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Journal of Advanced Materials and Technologies

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"Journal of Advanced Materials and Technologies" publishes original articles, reviews, short reports written by both renowned scientists and young researchers that contribute to the development of modern materials science.

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CONTENTS

Original papers

Advanced structural materials, materials for extreme conditions

98
108

Nanostructured, nanoscale materials and nanodevices

Pchel'nikov A. V., Pichugin A. P. Chemically resistant nanostructured protective coatings for metal	
surfaces	117

Manufacturing processes and systems

Zubov D. N., Sokolov S. A., Eganova E. M., Yakovlev V. B. Electron beam lithography using	
SiO ₂ as a sensitive layer	129
Degtyarev A. A., Trishina A. V., Rostova D. P. Theoretical investigation of the interaction	
mechanism of trialkylamine derivatives with the copper phthalocyanine surface	141

Materials for energy and environment, next-generation photovoltaics, and green technologies

Kadum A. H. K., Burakova I. V., Badin D. A., Rybakova S. O., Timirgaliev A. N., Yarkin V. O.,Kuznetsova T. S., Dyachkova T. P., Burakov A. E. Sorption dynamics of organic dyes fromaqueous solutions using activated carbon derived from peach modified with carbonnanotubes.154

Reviews

Materials for energy and environment, next-generation photovoltaics, and green technologies

СОДЕРЖАНИЕ

Оригинальные статьи

Современные конструкционные материалы, материалы для экстремальных условий

Столин А. М., Стельмах Л. С. Кинетика холодного уплотнения композиционного материала					
на основе политетрафторэтилена с учетом структурных факторов в режимах постоянного					
усилия на плунжере пресса или его постоянной скорости	98				
Малахов А. Ю., Серопян С. А., Денисов И. В., Шахрай Д. В., Боярченко О. Д.,					
Малахов А. Ю., Серопян С. А., Денисов И. В., Шахрай Д. В., Боярченко О. Д., Ниезбеков Н. Н., Волченко Е. И. Исследование влияния титана на образование соединения					

Наноструктурированные, наноразмерные материалы и наноустройства

Пчельников	A. B.,	Пичугин	А. П.	Химостойкие	наноструктурированные	защитные	
покрытия для	металли	ческих пове	рхносте	ей			117

Производственные процессы и системы

Зубов Д. Н., Соколов С. А., Еганова Е. М., Яковлев В. Б. Электронно-лучевая литография	
с использованием SiO ₂ в качестве чувствительного слоя	129
Дегтярев А. А., Тришина А. В., Ростова Д. П. Теоретическое изучение механизма взаимо-	
действия производных триалкиламинов с поверхностью фталоцианина меди	141

Материалы для энергетики и окружающей среды, фотоэлектрическая энергия следующего поколения и зеленые технологии

Обзор

Материалы для энергетики и окружающей среды, фотоэлектрическая энергия следующего поколения и зеленые технологии

Чабан В. В., Андреева Н. А. Проектирование сорбентов диоксида углерода в рамках концеп-	
ции ландшафта потенциальной энергии	167

Original papers

Advanced structural materials, materials for extreme conditions

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Kinetics of cold compaction of polytetrafluoroethylene-based composite material taking into account structural factors in constant force modes on press plunger or its constant speed

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Abstract: The article discusses the results of mathematical modeling of the one-sided pressing technological process of powder fluoropolymer materials. The peculiarity of the theoretical description is the consideration of rheodynamics, structuring and kinetics of compaction of the compressed medium. An important point of such a description is the choice of rheological equations. In what follows, it is assumed that the compaction of the material occurs according to the mechanism of viscous flow of the mass into pores (according to the theory of Ya.I. Frenkel). The rheological properties of such a medium, i.e. the ability to deform and flow, are determined by the properties of the solid phase, the presence and degree of porosity. Two variants of the technological process of a constant specified force or its constant speed. The analysis of numerical calculations for each of these modes made it possible to identify their fundamental features. It was found that in the mode of a specified force, progressive autobraking of the compaction process occurs over time. It is shown that for pressing materials in both modes it is necessary to select such parameters when the time of structural transformations is longer than the compaction time. The conducted analysis allowed to develop specific recommendations for forecasting rational modes of one-sided pressing of powder materials.

Keywords: fluoropolymers; polytetrafluoroethylene; structural model; cold pressing; rheodynamics; structurization.

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Кинетика холодного уплотнения композиционного материала на основе политетрафторэтилена с учетом структурных факторов в режимах постоянного усилия на плунжере пресса или его постоянной скорости

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Аннотация: Обсуждаются результаты математического моделирования технологического процесса одностороннего прессования порошковых фторполимерных материалов. Особенностью теоретического описания является учет реодинамики, структурирования и кинетики уплотнения сжимаемой среды. Важный моментом такого описания – выбор реологических уравнений. В дальнейшем предполагается, что уплотнение материала происходит по механизму вязкого течения массы в поры (согласно теории Я. И. Френкеля). Реологические свойства такой среды, то есть способность к деформированию и течению, определяются свойствами твердой фазы, наличием и степенью пористости. Рассмотрены два варианта технологического процесса прессования в зависимости от задаваемых извне условий на перемещение плунжера пресса: режимы постоянного заданного

усилия или его постоянной скорости. Анализ численных расчетов для каждого из этих режимов позволил выявить их принципиальные особенности. Установлено, что в режиме заданного усилия происходит прогрессивное автоторможение процесса уплотнения во времени. Показано, что для прессования материалов в обоих режимах следует выбирать такие параметры, когда время структурных превращений больше времени уплотнения. Проведенный анализ позволил выработать конкретные рекомендации прогноза рациональных режимов одностороннего прессования порошковых материалов.

Ключевые слова: фторполимеры; политетрафторэтилен; структурная модель; холодное прессование; реодинамика; структуризация.

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1. Introduction

It is known that deformation has a strong effect on the structure of the forming polymer and on the kinetics of viscosity changes during technological processes. Despite the successes achieved and a large number of published works in this area, there are still phenomena and dependencies which nature is still unclear. This is quite understandable if we take into account the fact that problems of structuraldeformational dependencies cover a wide range of processes, phenomena and objects in the chemistry and mechanics of polymers [1, 2]. During shear fluid deformation of structured systems, a phenomenon of viscosity superanomalies, named so by the founder of domestic polymer rheology G.V. Vinogradov, is realized [3]. This phenomenon is associated with a decrease in resistance to deformation with an increase in the deformation rate. In this case, the rheological curve in the coordinates of stress from the shear rate has an N-shaped form, and one of the branches of this curve has a negative slope (negative differential viscosity). It should be noted that under conditions of super-anomaly of viscosity, a sudden transition through the critical value is possible, which leads to the fact that the deformation mode with an almost intact structure and high viscosity abruptly changes to the deformation mode with an extremely destroyed structure and low viscosity.

Previously, a theoretical analysis of the process of one-sided pressing under conditions of a constant speed on the press plunger and constant pressure of powder composite polymer materials based on polytetrafluoroethylene (PTFE) with small additives (less than 5 %), such as silicon dioxide SiO₂, kaolinite Al₄[Si₄O₁₀](OH)₈, carbon nanotubes, carbon fiber was carried out. New visual ideas about the kinetics of compaction of powder materials based on polytetrafluoroethylene under conditions of constant pressure and speed of the press plunger were established [4]. This paper presents a mathematical model of the process of cold pressing of a viscous structured material. Previously developed rheodynamic models of solid-phase pressing of materials [4, 5] are supplemented by taking into account the dependence of viscosity on the structural parameter.

