DEVELOPMENT OF A NEW SUSPENSION ELECTROLYTE BASED ON METHANE-SULPHONIC ACID FOR THE ELECTRODEPOSITION OF Cu–TiO₂ COMPOSITES

Electrodeposition of composite coatings based on copper is a promising direction in the creation of advanced materials for multifunctional purposes. An important area of composites application is to use them in the treatment systems for gas emissions and wastewater. It is advisable to use semiconductor oxide materials, in particular titanium dioxide, as the photocatalysts in the photo destruction of organic pollutants of wastewater. The structural features of wastewater treatment equipment require that titanium dioxide particles should be fixed in a rigid matrix. Resolving the task of fixing photosensitive elements at the surface of a certain configuration implies the electrodeposition of coatings by composites, in particular Cu–TiO₂. An important factor affecting the functional characteristics of composites and their manufacturing technology is the nature of the electrolyte. It has been shown that the electrodeposition of Cu–TiO₂ composites from methane-sulfonate electrolytes makes it possible to reduce the coagulation of the dispersed phase and to obtain coatings with a high content of titanium dioxide from a suspension solution containing no more than 4 g/l of TiO₂. It was established that the content of the dispersed phase in the composite made at a current density of 2 A/dm² and the concentration of titanium dioxide in the electrolyte at the level of 4 g/l is 1.3 % by weight, which is twice as much as when using a sulfate electrolyte. It has been shown that the increase in the content of the dispersed phase in the coatings from 0.1 to 1.3 % by weight is accompanied by an increase in the degree of photo destruction of the colorant from 6 to 15.5 %. The micro-hardness of coatings increases, in this case, by 30 %. The proposed electrolyte to make the Cu–TiO₂ composites is an important contribution to the development of the synthesis of wear-resistant high-performance photocatalysts for treating wastewater from organic pollutants

Keywords: methane-sulfonate electrolyte, composite coatings, titanium dioxide, photocatalysis, micro-hardness

I. S k n a r
PhD, Associate Professor*
E-mail: juventa2011@gmail.com

Y. S k n a r
Doctor of Chemical Sciences, Professor*
E-mail: yuriy.sknar@gmail.com

T. H r y d n i e v a
PhD, Senior Lecturer*
E-mail: tasya.gridneva@gmail.com

P. R i a b i k
PhD, Associate Professor*
E-mail: pavelriabik@gmail.com

O. D e m c h y s h y n a
PhD, Associate Professor
Department of Mineral Processing and Chemistry
Kryvyi Rih National University
Vitaliya Matusevycha str., 11, Kryvyi Rih, Ukraine, 50027
E-mail: demchyshynaov@gmail.com

D. G e r a s i m e n k o
Department of Physics
Dnipro National University of Railway Transport
named after Academician V. Lazaryan
Lazaryana str., 2, Dnipro, Ukraine, 49010
E-mail: dvg7560@gmail.com
*Department of Processes, Apparatus
and General Chemical Technology
Ukrainian State University of Chemical Technology
Gagarina ave., 8, Dnipro, Ukraine, 49005

1. Introduction

An important aspect in preserving the environment is the complete neutralizing of industrial emissions. The quantitative and qualitative composition of industrial wastewater is quite diverse and depends on the industry and its technological processes [1]. Pollutants of reservoirs by organic substances include the production of leather, as well as the cellulose and paper industry. In addition, organic waste forms during the production of dyes and pigments, at sugar plants and breweries, at the meat and dairy enterprises, in the canning and confectionery industries, etc. Wastewater treatment from organic pollutants is based on methods of their destruction [2]. Specifically, oxidation, which makes it possible to receive water with very low levels of pollution. In addition, a common method of neutralizing organic

pollutants is the treatment of wastewater with ultraviolet radiation [3], which typically requires the use of a catalyst. Metal oxides such as TiO_2, CuO, WO_3, etc. are applied to purify water and air from organic contamination, as well as to destroy bacteria [4]. Titanium dioxide is characterized by high photosensitivity. As a photocatalyst, the priority is the use of the crystalline modification of anatase-type titanium dioxide [5]. Given that TiO_2 is chemically and biologically inert and is not pricey, titanium dioxide is currently considered to be the most promising photocatalyst [6]. Wastewater treatment with ultraviolet light in the presence of TiO_2 is regarded to be one of the best disinfection technologies, since, unlike other similar technologies, it does not produce carcinogenic or mutagenic compounds [7].

The greatest prospects for the use of titanium dioxide as a photocatalyst are expected in the technological processes for treating wastewater that contains dyes of synthetic and organic origin. Such wastewater is common in the textile, cosmetic, and food industries [7]. The application of photocatalysts makes it possible not only to discolor the dyes but also to destroy them [8].

