experimental results for registration of a patent for a useful model No. 5088 (Publ. In bull. No. 5088 of 06.26.2020) for a Method of activating the surface of dielectrics before chemical metallization.

The doctoral student was directly involved in obtaining experimental data, processing and interpreting the results of experiments for issuing an inventor's certificate for the method of photochemical reduction of copper metal halides (No. 4911 08/14/2019).

Information about publications. According to the results of the study, 1 monograph, 16 articles, including 3 articles in publications approved by the order of the Committee for Control in the Sphere of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, 2 article in high-ranking reference journals. (included in Scopus and Web of Science), 7 articles published at international scientific and practical conferences abroad, 2 articles in scientific works of M. Auezov SKU, 3 articles in the collection of scientific works of undergraduates, PhD students and young applicants of M. Auezov SKU. A patent certificate was received for 2 utility models of the Republic of Kazakhstan (patent UM No. 4342 published on 04.10.2019; patent UM No. 5088 published on 26.06.2020). In addition, according to the results of research work, 2 copyright certificates were obtained (No. 949 dated December 13, 2018; No. 4911 dated August 14, 2019) for published works.

The structure and volume of the dissertation. The scientific work consists of an introduction, 4 chapters, a conclusion, a bibliography and an appendix. The thesis is presented on 152 pages, includes 67 figures, 24 tables. The bibliography contains a list of scientific and technical literature, consisting of 179 original works by domestic and foreign authors.