It is assumed that under the action of external loads the structure of the material can be destroyed. The processes of structural transformations, namely, the destruction and restoration of the structure, are similar to the process of a chemical reaction occurring in the forward and reverse directions [3, 6, 7]. But rheodynamics was not taken into account in the theoretical description of these processes.

The structural approach allows us to analyze the dynamics of the deformation processes of structured systems and explain the nature of various critical (threshold) phenomena and oscillatory modes [7, 8]. This approach made it possible to analyze the dynamics of the deformation process of structured systems. Based on a numerical study of the problem posed for the process parameters corresponding to solid-phase pressing of fluoropolymers, the possibility of various deformation modes was theoretically shown.

2. Process model and problem statement

The compaction of a viscous porous material in a cylindrical chamber limited from above by a moving piston should be considered. The axis of symmetry of the work piece is taken as the z axis, the positive direction of which is opposite to the direction of piston movement.

The rheodynamic model of the process, which does not take into account structural transformations, is presented in [4]. The formulation of the problem taking into account structural transformations includes equations, equilibrium (1), continuity (2), rheological relationships (3), (4), and a kinetic equation describing the change in structure (5):

$$\frac{\partial \sigma_{zz}}{\partial z} = 0; \tag{1}$$

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho V)}{\partial z} = 0; \qquad (2)$$

$$\sigma_{zz} = \left(\frac{4}{3}\mu + \xi\right) \frac{\partial V}{\partial z}; \qquad (3)$$

$$\sigma_{rr} = \sigma_{\theta\theta} = \left(-\frac{2}{3}\mu + \xi\right)\frac{\partial V}{\partial z}; \qquad (4)$$

$$\frac{\partial(a\rho)}{\partial t} + \frac{\partial(a\rho V)}{\partial z} = \varphi(a\sigma_{zz}), \qquad (5)$$

where $\sigma_{zz}, \sigma_{rr}, \sigma_{\theta\theta}$ are axial, radial and tangential stresses; ρ is relative density of the material; μ , ξ is shear and bulk viscosity of the material; *V* is flow rate of the material; ρ is density of the incompressible base of the material, *a* is a degree of structural changes. Due to the high viscosity of fluoropolymers, the Reynolds criterion is small [8, 9], therefore, for cold pressing of fluoropolymers, the equilibrium equation (1) can be used instead of the equation of motion.

To study the process of structural transformations, we use a model of the flow of a two-component liquid taking into account the kinetics of the mutual transformation of structural units [8].

Let the rheological system consist of structures of types A and B, mutually transforming into each other $A \xrightarrow{\longrightarrow} B$ under the action of an applied \leftarrow

mechanical field with their concentration in the volume *a* and b = 1 - a. In this case, the kinetic equation for the change in structure is written as (5). We assume that the processes of restoration and destruction of the structure are activation processes, the rates of destruction and restoration of structures can be written as:

$$k_{1} = k_{10} \exp\left(-\frac{U_{1} - E_{1}}{RT}\right);$$

$$k_{2} = k_{20} \left(-\frac{U_{1} + E_{1}}{RT}\right),$$

where *T* is the sample temperature; U_1 is the activation energy of viscous flow; *R* is a universal gas constant; E_1 is the effective activation energy; k_{10} , k_{20} are constants of destruction and restoration of the structure, respectively. For cold pressing, the

temperature does not change during the process and is equal to the ambient temperature (293 K).

Then the total rate of structural transformations:

$$\varphi(a\sigma_{zz}) = -k_1a + k_2(1-a).$$

Under the influence of a mechanical field, deformation of bonds in the structure being destroyed occurs, depending on the magnitude of the stress, and the orientation of randomly directed molecular-kinetic units, depending on the velocity gradient. In this case, the effective activation energy $E_1 = p_1 \sigma_{zz}$, where p_1 is the constant of the destruction intensity. Due to the high viscosity of fluoropolymers $(10^8-4\cdot10^9 \text{ Pa·s})$, orientational rotation is difficult and the effective activation energy decreases only under the action of compressive (or tensile) stress (this applies to the mechanical destruction of polymers).

In this paper, the generalized Newton model is used to describe the viscoelastic behavior of the material:

$$\sigma_{zz} = \left(\frac{4}{3}\mu + \xi\right) \frac{\partial V}{\partial z},$$

where $\mu = \mu(a) = \mu_0 \exp(ka)$ is the viscosity depending on the degree of structural transformations *a* (the concentration of intermolecular crosslinks).

Usually, different deformation modes are set in the experiment: a mode with constant force (a constant pressure *P* is set on the piston) and a mode with a constant deformation rate (a constant piston speed is set): $\sigma_{zz}|_{z=H(t)} = -P$, $V_{zz}|_{z=H(t)} = V$.

In this paper, both deformation modes are considered.

The problem is characterized by the presence of a moving boundary: the upper boundary of the solution region (Z = H), corresponding to the press plunger

$$\frac{dH}{dt} = -V_H \; .$$

The problem has two viscosity coefficients – shear (μ) and volume (ξ), depending on the density and structural parameter (*a*):

$$\mu(\rho, T, a) = \mu_0 \rho^m \exp(ka);$$

$$\xi(\rho, T) = \frac{4}{3} \mu(\rho, T, a) \rho / (1 - \rho) = \frac{4}{3} \mu_0 \rho^{m+1} / (1 - \rho) \exp(ka).$$

At the initial moment of time, the density distribution by the pressing height is given $\rho(z, 0) = \rho_0(z) = \rho_0 + (\rho_m - \rho_0)z/H_0$ and the initial distribution of the structure by sample $a(z, 0) = a_0(z)$.

Boundary conditions:

z = 0: V = 0;

 $z = H_0$: $\sigma_{zz} = -P$ (for the case of a given force on the press plunger);

 $z = H_0$: $V_n = V_0$ (for the case of a given speed on the press plunger).

For the numerical solution of the problem, Lagrangian coordinates associated with the medium for stopping the upper moving boundary of the sample were used. Lagrangian coordinates (q; t) have the following meaning: $t_L = t$ is real time, mass coordinate q has the meaning of the relative mass between the lower boundary of the mold and the upper moving boundary z:

$$q = \int_{0}^{z} \rho(z, t) dz$$

 $q_0 = \int_{0}^{H_0} \rho(z,0) dz$ is the initial coordinate, which is the

total mass of the sample, expressed in linear units. The problem statement in Lagrange coordinates has the following form:

$$\begin{aligned} \frac{\partial \sigma_{zz}}{\partial q} &= 0; \\ \frac{\partial \rho}{\partial q} + \rho^2 \frac{\partial (V)}{\partial q} &= 0; \\ \sigma_{zz} &= \left(\frac{4}{3}\mu + \xi\right)\rho \frac{\partial V}{\partial q}; \\ \sigma_{rr} &= \sigma_{\theta\theta} = \left(-\frac{2}{3}\mu + \xi\right)\rho \frac{\partial V}{\partial q}; \\ \frac{\partial (a)}{\partial t} &= \phi(a, \sigma_{zz})/\rho_1\rho. \end{aligned}$$

Boundary conditions:

q = 0: V = 0;

 $q = q_0$: $\sigma_{zz} = -P$ (for the case of a given force on the press plunger);

 $q = q_0$: $V_n = V_0$ (for the case of a given speed on the press plunger).