A promising direction in the development of photocatalysts is the production of composite coatings with photocatalytic-active particles incorporated into the metallic matrix [9, 10]. Composites can be applied onto the surface of the predefined shape, which ensures contact with the pollutant.

Composites are a structure consisting of a metallic matrix and evenly distributed particles of another phase in it. Typically, incorporated particles significantly improve the hardness and wear resistance of coatings [11]. The properties of the composites depend on the shape and size of the particles of the dispersed phase in the electrolyte, their distribution inside the composite [12].

Among the basic techniques for making composite coatings, one should note the chemical and electrochemical techniques. The formation of composite coatings chemically ensures the uniformity of their application and low porosity. However, the solutions used in such processes are expensive and not stable. In addition, the chemical application of coatings takes place at elevated temperatures.

In contrast to the chemical technique, the electrochemical application of composite coatings proceeds at a noticeably higher speed. In addition, the electrodeposition of coatings is characterized by the manageability and reliability of the technological process.

It should be noted that copper-based composite coatings have become common. This is due to their high physicochemical characteristics, enhanced hardness, wear resistance, and strength at high temperatures. Copper-based coatings provide high values of electrical conductivity, thermal conductivity, ductility [13].

Given this, we find it relevant to study the photocatalytic and physicochemical properties of the $Cu–TiO_2$ composites produced by using an electrochemical technique.

2. Literature review and problem statement

Composite coatings based on the metallic matrix and nonmetallic phase particles incorporated into it ensure the necessary physicochemical properties of the surface of parts onto which they are applied, and do not change the shape of these parts. Such coatings are produced from suspension electrolytes containing the dispersed nonmetallic phase. To maintain the dispersed phase in a suspended state, the electrolyte is stirred, or its intense circulation is ensured.

The most common material used as a composite filler is titanium dioxide. Titanium dioxide acts as a dispersing phase in the electrodeposition of composites with various base metals, for example, Cu, Zn, Ni, etc. [13–16]. The choice of material of the metal matrix depends on the conditions of use of composites. However, as a rule, these are the wear-resistant composites; no studies into the photocatalytic properties of such coatings were performed.

The advantages of titanium dioxide are affordability, non-toxicity, photocatalytic activity, etc. [17]. Titanium dioxide also attracts attention as a reinforcement agent of the metal matrix to improve hardness, as well as anti-corrosion intensity [15]. In particular, titanium dioxide particles incorporated into the copper matrix are used to strengthen copper coating [18], the use of which is strategically important in electronics and robotics [19]. Another important area of employing the $Cu–TiO_2$ composites is the formation of layers of photocatalysts for the decomposition of organic wastewater pollutants. However, this issue was not investigated in the cited works.

The physical and mechanical properties of $Cu–TiO_2$ samples were studied in [20]. It was shown that the density, specific electrical conductivity, the values of hardness, and wear rate vary significantly depending on the amount of TiO_2 in the copper matrix [20]. As the amount of TiO_2 in the metal matrix increases, the hardness and specific electrical resistance grow while the density of $Cu–TiO_2$ composites decreases. The influence of the composition of the sulfate electrolyte of deposition and electrolysis conditions on the composition of $Cu–TiO_2$ composites was investigated in [21]. It was shown that an increase in the concentration of titanium dioxide in the electrolyte to 20 g/l leads to an increase in its content in the composite to 2.26 % by weight. Increasing the density of the current and reducing the pH of electrodeposition helps reduce the content of the dispersed phase in composites. With an increase in the concentration of titanium dioxide in the sulfate electrolyte to 50 g/l, the authors of [22] managed to make coatings with a $Cu–TiO_2$ composite containing a disperse phase at the level of 4.2 % by weight. The correlation between the content of titanium dioxide in $Cu–TiO_2$ composites and their micro-hardness was established in [23]. It was shown that with an increase in the dispersed phase in composites, a proportional increase in the values of the micro-hardness of coatings is observed. Consequently, it is possible to increase the content of titanium dioxide in $Cu–TiO_2$ composites and, at the same time, to improve the micro-hardness of the coatings only with the use of a high concentration of titanium dioxide in the electrolyte. However, the issues related to the increase in the content of titanium dioxide in composites during the use of electrolyte sufficiently diluted in the dispersed phase remained unresolved.

The reason for this is the objective difficulties associated with the fact that the two-charge sulfate anion provokes significant coagulation of the dispersed phase. This leads to the formation of large agglomerates, the incorporation of which into the coatings is difficult. Consequently, increasing the TiO_2 content in $Cu–TiO_2$ composites is problematic [24]. An option to overcome such difficulties may be the use of a horizontal cathode, which hosts the sedimentation of the dispersed phase. This approach was reported in work [24]. The

authors proposed applying the Cu–TiO$_2$ composite coatings on a horizontally positioned cathode, to which a jet of suspension electrolyte is fed. This course of the process makes it possible to significantly increase the content of titanium dioxide in the coatings. In the presence of 50 g/l of TiO$_2$ in the electrolyte, the content of titanium dioxide in composites reaches 7.25 % by weight. Accordingly, there is an increase in the micro-hardness of the coatings to 218.7 kg/mm^2. Another solution to the problem of significant coagulation of titanium dioxide particles in sulfate electrolyte is the use of surfactants. Work [25] notes that the presence of surfactants in the suspension electrolyte leads to its stabilization. This is due to an increase in the wettability and a change in the surface charge of the dispersed particles.

However, a radical solution that reduces the coagulation of the dispersed phase is the use of an electrolyte with a single-charge anion. Such an electrolyte is a solution based on methane sulfonic acid. Paper [26] shows that the particle size of ZrO$_2$ in the methane-sulfonate electrolyte is smaller than in the sulfate one. Methane-sulfonate electrolytes for the electrodeposition of metals, alloys, and composites [27–29] revealed a number of beneficial properties. In particular, the high solubility of salts, low overvoltage of metal release, high electrical conductivity. Work [30] shows that due to the high solubility of copper methane sulfonate, one can use solutions that are sufficiently concentrated by copper ions, which are characterized by high electrical conductivity. The application of the methane-sulfonate copper electrolyte makes it possible to produce small-crystal uniform copper coatings in a wide range of current densities.

Thus, when making Cu–TiO$_2$ composites from sulfate electrolytes, the complicating factor is the coagulation of the dispersed phase. As a result, it is not possible to manufacture high-content TiO$_2$ composites from electrolytes containing a small amount of the dispersed phase. At the same time, an increase in the concentration of titanium dioxide in electrolyte is accompanied by the sedimentation of particles of the dispersed phase. Accordingly, there is a need for more intensive agitation of the electrolyte. It seems possible to avoid these technological difficulties when using methane-sulfonate electrolyte whose anion's coagulating activity is significantly less than that of sulfate-anion. Based on this, it can be argued that it is advisable to conduct a study aimed at establishing patterns in the electrodeposition and the properties of Cu–TiO$_2$ composites obtained from methane-sulfonate electrolytes.

3. The aim and objectives of the study

The aim of this study is to develop a new methane-sulfonate electrolyte for the electrodeposition of Cu–TiO$_2$ composite coatings. This could make it possible to improve the technology of making composite coatings in terms of the technological simplification of the process and improving the photocatalytic and physicochemical properties of the coatings.

To accomplish the aim, the following tasks have been set:
– to investigate the influence of electrolyte composition and electrolysis modes on the content of the dispersed phase in the Cu–TiO$_2$ composite coatings obtained from methane-sulfonate solutions;
– to investigate the effect of electrolysis conditions on the photocatalytic and physicochemical properties of Cu–TiO$_2$

composite coatings obtained from methane-sulfonate electrolytes.

4. Materials and methods to study patterns in the electrodeposition of Cu–TiO$_2$ composites and their properties

Electrodeposition of the Cu–TiO$_2$ composite coatings was carried out from a methane-sulfonate electrolyte of the suspension type (Table 1) onto a copper foil of 3×2 cm^2 at a temperature of 293 K. To make the Cu–TiO$_2$ coatings, we used the powdered titanium dioxide P 25 (Degussa) [31]. The commercially-available powder is a mixture of the allotropic modifications of titanium anatase dioxide and rutile in the ratio of 80:20, respectively. The claimed average particle size of titanium dioxide is 31 nm. Methane sulfonic acid (70 % by weight) and copper(II) methane-sulfonate (40 % by weight) produced by BASF.

Table 1

The composition of electrolytes for the electrodeposition of Cu–TiO$_2$ composite coatings

Electrolyte component	Concentration of electrolyte component, mol/l
Cu(CH$_3$SO$_3$)$_2$	0.6
CH$_3$SO$_3$H	0.6
TiO$_2$, g/l	0.1; 0.2; 0.5; 1.0; 2.0; 4.0

The electrodeposition of the Cu–TiO$_2$ composite was carried out under steady hydraulic conditions. The process involved the agitation of the electrolyte using a magnetic stirrer (Fig. 1). The agitation speed was 500 rpm. Stable current was generated by the BVP Electronics Home Tools (Ukraine) power source. The operating current density was, A/dm^2: 2, 3, 5, 7.
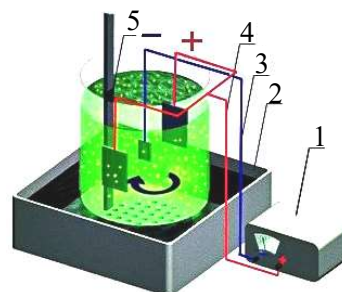

Fig. 1. Schematic of the installation for the electrodeposition of a Cu–TiO$_2$ composite: 1 — current source; 2 — thermostated water bath; 3 — cathode current drive; 4 — anode current drive; 5 — thermometer

The content of titanium dioxide was determined using an X-ray fluorescent method [32] at the X-ray energy dispersion spectrometer SEF–01–M–1 "SPRUT" (Ukraine).