Initial conditions:

$$\rho(q, 0) = \rho_0(q);$$

 $a(q, 0) = a_0(q).$

The equations were reduced to dimensionless form and solved numerically using a conservative balance scheme. This scheme ensures exact (without taking into account the rounding error) fulfillment of conservation laws on any grid in a finite region containing an arbitrary number of nodes of the difference grid [10]. The grid is non-uniform in space and time. Then the resulting algebraic equations are solved using the sweep method.

As a result of the solution, unknown stresses $(\sigma_{zz}, \sigma_{rr}, \sigma_{\theta\theta})$, relative density (ρ), velocity (V), structural parameter (a) were found, which are functions of the coordinate (q) and time (t).

The problem has two scales of characteristic times: compaction $t_c = 4\mu_1/3P$, structuring $t_a = 1/k_{10}$, where μ_1 is viscosity of the incompressible base material, q_0 is the relative initial mass of the material, P is the pressure on the piston. Depending on the relationships between these scales, various modes of compaction and structural changes are possible.

Parameters (technological parameters and properties of polytetrafluoroethylene) vary within the following limits: $P = 10^7 - 5 \cdot 10^8$ Pa, $V = 8 \cdot 10^{-6} - 2 \cdot 10^{-3}$ m·s⁻¹, $\rho_1 = 2.25 \cdot 10^3$ kg·m⁻³, $\mu_1 = 10^7 - 4 \cdot 10^9$ Pa·s, $q_0 = 1.5 \cdot 10^{-2} - 3 \cdot 10^{-2}$ m, $k_{10} = 1 \cdot 10 - 1 \cdot 10^{-3}$. The characteristic times corresponding to these parameter values vary in the following intervals: $t_c = 3 \cdot 10^{-2} - 5 \cdot 3 \cdot 10^2$ s, $t_a = 10^{-1} - 10^3$ s.

3. Results and Discussion

3.1. Pressing mode with constant force on the press plunger

In general, the deformation mode is determined by the ratio of characteristic times. The limiting values of density and degree of structural changes are affected by the main parameters of the process.

Below are the results of numerical calculations for plunger cold pressing with a given force on the press plunger. Fig. 1 shows the dependences of density (ρ and structural parameter *a* on time *t*) for two limiting cases: the time of structural changes is much longer than the deformation time (Fig. 1*a*) and the time of structural changes is shorter than the deformation time (Fig. 1*b*). In the first case, the samples are dense, but not completely structured, and in the second case, the samples are not compacted to the maximum value.

Transitional modes of structuring and compaction lie between these extreme cases (Fig. 2).

It can be assumed that in the case when the characteristic time of complete structuring t_a is comparable with the deformation time t_c , the samples are smoother, but not compacted.



Fig. 1. Dependence of relative density ρ (curve *l*) and structural parameter *a* (curve *2*) on pressing process time *t*: $a - t_c << t_a, b - t_c >> t_a$

For the pressing mode with a given force on the press plunger, the dependence of the time to reach the maximum density value on the pressure on the press plunger is shown in Fig. 3*a*. It is evident that for pressure values less than 100 MPa, this time is very long (more than 25 min, and the characteristic compaction time is much longer than the structuring time. The material will be uncompacted.

The characteristic times of compaction and structuring strongly depend on the applied pressure on the press plunger (Fig. 3b). If the pressure is less than 100 MPa, the characteristic time of compaction is significantly longer than the structuring time, and when the pressure is greater than 130 MPa, the

characteristic times are comparable. In these cases, the material is undercompacted and understructured. Between these modes (pressure from 100 to 130 MPa), the characteristic time of compaction is shorter than the structuring time, but the material has time to undergo these processes and the material should be of better quality.

3.2. Pressing mode with constant speed on the press plunger

When pressing in the mode with a constant speed on the press plunger, the material always reaches the ultimate density value [6].



Fig. 2. Relative density ρ (curve *I*) and structural parameter *a* (curve *2*) versus pressing process time *t*: $t_c \cong t_a$



Fig. 3. Pressure dependence P on the press plunger: *a* – time *t* to reach the limit value of density; *b* – characteristic compaction times (curve I) and structuring (curve 2)

But in the case when the time of structural transformations is significantly longer than the compaction time, the material is compacted to the ultimate density, but the structuring process does not have time to complete (Fig. 4). In a large range of speeds (Fig. 3a, $V = 2 \cdot 10^{-3}$ m·s⁻¹, Fig. 3b, $V = 2 \cdot 10^{-5}$ m·s⁻¹) used in practice, this is exactly the case. In Fig. 4*a*, the characteristic compaction time (0.025 s) is much less than the structuring time (10 s), and in Fig. 3*b*, the characteristic compaction time (2.5 s) is slightly less than the structuring time (10 s), and in both cases, the density reaches its ultimate value, and structuring is not complete.

Figure 5 shows the case of pressing at a constant speed, when the characteristic times of structuring and compaction are comparable. It can be assumed that in this case the material will be less durable than in the case when the material is quickly compacted (Fig. 4a), although the structuring process is not finished.

The most acceptable case is when the compaction time is several times (3 or 4 times) longer than the structuring time. In this case (Fig. 4b) the material reaches the limit value, the structuring process is almost finished and the compaction process itself is smoother than in the case of high speeds on the press plunger, which should affect the quality of the obtained samples towards its improvement.

Figures 6, 7 show the dependences of the density and structural parameter on time for cases when the characteristic compaction time is slightly less than the structuring time ($t_c < t_a$) (Fig. 6), the characteristic compaction time is much less than the characteristic structuring time ($t_c << t_a$) (Fig. 7).



Fig. 4. Dependence of relative density ρ (curve *I*) and structural parameter *a* (curve *2*) on pressing process time *t*: $a - V = 2 \cdot 10^{-3} \text{ m} \cdot \text{s}^{-1}, t_c << t_a; b - V = 2 \cdot 10^{-5} \text{ m} \cdot \text{s}^{-1}, t_c < t_a$





Fig. 6. Dependence of relative density $\rho(a)$ and structural parameter *a* (*b*) on pressing process time *t* at three different points: top is a blue curve *1*, middle is a red curve *2*, bottom is a green curve *3*, $t_c < t_a$

In the first case, the material reaches the limit value of density and the end of structuring, and the difference in the value of the structural parameter of the top and bottom of the material by the end of pressing is no more than 0.05 (Fig. 7*a*). And for the second case, the structuring is not finished, and it can be assumed that there will be a non-uniform surface (the plunger speed in this case is $2 \cdot 10^{-3} \text{ m} \cdot \text{s}^{-1} = 120 \text{ mm} \cdot \text{min}^{-1}$). Therefore, the option when the speed is 12 mm $\cdot \text{min}^{-1}$ is preferable (Fig. 6).

4. Conclusion

The development of the cold solid-phase pressing process depends on the ratio of the characteristic times of compaction and structural transformations. These times depend on the process parameters: the press plunger speed, the pressure on the plunger, the intrinsic properties of the material, the bulk and shear viscosities and their dependence on the density, the structural parameter, the geometry of the setup and the sample [11–14]. The averaging method used in this work and the application of Lagrangian coordinates make it possible to simplify the finding of the optimal region of parameters for the implementation of the most favorable modes from the technological point of view. For pressing materials in modes with a constant force on the press plunger and at a constant speed, such parameters should be selected when the time of structural transformations is slightly longer than the compaction time.