We determined the dispersed phase distribution based on particle size by the sedimentation method. The calculation of the TiO$_2$ particle size was carried out on the basis of data on the sedimentation rate of the dispersed phase.

We registered the sedimentation curve using a computer that acquired a signal from the digital torsion scales Vibra HT (Japan). During the experiments, titanium diox-

ide particles were deposited on a cup, which was positioned coaxially in a cylinder filled with a suspension electrolyte (Fig. 2).

Fig. 2. Installation for the suspension electrolyte analysis by a sedimentation method

The results obtained were treated by the Tsuryupa method [33]. The method implies establishing a differential function of particle distribution by size according to the following equation:

$$F = 4Q_m \cdot \frac{r \cdot r_0^4}{\left(r_0^2 + r^2\right)^3}, \qquad (1)$$

where Q_m is the constant that corresponds to the maximum amount of the dispersed phase settled on the cup over an infinitely long time, g; r is the radius of particles of the dispersed phase, m; r_0 is the constant.

The constant r_0 is calculated from the following equation:

$$r_0 = \sqrt{\frac{9\eta \cdot H}{2g \cdot (\rho - \rho_0) \cdot \tau_0}}, \qquad (2)$$

where η is the viscosity of the electrolyte; ρ, ρ_0 is the density of particles and electrolyte; H is the height of the suspension electrolyte column; τ_0 is half the time of particle deposition.

The Q_m value was found from the following equation:

$$\tau/m_\tau = \tau_0/Q_m + \tau/Q_m, \qquad (3)$$

where τ is the time of particle deposition; m_τ is the mass of particles of the dispersed phase settled on the cup over time τ.

The cotangent of the angle of inclination of the straight line in the $\tau/m_\tau - \tau$ coordinates relative to the τ axis equals Q_m. On the y-axis, the straight-line cuts a segment equal to τ_0/Q_m.

The interval corresponding to the particle sizes of the dispersed phase was determined by calculating the minimum and maximum radii of these particles from the following equations:

$$r_{min} = r_0 \cdot \left(0.1\sqrt{Q_m} - 1\right)^{1/2}, \qquad (4)$$

$$r_{max} = 3r_0. \qquad (5)$$

Given the particle radius values at the defined interval from r_{min} to r_{max}, we calculated the F function using equation (1) and built a differential distribution curve.

The Cu–TiO$_2$ photocatalytic activity was estimated according to the results from studying the degree of the photo destruction of methyl orange under the influence of ultraviolet radiation. The Cu–TiO$_2$ composite coatings, applied onto a copper plate with an area of 3 cm^2, were in contact with a solution of methyl orange when exposed to ultraviolet (Fig. 3).
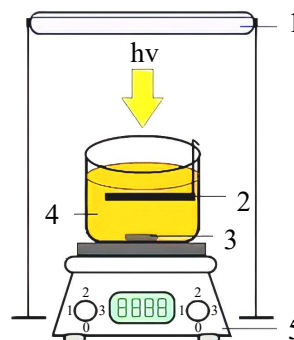

Fig. 3. Schematic of the installation for the dye photo destruction experiment in the presence of Cu–TiO$_2$ composites: 1 — ultraviolet lamp; 2 — plate with a composite coating; 3 — mixer; 4 — solution of methyl orange; 5 — magnetic stirrer

The Bactosfera Sun Universal lamp (Ukraine) was used as a radiation source. The radiation wavelength was 253.7 nm. The initial concentration of the dye was equal to 6 µmol/l. The concentration of the dye in the solution was determined according to data on the optical density of the methyl orange solution at the photo colorimeter KFK-2-UHL 4.2 (Russia) with a light filter of 490 nm.

The values of the optical density of the dye solution are directly proportional to its concentration in the electrolyte (Fig. 4). That is, the Beer–Lambert–Bouguer equation holds in the studied range of the concentrations of methyl orange.
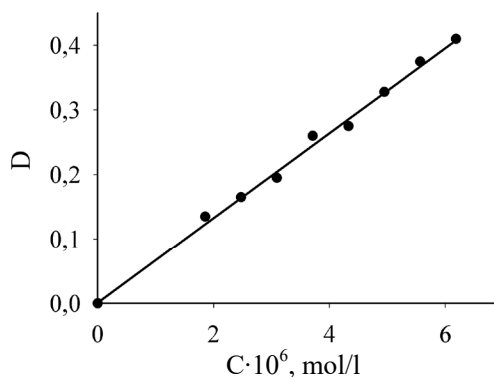

Fig. 4. The chart of dependence of the optical density of a methyl orange solution on its concentration

The micro-hardness of Cu–TiO$_2$ coatings by Vickers was determined when measuring at the PMT-3 device with a load of 50 g.

The micro-hardness values were calculated using a formula given in [27]:

$$H = \frac{1,854 \cdot P}{l^2}, \tag{6}$$

where l is the length of the diagonal of the indenter imprint, μm.

The value of the internal strains in the composites was determined by a method of the flexible cathode from the equation given in [28]:

$$\sigma = \frac{E_c \cdot d_c \cdot (d_c + d_{co}) \cdot z}{3l_p^2 \cdot d_{co}}, \tag{7}$$

where E_c is the module of elasticity of a cathode copper plate, MPa; d_c is the thickness of a cathode plate, m; d_{co} is the coating thickness, m; l_p is the length of the working part of a cathode plate, m; z is the deviation of the edge of the cathode plate from the starting position, m.

5. Developing a new methane-sulfonate electrolyte for the electrodeposition of Cu–TiO₂ composites

5. 1. Studying the influence of electrolyte composition and electrolysis modes on the content of the dispersed phase in the Cu–TiO₂ composite coatings obtained from methane-sulfonate solutions

Electrodeposition of the Cu–TiO₂ composites was carried out from the suspension methane-sulfonate electrolyte, which contained titanium dioxide powder in the range of 0.1–4 g/l. Electrolysis was performed with stirring at a speed of 500 rpm. The agitation of the studied suspension electrolytes ensured uniform distribution of the dispersed phase throughout the entire volume without the formation of sediment at the bottom of the cup (Fig. 5). Consequently, the total amount of the dispersed phase was in a suspended state and can be considered to be capable of participating in the formation of composite coatings.
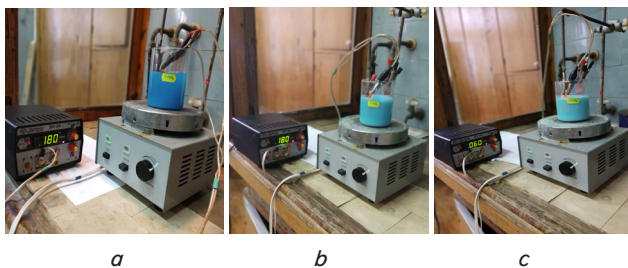

Fig. 5. General view of the suspension electrolyte containing titanium dioxide, g/l: *a* — 0.2; *b* — 2; *c* — 4

To establish the dependence of the content of titanium dioxide in composites on the concentration of TiO₂ particles in the methane-sulfonate electrolyte, we took the samples of coatings at a constant density of the current and various concentrations of the dispersed phase in the electrolyte. Such dependences were built for the current density of 2, 3, 5, 7 A/dm². The results of studying the content of the dispersed phase in the obtained samples are conveniently represented in the form of the dependence of TiO₂ content in the coatings on the concentration of

the dispersed phase in the electrolyte and the density of the electrodeposition current (Fig. 6).

Our study of the effect of electrolysis parameters on the composition of Cu–TiO₂ coatings has shown that an increase in the concentration of titanium dioxide in the electrolyte leads to an increase in the content of filler in the coatings (Fig. 6). The dependence of the amount of titanium dioxide in composites on the concentration of particles in the electrolyte turned out to be nonlinear. A significant increase in the content of the dispersed phase in sediment is observed with the initial adding to the copper electrolyte of the powdered titanium dioxide. With a further increase in the concentration of the dispersed phase in the suspension, the increase in the content of TiO₂ in composites occurs more slowly.
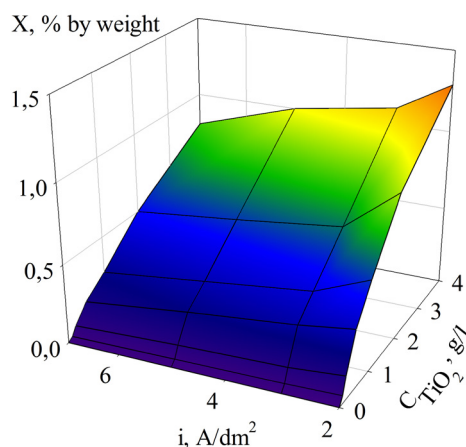

Fig. 6. Dependence of the content of titanium dioxide in Cu–TiO₂ composites on the concentration of the dispersed phase in the electrolyte and the density of electrodeposition current