Fig. 7. Dependence of relative density $\rho(\alpha)$ and structural parameter *a* (*b*) on pressing process time *t* at three different points: top is a blue curve *1*, middle is a red curve *2*, bottom is a green curve *3*, $t_c \ll t_a$

Then the samples are dense, although the structuring process is almost complete, the distribution of the structural parameter and density along the height of the sample is uniform.

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6. Conflict of interest

The authors declare no conflict of interest.

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Study of the influence of titanium interlayer on formation of AlMg6 – 12Cr18Ni10Ti weld interface during explosive welding

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Abstract: This paper presents the aspects of the formation of multilayer composite material (MCM) consisting of aluminium-magnesium alloy AlMg6, titanium VT1-0 and austenitic stainless steel 12Cr18Ni10Ti during explosive welding. This MCM has promising properties for use in various industries such as shipbuilding and automobile manufacturing. However, the production of this material presents certain difficulties due to different properties of the initial materials. In this paper, the effect of residual stresses occurring in MCM after explosive welding on the continuity of the joint was investigated. Using metallographic studies and electron microscopy, it was found that the high velocity impact process between different materials comprising MCM formed weld interfaces with straight and wavy profiles. There was also evidence of dynamic recrystallisation at the 12Cr18Ni10Ti–VT1-0 weld interface and the formation of vortex zones in wave crests. The microhardness of the layers was also measured. The measurement showed that hardening occurred in MCM layers with the maximum value in the 12Cr18Ni10Ti steel layer. The evaluation of tear strength revealed that the formation of cracks occurred at the interface between the VT1-0–AlMg6 weld interface, with an average strength of 160 MPa. The results of the study may be useful to specialists in materials science, mechanical engineering and other related fields.

Keywords: explosive welding; AlMg6; titanium; microhardness; weld interface; steel.

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Исследование влияния титана на образование соединения АМг6 – 12X18H10T в процессе сварки взрывом

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Аннотация: Рассматриваются особенности формирования в процессе сварки взрывом многослойного композиционного материала (МКМ), состоящего из алюминиево-магниевого сплава АМг6, титана ВТ1-0 и аустенитной коррозионностойкой стали 12Х18Н10Т. Данный МКМ обладает перспективными свойствами для использования в различных отраслях промышленности, таких как судостроение и автомобильная

108 Malakhov A.Yu., Seropyan S.A., Denisov I.V., Shakhray D.V., Boyarchenko O.D., Niyozbekov N.N., Volchenko E.I.

промышленность. Однако процесс получения такого материала сопряжен с определенными трудностями, связанными с различиями в свойствах исходных материалов. Проведено исследование влияния остаточных напряжений, возникающих в МКМ после сварки взрывом, на сплошность соединения. С помощью металлографических исследований и электронной микроскопии обнаружено, что в процессе высокоскоростного соударения между различными материалами, входящими в состав МКМ, формируются границы соединения с прямым и волнообразным профилем. Кроме того, получены данные о динамической рекристаллизации на границе соединения 12Х18Н10Т – ВТ1-0 и образовании вихревых зон в гребнях волн. Проведено измерение микротвердости слоев, которое показало, что в слоях МКМ произошло упрочнение, максимальное значение которого зафиксировано в слое из стали 12Х18Н10Т. Испытание прочности слоев на отрыв выявило, что разрушение происходило по границе соединения ВТ1-0 – АМг6 при средней прочности 160 МПа. Результаты исследования могут быть полезны для специалистов в области материаловедения, машиностроения и других смежных областей.

Ключевые слова: сварка взрывом; АМг6; титан; микротвердость; граница соединения; сталь.

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1. Introduction

Multilayer composite materials (MCM) consisting of aluminum alloy and steel are widely used in shipbuilding, automobile and railcar manufacturing due to their high specific strength and corrosion resistance [1, 2].

Currently, the most common technologies for producing steel/aluminum alloy pairs are mechanical connections (e.g. riveting, clamping, etc.) and adhesive connections [3]. Mechanical and adhesive connections are inferior in strength per unit area to direct metal connections between sheets of steel and aluminum alloy [4].

One of the technologies that allows obtaining a metallic connection between aluminum alloys and steels is explosive welding (EW) [5–7]. This technology uses the energy of explosives to accelerate a metal sheet called a projectile and collide it with a stationary sheet called a base sheet at high speed. During the collision, the surfaces of the sheets are cleaned of any oxides and contaminants, thereby providing a metallic connection.

However, due to the significant difference in the properties of aluminum alloys, and in particular aluminum-magnesium and steel, it is problematic to obtain a strong connection. First of all, this is due to the formation of brittle intermetallic phases of the Fe_xAl_y type at the boundary of the welded joint [8, 9]. For example, in [10], a bimetallic material of aluminum alloy Al1100 with low-carbon steel was obtained. Two types of intermetallic phases Al₃Fe and Al₅Fe₂ were formed at the boundary of the joint. To reduce the formation of intermetallic phases at the interface of the aluminum alloy and steel, an interlayer is used [4]. Typically, ductile materials,

pure aluminum, titanium, etc., act as an interlayer, which allow achieving high strength and ductility of the material [4, 11]. The use of an interlayer of refractory materials (tantalum, vanadium, titanium, etc.) helps prevent the formation of intermetallic compounds during heating during further technological processing and operation of the product [2]. For example, in [11], the authors showed that a titanium interlayer prevents the formation of brittle intermetallic phases Fe_xAl_y. Moreover, intermetallic phases Ti_xAl_v are formed, which have a higher initial temperature and a longer growth time than Fe_rAl_v.

A review of the work shows that most studies of EW were carried out for aluminum alloys with a magnesium content of less than 5 %. Explosion welding of AlMg6 with stainless steel and titanium has not been sufficiently studied.

The aim of the work was to study the influence of the titanium interlayer on the microstructure and mechanical properties of AlMg6–12Cr18Ni10Ti.

2. Materials and Methods

2.1. Initial materials

The following source materials were used to obtain MCM: base sheet – aluminum-magnesium alloy AlMg6 ($4 \times 200 \times 300$ mm); interlayer – titanium VT1-0 ($1 \times 200 \times 300$ mm), rolled sheet – austenitic corrosion-resistant steel 12Cr18Ni10Ti ($3 \times 200 \times 300$ mm).

Table 1 shows physical and mechanical properties of the source materials, such as density (ρ), melting point (T_m), yield strength σ_y , tensile strength σ_t , Brinell hardness (HB) and relative elongation (δ).

Material	Thickness, mm	ρ , kg·m ⁻³	T_m , °C	σ _y , MPa	σ_t , MPa	HB	δ, %
AlMg6	4	2640	630	160	350-355	81	17.9–20.7
Titanium	1	4500	1670	_	395–400	163	67–71
12Cr18Ni10Ti	3	7900	1450	205	530	106	52-56

Table 1. Physical and mechanical properties of the source materials



Fig. 1. Experimental scheme of the explosive welding experiment

The microstructure of AlMg6 consists of the α -phase with a grain size of ~50 µm and the β -phase of Mg₂Al₃ located mainly along the grain boundaries of the α -phase. AlMg6 contains insoluble inclusions of the type (Fe, Mn). The microstructure of 12Cr18Ni10Ti consists of austenite with a small amount of ferrite. The size of the austenite grains is 30–40 µm throughout the thickness of the material. The microstructure of titanium mainly consists of the α -phase, which has a fine-grained structure with a grain size of 7 to 20 µm [12].