With an increase in the density of the electrodeposition current of Cu–TiO₂ composite coatings, less intensive incorporation of TiO₂ into the copper matrix occurs, and the content of the dispersed phase decreases. To explain the nature of the influence of the concentration of the dispersed phase in the electrolyte and the density of the electrodeposition current on the particle content of titanium dioxide in composites, the peculiarities of composite formation should be taken into consideration. Those particles that are on the surface of the cathode over a sufficient period for their incorporation enter the metal matrix. The degree of filling the cathode surface with particles is the finite value. Consequently, an increase in the concentration of the dispersed phase in the electrolyte should lead to an increase in its content in composites not linearly; at high concentrations in the electrolyte, the particle content in the coatings asymptotically approaches the maximum value. The formation of the composite occurs through the electrodeposition of the metal matrix and the inclusion of inert particles into it. Titanium dioxide particles partially shield the surface of the cathode and the distribution of force lines of the electric field on this surface is not uniform. This, in fact, predetermines the incorporation of titanium dioxide particles into the copper matrix. Increasing the density of the current, probably, leads to the redistribution of the current density over the cathode surface with a decrease in the differences in the values of the current densities on the free and partially occupied by the

dispersed phase of the cathode surface. This may explain the decrease in the content of titanium dioxide in Cu–TiO$_2$ composites with an increase in the electrodeposition current density.

5. 2. Studying the influence of electrolysis conditions on the photocatalytic and physicochemical properties of the Cu–TiO$_2$ composite coatings obtained from methane-sulfonate electrolytes

The inclusion of titanium dioxide particles in a metal matrix renders the Cu–TiO$_2$ composite photocatalytic properties. We studied the photocatalytic activity of composites using a model solution of methyl orange dye. The degree of photo destruction of the dye was determined from the following equation

$$Y = \frac{C_0 - C}{C_0},\qquad(8)$$

where C_0 is the initial concentration of orange methyl in solution; C is the current concentration of methyl orange in solution.

Fig. 7 shows that the degree of the photo destruction of methyl orange under the action of ultraviolet light without a photocatalyst does not exceed one percent. The introduction of Cu–TiO$_2$ into the composite coating system leads to a significant increase in the degree of photo destruction.
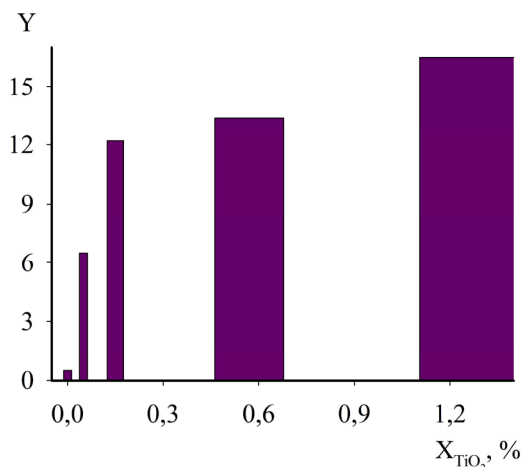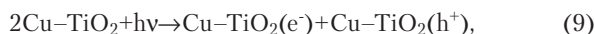

Fig. 7. Dependence of the degree of photo destruction of methyl orange on the content of titanium dioxide in Cu—TiO$_2$ composites

Increasing the content of titanium dioxide in the coatings naturally enhances the photocatalytic effect of dye decomposition; its concentration decreases.

Apparently, the increase in the content of titanium dioxide in the composite causes a proportional increase in the free surface of titanium dioxide, which is in contact with a solution of methyl orange. According to [34], the following processes take place:

$$2Cu–TiO_2 + h\nu \rightarrow Cu–TiO_2(e^-) + Cu–TiO_2(h^+),\qquad(9)$$

$$Cu–TiO_2(h^+) + H_2O_{ads} \rightarrow Cu–TiO_2 + {}^{\bullet}OH_{ads} + H^+,\qquad(10)$$

$$MO + {}^{\bullet}OH_{ads} \rightarrow \text{destruction products}.\qquad(11)$$

Ultraviolet irradiation converts electrons at the surface of Cu–TiO$_2$ from the valence zone to the conduction zone. This leads to the formation of a pair electron-hole. The resulting hole migrates to the surface of the particle of titanium dioxide and decomposes the adsorbed water molecule. Hydroxyl radical is formed. The high reactive activity of the radical predetermines its interaction with the Cu–TiO$_2$ methyl orange (MO) molecules adsorbed on the surface of the composite.

To use photocatalytic composites in wastewater treatment, such coatings should be wear-resistant enough and well-glued to the base. Continuous water supply in the corresponding devices causes the friction of liquid against the surface of the photocatalyst. Consequently, it is necessary to assess the effect of the dispersed phase on the micro-hardness and internal stresses of Cu–TiO$_2$ coatings.

The micro-hardness of Cu–TiO$_2$ composites derived from methyl sulfate electrolytes increases with an increase in the content of titanium dioxide in the composites (Fig. 8).
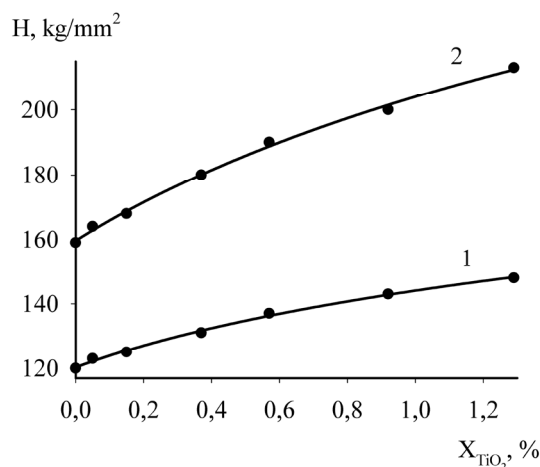

Fig. 8. Dependence of the micro-hardness of Cu—TiO$_2$ composites on the concentration of the dispersed phase in the electrolyte, obtained at a current density of, A/dm^2: 1 — 2; 2 — 7

An increase in current density leads to an increase in the micro-hardness of pure copper, and in the presence of titanium dioxide in the electrolyte, these indicators for deposited composites are even greater. Consequently, the dispersed phase helps increase the micro-hardness of composites. This is due to both the curvature of the crystalline lattice and the strengthening caused by the greater hardness of the oxide phase compared to copper.

Fig. 9 shows the dependences of internal stresses in the Cu–TiO$_2$ composites, electrodeposited from methyl sulfonate suspension electrolytes.

As can be seen from the figure, an increase in the content of the dispersed phase in Cu–TiO$_2$ composites causes an increase in the internal stresses of the stretching of the coatings. It is likely that the increase in internal stresses occurs as a result of the curvature of the crystalline lattice of copper by the incorporated particles of the dispersed phase; this effect is greater, the greater the content of the dispersed phase in the coatings. A certain increase in the internal stresses of the composite coatings is an undesirable effect. However, the maximum value of these stresses does not exceed 50 MPa while the adhesion between composite coatings and the plate is good.
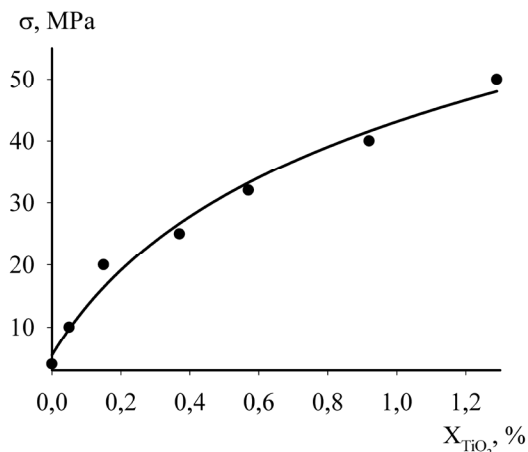
σ, MPa

Fig. 9. Dependence of the internal stresses in composites on the content of TiO₂ in the Cu–TiO₂ coatings obtained at i=2 A/dm²

6. Discussion of results of studying the patterns in the formation of Cu–TiO₂ composites obtained from methane-sulfonate electrolytes

The resulting dependences of the content of titanium dioxide in Cu–TiO₂ coatings, derived from methane-sulfonate electrolytes, on the conditions of electrolysis indicate significant incorporation of the dispersed phase. Thus, at the concentration of TiO₂ in an electrolyte equal to 4 g/l, the content of the dispersed phase is 1.3 % by weight. At the same time, at the concentration of titanium dioxide of 5 g/l in the sulfate electrolyte, the content of the dispersed phase in the coatings is 0.81 % [21]. This is because the content of the dispersed phase in composites is determined by the size of the particles in the suspension electrolyte. In this context, it is important that methane-sulfonate-anion has a less coagulating effect on the dispersion of titanium dioxide in the electrolyte.

To determine the distribution of particles of titanium dioxide by size in the methane-sulfonate electrolyte, we performed a sedimentation study Fig. 10 shows the differential dependences of particle distribution by size, which are obtained immediately after the introduction into the electrolyte of TiO₂ powder and from an electrolyte stirred for 30 minutes. The differential curves are extreme in nature, indicating the polydispersity of the system. The curve obtained from the suspension electrolyte without pre-agitation has a blurred maximum corresponding to particles with a dominating size of 14 μm. Agitating the suspension electrolyte contributes to a narrowing of the range of sizes of the dispersed phase; the dominating particle size is halved.