2.2. Production of multilayer composite materials

The experimental scheme for obtaining MCM is shown in Fig. 1. A mixture of ammonium nitrate and diesel fuel was used as explosive.

The parameters of EW were calculated using formulas (1) and (2) [13]:

$$V_0 = 1.2D \frac{\sqrt{1 + \frac{32}{27}r} - 1}{\sqrt{1 + \frac{32}{27}r} + 1};$$
 (1)

Table 2. Explosive welding parameters of AlMg6 ++ Titanium + 12Cr18Ni10Ti

$D, \mathrm{m} \cdot \mathrm{s}^{-1}$	$V_0/V_1, {\rm m} \cdot {\rm s}^{-1}$	r	γ0/γ1, °
2600	686/508	1,16	13,8/10,7
	$\gamma = 2 \arcsin($		(2)

where V_0 is the velocity of the plate being thrown; D is the detention velocity of the avalasive: r is a

is the detonation velocity of the plate being thrown, Ddimensionless parameter equal to the ratio of the mass of the explosive charge to the mass of the plate being thrown, γ is the impact angle.

The design parameters of EW are presented in Table 2.

2.3. Quality control methods for welded joints

Ultrasonic testing (UT) was performed using a UD2 BP flaw detector with a DF5012 sensor to assess the continuity of the welded joint. Ultrasonic testing was performed in 3 stages: after EW, 14 days after EW and after heat treatment (HT). HT was

110 Malakhov A.Yu., Seropyan S.A., Denisov I.V., Shakhray D.V., Boyarchenko O.D., Niyozbekov N.N., Volchenko E.I.

performed in an SNOL 8.2/1100 electric muffle furnace at a temperature of 450 °C and held for 1 hour while cooling with the furnace.

Samples for metallographic testing were cut using a DK7725 electrical discharge machine from areas with satisfactory weld continuity in accordance with the ultrasonic testing maps. The samples were ground on abrasive paper with a grain size of 120 to 2500, then polished on felt with diamond paste with a grain size of 1–2 μ m on a LAP-1000 automatic grinding and polishing machine. Final polishing was performed on an AEP 2.2 electrochemical polishing machine.

Metallographic testing of sections was performed on a METAL LV-34 optical microscope. The images were obtained using an MC-5.3 camera. Microhardness was measured using the Vickers method on a PMT-3M microhardness tester under a load of 50 g using the MMC-Hardness software package. Energy dispersive microanalysis of structural components was performed on a Zeiss ULTRA plus electron microscope with an INCA 350 XT Oxford Instruments attachment for X-ray microanalysis. The tear strength of the samples was studied on an Instron 1195 universal testing machine. Samples for metallographic studies and tear strength studies were selected according to the corresponding schemes presented in [12].

3. Results and Discussion

After the UT, maps were compiled (Fig. 2), where the continuity zones are shown as green areas. The continuity of the joint after the UT was 35 % of the total plate area (Fig. 2a).

After the EW, residual stresses arise in the material. They arise as a result of local deformations of the metal due to uneven heating during EW. Residual stresses are mainly concentrated at the weld interface [14]. If the level of residual stresses exceeds the strength of the joint, this can lead to delamination of the material. To determine the effect of residual stresses on the continuity of the joint, UT was carried out immediately after the UT and 14 days after the UT experiments. In the second case, the continuity of the joint was about 30 % of the total plate area (Fig. 2*b*). The presence of residual stresses in the material led to a decrease in the continuity of the joint.

Subsequent maintenance and UT showed that the continuity of the joint did not change. Thus, it can be concluded that within 14 days, complete relaxation of residual stresses occurs in the weld joint boundary area.



Fig. 2. Ultrasonic testing maps of joint continuity: a – immediately after EW; b – 14 days after EW

Further studies of the microstructure were carried out on samples after the HT. It is known that during the HT process, new phases can form at the boundary of the connection of dissimilar materials, which can affect the properties of the connection [15-17].

Figure 3 shows the boundary of the 12Cr18Ni10Ti - Titanium - AlMg6 joint, which has a rectilinear profile between AlMg6 and titanium, and a wave-like profile between titanium and 12Cr18Ni10Ti. The wavelength at the boundary of the 12Cr18Ni10Ti - titanium joint is about $150 \mu m$, and the height is about $25 \mu m$.

Figure 4 shows the microstructure of the 12Cr18Ni10Ti-Titanium joint boundary [18, 19]. During the EW process, vortex zones were formed (area 1), around which dynamic recrystallization



Fig. 3. Weld interface of 12Cr18Ni10Ti – Titanium – AlMg6



Fig. 4. Microstructure of 12Cr18Ni10Ti – Titanium weld interface

zones were found (area 2). It is known that a large amount of heat is released in the vortex zones, which promotes the formation of dynamic recrystallization zones in titanium. This process is typical for materials with low thermal conductivity [18, 19].

Localized shear bands (LSB) were also found (area 3). LSBs were formed in titanium at the joint boundary, at an angle of approximately 45°. It is known that LSBs are one of the failure mechanisms that occur in some materials at high deformation rates, for example, during EW. This term describes a sharp increase in temperature and the transfer of heat to a narrow region [20].

Figure 5 shows the microstructure and EDS analysis results of the weld interface. The results show that the titanium interlayer limits mutual diffusion between 12Cr18Ni10Ti and AlMg6 (Fig. 5*a*). The vortex zone consists of areas of brittle



Na			Ele	ement c	ontent, at	. %		
INO.	0	Mg	Al	Si	Ti	Cr	Fe	Ni
1	2	0.4	3.3	0.8	0.5	18.4	65.3	9.3
2	3	0.1	2.3	1.5	0.4	18.3	64.6	9.8
3	_	_	2.3	_	97.5	0.1	0.1	_
4	_	0.2	2	_	97.3	_	0.2	0.3
5	4.1	6.7	88.7	0.3	-	-	0.2	_
6	2	6.7	91.2	_	_	_	0.1	_



No.	Element content, at. %							
	Al	Ti	Cr	Fe	Ni			
1	3.2	0.3	18.8	67.4	10.3			
2	3.4	0.3	18.9	67.7	9.7			
3	1.9	97.7	0.1	0.2	0.1			
4	2.6	97.2	0.2	_	—			
5	2.4	96.8	0.1	0.5	0.2			

(b)

Fig. 5. SEM-images and results of EDS analysis of MCM 12Cr18Ni10Ti – Titanium – AlMg6: *a* – microstructure MCM; *b* – vortex zone of weld interface 12Cr18Ni10Ti – Titanium intermetallic phases and a mechanical mixture of titanium with elements of corrosion-resistant steel 12Cr18Ni10Ti (Fig. 5*b*, No. 5). Such a structure is usually observed in pairs of materials with close density values, such as Al/Al [21], steel/steel [22].

Figure 6 shows the microstructure of the interface between 12Cr18Ni10Ti and titanium. During EW, a melted zones of about 3 µm thickness was formed at the interface. According to the Fe–Ti phase diagram and the results of EDS analysis (Fig. 6, point 2), it was established that the molten layer consists of the brittle intermetallic phase TiFe [23].

Figure 7 shows the Titanium – AlMg6 bond boundary. During the EW process, a melted zone up to 20 μ m thick was formed (Fig. 7*a*). The results of the EDS analysis showed that the melt consists of titanium particles surrounded by the AlMg6 alloy (Fig. 7*b*).

The study of the MCM microhardness showed that near the boundary of the 12Cr18Ni10Ti – Ttitanium joint an increase in microhardness occurs, which is associated with the formation of a hardening zone with a width of about 200 µm (Fig. 8).



No	Element content, at. %								
INO.	Al	Si	Ti	Cr	Fe	Ni			
1	2.6	1.4	0.9	18	67.5	9.6			
2	2.9	0.9	40.6	11.4	37.9	6.3			
3	2.2	0.4	97.1	0.1	0.1	0.1			

Fig. 6. SEM-images and results of EDS analysis of weld interface 12Cr18Ni10Ti - Titanium

(a)



No.	Element content, at. %						
	0	Mg	Al	Ti			
1	13.6	0.2	2	84.2			
2	14	6	75.3	4.7			
3	3.2	6.4	90.4	_			



No	Element content, at. %							
INO.	0	Mg	Al	Ti	Fe			
1	8.1	_	1.9	89.8	0.2			
2	13.9	0.2	2	83.9	_			
3	2.2	6.1	91.6	0.1	_			
4	2.6	5.8	91.5	0.1	_			
5	1.1	4	90	1.4	3.5			
6	3.1	5.2	88	0.2	3.5			
7	3.8	6.6	85.9	3.5	0.2			
8	10	6.4	80.7	2.9	_			
9	3.7	3.5	50.2	42.6	_			
10	14.5	3.9	47.9	33.7	_			
11	8	2.6	21.8	67.5	0.1			
<i>(b)</i>)							

Fig. 7. SEM-images and results of EDS analysis of weld interface Titanium – AlMg6: a – microstructure weld interface; b – microstructure of melted zone



Fig. 8. Microhardness of 12Cr18Ni10Ti - Titanium - AlMg6



Fig. 9. Tear strength distribution along the MCM length

Figure 9 shows a graph of the strength distribution along the MCM length. It is evident from the graph that the strength value is unevenly distributed along the MCM length. As the distance from the initiation point increases, the strength of the joint increases to 230 MPa, and from a distance of 200 mm it decreases to 172 MPa, which is apparently due to the spread of explosives and the influence of unloading waves. At the same time, the average tear strength was 160 MPa. The destruction of the samples occurred along the titanium-AlMg6 joint boundary.

4. Conclusion

In the course of the work, a multilayer composite material consisting of 12Cr18Ni10Ti, titanium and AlMg6 layers was obtained using the EW method. As a result of the study, it was found that the continuity zone of the welded joint is located in the central part of the multilayer composite material and occupies 35% of the total area of the material. It is shown that after EW, the continuity of the joint is affected by residual stresses, which over time lead to a decrease in the area of the continuity of the joint. The study of the microstructure of the multilayer composite material showed that the boundary of the joint between AlMg6 and titanium has a rectilinear profile, and between titanium and 12Cr18Ni10Ti wavy with a length of 150 μ m and a height of 25 μ m. At the boundary of the 12Cr18Ni10Ti - titanium joint, areas of dynamic recrystallization and vortex zones with plastically deformed layers around them are observed at the tops of the waves. It was found that melted areas were formed at the AlMg6-titanium joint boundary, which were titanium particles surrounded by AlMg6 alloy.

It was revealed that in the 12Cr18Ni10Ti steel layer near the joint boundary, hardening occurred to a depth of \sim 200 µm. The average tear strength of the multilayer composite material was 160 MPa.

Thus, this study allows us to better understand the fundamental features of the EW process of the 12Cr18Ni10Ti – Titanium – AlMg6 multilayer composite material.

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6. Conflict of interest

The authors declare no conflict of interest.

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Chemically resistant nanostructured protective coatings for metal surfaces

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Abstract: The aim of this study is to develop nanostructured protective coatings with high chemical resistance for metal surfaces. To modify paints and varnishes, compositions based on carbon nanotubes (CNTs), bismuth oxide nanoparticles, silicon dioxide, titanium dioxide, magnesium hydroxide and aluminum hydroxide were used. The introduction of nanomaterials into acrylic paint and varnish material helps to increase the adhesive strength of coatings, so the best effect was determined with the introduction of CNTs in the amount of 0.1 % – the adhesive strength increased from 2.0–2.2 MPa to 2.9–3.1 MPa with a change in the nature of the separation of the paint and varnish coating from the substrate from fully adhesive (100 %) to adhesive-cohesive. Evaluation of the chemical resistance of nanostructured paint and varnish coatings modified with CNTs showed that when the coatings were exposed to an herbicide solution, they retained their weight regardless of the concentration of the modifier, while their hardness did not change (H). Evaluation of the equilibrium swelling rate made it possible to determine that paint and varnish coatings modified with bismuth oxide nanoparticles and CNTs are resistant to solvents and acquire a more mesh structure in relation to coatings without additives. Scanning of various sections of the sample surface becomes smoother, and the nanometer roughness decreases from 50–60 nm to 20–30 nm. A more significant reduction in protrusions is observed in coatings modified with CNTs, which indicates that the coating is strengthened by reducing the size of depressions and pores.

Keywords: nanomaterials; nanostructured coatings; paint and varnish coatings and materials; adhesive strength; chemical resistance; metal structures; carbon nanotubes; bismuth oxide.

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Химостойкие наноструктурированные защитные покрытия для металлических поверхностей

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Аннотация: Цель работы заключается в разработке наноструктурированных защитных покрытий с высокой химической стойкостью для металлических поверхностей. Для модификации лакокрасочных материалов применялись составы на основе углеродных нанотрубок (УНТ), наночастиц оксида висмута, диоксида кремния, диоксида титана, гидроксида магния и алюминия. Введение в акриловый лакокрасочный материала наноматериалов способствовало увеличению адгезионной прочности покрытий, так наилучший эффект определен при введении УНТ, в количестве 0,1 % – адгезионная прочность повышается с 2,0...2,2 до 2,9...3,1 МПа при изменении характера отрыва лакокрасочного покрытия от подложки с полностью адгезионного (100 %) на адгезионно-когезионный. Оценка химической стойкости наноструктурированных лакокрасочных покрытий с УНТ показала, что при воздействии на покрытия раствора гербицида, они сохраняют свою массу вне зависимости от концентрации модификатора, при этом их твердость не изменяется (Н). Оценка равновесной степени набухания

позволила определить, что лакокрасочные покрытия с наночастицами оксида висмута и УНТ обладают устойчивостью к растворителям и приобретают более сетчатую структуру по отношению к покрытиям без добавок. Сканирование различных участков поверхностей образцов на АСМ показало, что при модификации нанодобавками оксида висмута и УНТ поверхность становится более гладкой, нанометровая шероховатость уменьшается с 50...60 до 20...30 нм. Более существенное уменьшение выступов наблюдается у покрытий модифицированных УНТ, что говорит об упрочнении покрытия за счет уменьшения размеров углублений и пор.

Ключевые слова: наноматериалы; наноструктурированные покрытия; лакокрасочные покрытия и материалы; адгезионная прочность; химическая стойкость; металлические конструкции; углеродные нанотрубки; оксид висмута.