Obviously, the electrolyte for the electrodeposition of Cu–TiO₂ composites contains the TiO₂ particles of different sizes within the established range (Fig. 10). Initial particles measuring 31 nm have excess surface energy and form agglomerates. In the electrolyte, when stirred, these agglomerates are crushed. At the same time, a double electrical layer is formed in the electrolyte on the particle surface, in the formation of which ions that are present in the electrolyte take part. Reducing the thickness of the double electrical layer leads to particle coagulation. Consequently, the agglomerates of powdered titanium dioxide in the electrolyte

are involved in two opposite processes. They are destroyed at agitation; smaller particles are partially enlarged as a result of coagulation. The resulting differential curves of particle distribution of titanium dioxide by size correspond to some quasi-state of the dispersed system.
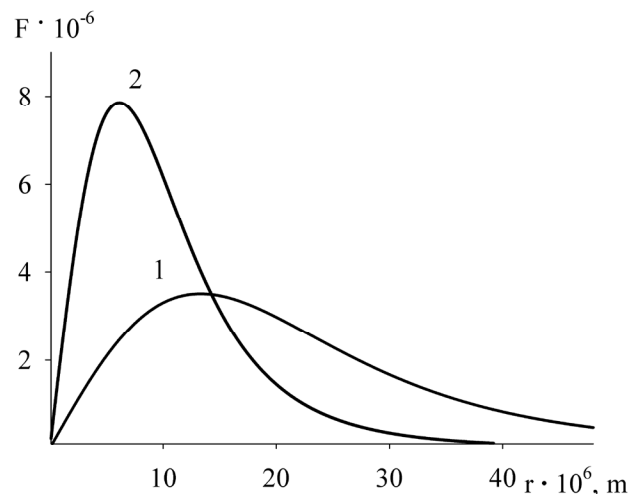
F · 10⁻⁶

Fig. 10. Differential curves of the TiO₂ particle distribution by size obtained in methane-sulfonate copper electrolyte containing 2 g/l of titanium dioxide: 1 — without pre-agitation; 2 — with a pre-agitation of the electrolyte for 30 minutes

A greater concentration of fine TiO₂ particles in the methane-sulfonate electrolyte compared to the sulfate electrolyte causes a greater content of titanium dioxide in composite coatings. Accordingly, composites with high photocatalytic activity and significant micro-hardness can be received from less titanium-dioxide-concentrated suspension electrolytes. That is, the use of the developed electrolyte greatly simplifies the technological execution of the process, at which there is no need to introduce complex structural solutions to maintain the high concentration dispersion in a balanced state.

It should be noted that despite the decrease in the size of the dispersed phase in the methane-sulfonate electrolyte, the initial nanoparticles of titanium dioxide are consolidated as a result of coagulation. To resolve the issue of further grinding of particles of the dispersed phase in methane-sulfonate electrolyte in the future, it is advisable to investigate the effect of surfactants on this process.

7. Conclusions

1. We have established the dependences of the content of the dispersed phase in Cu–TiO₂ composites on the concentration of titanium dioxide in the electrolyte and the density of electrodeposition current. Increasing the concentration of TiO₂ to 4 g/l leads to an increase in the content of the dispersed phase in sediment to 1.3 % by weight at a current density of 2 A/dm². With an increase in the current density, the content of titanium dioxide in the Cu–TiO₂ coatings is slightly reduced We have proposed an explanation of the detected patterns based on ideas about the partial filling of the cathode surface with a dispersed phase during electrol-

ysis and an uneven distribution of current density on a free and partially particle-occupied cathode surface. Using the sedimentation method of analysis, it was established that the predominant particle size of titanium dioxide in the methyl sulfonate electrolyte for the electrodeposition of Cu–TiO$_2$ composites is 7 µm. It has been shown that the equilibrium particle size is determined by the processes of grinding agglomerates in the electrolyte at agitation and coagulating particles. It was found that in methane-sulfonate electrolyte, the coagulative effect of the anion is less compared to sulfate electrolyte, which has a positive effect on the incorporation of the dispersed phase into the coatings.

2. The photocatalytic activity of Cu–TiO$_2$ composites deposited from methane-sulfonate electrolyte in the process of photo destruction of methyl orange was studied. It has been shown that an increase in the content of titanium dioxide in Cu–TiO$_2$ coatings leads to an increase in their photocatalytic activity. The expediency of increasing the free surface of

titanium dioxide in contact with the dye solution in view of the mechanism of photocatalysis has been substantiated. The incorporation of titanium dioxide particles into the copper matrix leads to an increase in the micro-hardness of the coatings by 20–30 % due to the curvature of the metal crystalline lattice and strengthening due to the high hardness of TiO$_2$. The presence of a dispersed phase in the coatings somewhat increases the internal stresses at stretching. However, the Cu–TiO$_2$ composite coatings derived from methane-sulfonate electrolyte are plastic enough and well-glued to the base. We have developed a methane-sulfonate electrolyte for the electrodeposition of Cu–TiO$_2$ composites, which includes 0.6 mol/l Cu(CH$_3$SO$_3$)$_2$, 0.6 mol/l CH$_3$SO$_3$H, 4 g/l TiO$_2$. The established indicators of the photocatalytic activity and the physicochemical properties of the obtained Cu–TiO$_2$ composites indicate good prospects of using them as photocatalysts in wastewater treatment from pollutants of organic origin.

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