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1. Introduction

The surfaces of various metal products and structures operating in industrial environments are constantly exposed to aggressive action of various environments: acids, alkalis, fuels and lubricants, salt solutions, etc. Thus, one of the most important properties of protective coatings of metal surfaces is chemical resistance. The use of chemical-resistant protective coatings is widespread in the oil and chemical industries, and is also relevant, for example, for anti-corrosion protection of structures at mineral fertilizer production plants [1–3].

The need to address the issues of developing chemical-resistant protective coatings for metals is explained by a number of factors [1, 3-5]:

- corrosion damage (active exposure to liquids and gases in chemical and petrochemical plants, under the influence of severe temperature loads, negatively affects the condition of metal structures, pipes, tanks and other equipment);

 economic losses caused by corrosion damage, leading to the need to replace or repair parts and equipment;

- threat to human safety, including in the event of damage to bridges, oil pipelines, aviation equipment;

- negative impact on the environmental system and human health due to uncontrolled destruction, which can lead to leaks of hazardous substances into the environment.

Hence, the use of chemically resistant coatings can increase the service life of individual elements, reduce the costs of repair work and reduce the likelihood of the development of corrosion changes inside structures.

One of the most effective methods for improving technological and operational characteristics of materials is their nanomodification, which has become the basis for this study and was discussed in the works of many researchers, who presented the results of using nanomodifiers to create highly effective composite materials for various purposes [3-17].

Thus, the study aims to develop nanostructured protective coatings with high chemical resistance for metal surfaces.

2. Materials and Methods

2.1. Materials

Acrylic and pentaphthalic paints and varnishes (AC-182, PF-115 - manufactured by LKZ Kolorit Ltd., Russia) were used in the tests. They are widely used for painting metal products and structures and their choice was justified in other studies [3, 18, 19]. The paints and varnishes were modified using compositions based on carbon nanotubes (CNT) (Tuball Matrix 203 – Russia, OcSiAl), bismuth oxide nanoparticles (BO) (Dongguan SAT nano technology material Co., Ltd. - China), silicon dioxide (SiO₂) (Tarkosil T-20 – Russia), titanium dioxide (TiO₂) (Zhengzhou Kelai Chemical Co., Ltd - China), magnesium hydroxide $(Mg(OH)_2)$ and aluminum hydroxide (Al(OH)₃) (Zibo Aotai New Material Technology Co., Ltd. - China). The method of dispersing nanomaterials is mechanical mixing [3].

2.2. Control methods

The chemical resistance of paint and varnish coatings was assessed in accordance with Russian Standard 9.403-2022. The adhesive strength of paint and varnish coatings was determined in accordance with Russian Standard 32299–2013. The hardness of the coatings was assessed in accordance with Russian Standard R 54586–2011.

Also, one of the simple and reliable methods for determining the chemical resistance, as well as the topological structure of coatings is the equilibrium swelling method or the Flory-Rehner method, based on the swelling of the coating in a solvent, followed by an assessment of the equilibrium swelling rate [16]:

$$\Delta \mu = RT \left(\ln(1-\phi) + \phi + x_1 \phi^2 + \frac{\rho_2 V}{M_c} \left(\phi^{1/3} - \frac{2\phi}{f} \right) \right), \quad (1)$$

where ρ_2 is polymer density, g·cm⁻³; *V* is volume of absorbed liquid, cm³; *f* is mesh functionality; M_c is average molecular weight of chain segments; x_1 is polymer-solvent interaction parameter (known for different polymer-solvent systems); *RT* is the energy required to transfer one molecule of solvent into the polymer; φ is volume fraction of polymer in the swollen sample.

The volume fraction of the polymer in the swollen sample is found using formula (2):

$$\varphi = \frac{m_0/\rho}{m_0/\rho + V_1},\tag{2}$$

where V_1 is volume of solvent absorbed at equilibrium at the end of the experiment, cm³.

The main consequences of the calculations in accordance with the Flory-Rehner equation and the tests carried out are [20]:

- mesh polymer swelling is always limited;

- the degree of swelling of a mesh polymer depends on the thermodynamic affinity of the components and the density of the mesh;

- increasing the mesh density leads to a decrease in the degree of swelling.

The tests were carried out by processing the obtained data by calculating the equilibrium swelling rate of specimens, excluding the estimation of the mesh density parameter. Indicators for comparing the test results of the specimens were carried out by means of formulas 3 and 4, according to which the equilibrium swelling rate is calculated.

$$\alpha = \frac{m - m_0}{m_0} 100 \%;$$
 (3)

$$\alpha = \frac{V \rho}{m_0} 100 \%, \tag{4}$$

where *m* is weight (volume) of swollen specimen, g; m_0 is weight (volume) of the initial specimen, g; *V* is volume of absorbed liquid, cm³; ρ is solvent density, kg·m⁻³.

According to the equilibrium swelling method, the specimens were exposed in the solvent and the changes in the parameters of mass, thickness, length and width of the specimens were monitored at regular intervals. The tests were continued until the equilibrium state was reached, when the parameters became unchanged. Based on the Flory-Rehner theory, an increase in the mesh density leads to a decrease in the degree of swelling, i.e. the smaller the equilibrium swelling rate, the more mesh-like the coating structure.

2.3. Analytic methods

The study of the linear dimensions of the elements of the micro- and nanorelief surface structures of the nanomodified coatings was carried out using an atomic force microscope (AFM) based on the INTEGRA Aura probe nanolaboratory platform of NT-MDT company. A semi-contact (intermittent-contact) method was used to produce images; to increase the goodness of cantilever oscillations and, consequently, to increase the sensitivity, reliability, and validity in the measurements of weak forces between the probe and the specimen, the study was carried out under low vacuum conditions.

3. Results and Discussion

When determining the effect of nanomaterials on the physical and mechanical properties of the resulting coatings, it was found that the best adhesion strength has coatings based on acrylic paint material (AC-182) than on the basis of pentaphthalic (PF-115). At the same time, the introduction of nanomaterials contributes to an increase in the adhesive strength of the coating. So, the best effect is determined by the introduction of CNTs, in the amount of 0.1 % – the adhesive strength increases from 2.0-2.2 to 2.9-3.1 MPa with a change in the nature of detachment of the paint coating from the substrate from fully adhesive (100 %) to adhesioncohesive (Table 1).

Tests on the chemical resistance of paint coatings were carried out by exposing paint coatings to various chemical media (solvents, fuels and lubricants, acids, alkalis, etc.). At the first stage of the research rational concentration of chemical solutions was determined. So, for example, 40 % aqueous solution of herbicide (a mixture of dimethylamine, potassium, sodium salts) was chosen, at which changes in the properties of coatings occur, at which it is possible to most adequately trace the different effects of chemical solution on the coating. Nanostructured paint coatings based on AS-182 enamel showed the greatest chemical resistance, the results of the studies of which are presented in Table 2.

Introduced additives	Adhesion strength, MPa / Detachment character (adhesive (A) – cohesive (K)), $\%$			
	AC-182	PF-115		
No additives	1.7 – 1.9 / A100 – K0	1.6 – 1.8 / A100 – K0		
BO-0.5 %	2.6 - 2.8 / A30 - K70	2.4 - 2.6 / A30 - K70		
BO – 1 %	2.9 – 3.1 / A10 – K90	2.5 – 2.7 / A10 – K90		
BO – 2 %	2.4 – 2.6 / A30 – K70	2.3 – 2.5 / A20 – K80		
SiO ₂ -0.5 %	2.0 - 2.2 / A80 - K20	1.9 – 2.1 / A80 – K20		
SiO ₂ – 1 %	2.3 - 2.5 / A80 - K20	2.1 - 2.2 / A80 - K20		
SiO ₂ – 2 %	2.0 - 2.2 / A80 - K20	1.9 - 2.1 / A20 - K80		
CNTs - 0.01 %	2.7 – 2.9 / A90 – K10	2.4 - 2.6 / A70 - K30		
CNTs - 0.05 %	2.9 – 3.1 / A90 – K10	2.8 - 3.0 / A70 - K30		
CNTs - 0.1 %	3.2 – 3.4 / A50 – K50	3.0 - 3.2 / A75 - K25		
$Mg(OH)_2 - 0.5$ %	1.8 – 2.0 / A100 – K0	1.6 – 1.8 / A90 – K10		
Mg(OH) ₂ - 1 %	2.0 - 2.2 / A80 - K0	1.7 – 1.9 / A100 – K0		
Mg(OH) ₂ - 2 %	1.9 – 2.1 / A90 – K10	1.8 – 2.0 / A100 – K0		
Al(OH) ₃ – 0.5 %	1.6 – 1.8 / A100 – K0	1.7 – 1.9 / A100 – K0		
Al(OH) ₃ – 1 %	1.7 – 1.9 / A100 – K0	1.6 – 1.8 / A90 – K10		
Al(OH) ₃ – 2 %	1.5 – 1.7 / A100 – K0	1.7 – 1.9 / A100 – K0		

Table 1. Results of adhesive strength of paint and varnish coatings

Table 2. Chemical resistance of nanostructured coatings based on enamel AC-182 when exposed to herbicides

		Befo	ore testing	After testing		
Additive type	Weight, g	Hardness	A micrograph specimen (X230)	Weight, g	Hardness	A micrograph specimen (X230)
1	2	3	4	5	6	7
No additives	2.173	HB		2.159	В	
CNTs – 0.01 %	2.104	Н		2.104	Н	
CNTs – 0.05 %	2.063	Н		2.063	Н	

Pchel'nikov A.V., Pichugin A.P.

Continuation of Table 2

1	2	3	4	5	6	7
CNTs – 0.1 %	2.116	2Н		2.115	2Н	
Mg(OH) ₂ – 0.5 %	2.169	Н		2.162	Н	
Mg(OH) ₂ – 1 %	2.189	Н		2.186	HB	
Mg(OH) ₂ – 2 %	2.113	Н		2.108	HB	
Al(OH)3 – 0.5 %	2.150	2Н		2.143	2Н	
Al(OH)3 – 1 %	2.138	2Н		2.136	2Н	
Al(OH)3 – 2%	2.127	3Н		2.120	2H	

Continuation of Table 2

1	2	3	4	5	6	7
SiO ₂ – 0.5 %	2.084	Н		2.080	Н	
SiO ₂ – 1 %	2.126	2Н		2.120	Н	
SiO ₂ – 2 %	2.160	2Н		2.151	Н	
BO-0.5 %	2.191	2Н		2.190	Н	
BO-1%	2.166	2Н		2.166	Н	
BO – 2 %	2.132	2Н		2.132	Н	

Table 2 presents data on chemical resistance of paint coatings with different additives before and after exposure to herbicide. The results of data analysis revealed that the mass of the specimen without additives decreased by 0.014 g, also the coating became softer, as evidenced by the change in hardness from HB to B. Nanostructured paint coatings with carbon nanotubes retain mass according to the test results, and regardless of the concentration of the additive.

At the same time the hardness of such coatings does not change (H), which indicates high chemical stability of CNTs nanostructured coating. Also modification of the paint material with bismuth oxide nanoparticles leads to chemically stable coatings, as evidenced by the mass retention of the specimens and insignificant change in their hardness from 2H to H.

According to the results of studies of the equilibrium swelling rate (Tables 3, 4, Fig. 1), it was also determined that the paint coating modified with

bismuth oxide nanoparticles and carbon nanotubes has resistance to solvents, and also acquires a more reticulated structure in relation to coatings without additives, which also depends on the amount of introduced additives.

Specimen	Soaking time of specimens in solvent, min	Change in specimen weight, g	Change in specimen thickness, mm
	0	0.47	1.13
	20	0.57	1.21
No additives	40	0.60	1.23
	60	0.63	1.23
	80	0.63	1.24
	0	0.45	1.03
	20	0.55	1.12
CNTs 0,05 %	40	0.59	1.17
	60	0.60	1.17
	80	0.60	1.17
	0	0.51	1.23
	20	0.62	1.30
CNTs 0,1 %	40	0.67	1.33
	60	0.69	1.35
	80	0.69	1.35
	0	0.59	1.33
	20	0.70	1.40
TiO ₂ 0.5 %	40	0.78	1.45
	60	0.80	1.47
	80	0.81	1.47
	0	0.63	1.56
	20	0.69	1.64
TiO ₂ 1%	40	0.77	1.66
	60	0.79	1.75
	80	0.81	1.81
	0	0.64	1.46
	20	0.74	1.535
BO 0.5 %	40	0.79	1.615
	60	0.82	1.72
	80	0.84	1.72
	0	0.42	1.0
	20	0.5	1.03
BO 1%	40	0.53	1.07
	60	0.54	1.1
	80	0.56	1.1

Table 3. Results of tests of nanostructured coatings by the swelling method. Part 1

Pchel'nikov A.V., Pichugin A.P.

Specimen	Soaking time of specimens in solvent, min	Change in specimen length, mm	Change in specimen width, mm	Volume equilibrium swelling rate (α)
	0	26.30	9.65	
	20	27.05	9.90	
No additives	40	27.60	10.20	0.27
	60	27.80	10.35	
	80	28.20	10.40	
	0	26.70	9.55	
	20	27.30	9.80	
CNTs 0.05 %	40	27.90	10.50	0.22
	60	27.90	10.50	
	80	27.90	10.50	
	0	26.50	9.68	
	20	27.40	9.77	
CNTs 0.1 %	40	27.50	10.20	0.21
	60	27.50	10.30	
	80	27.50	10.30	
	0	26.30	9.83	
	20	26.60	10.25	
TiO ₂ 0.5 %	40	27.65	10.55	0.27
	60	27.70	10.80	
	80	27.70	10.80	
	0	26.60	9.58	
	20	27.50	9.64	
TiO ₂ 1%	40	28.20	9.81	0.29
	60	28.30	10.00	
	80	28.50	10.00	
	0	26.55	10.10	
	20	27.45	10.30	
BO 0.5 %	40	27.70	10.45	0.24
	60	27.80	10.60	
	80	28.00	10.60	
	0	26.70	10.18	
	20	26,8	10,82	
BO 1%	40	27,00	11,00	0.24
	60	27,6	11,05	
	80	27,6	11,15	

Table 4. Results of tests of nanostructured coatings by the swelling method. Part 2



Fig. 1. The degree of swelling of modified acrylic protective coatings, depending on the duration of swelling: $l - \text{modification TiO}_2 1 \%$; 2 - without modifier; $3 - \text{Bi}_2\text{O}_3 1 \%$ modification; 4 - CNTs modification 0.1 %

When bismuth oxide was added to the enamel, the meshiness of the coating increased, as indicated by the volume equilibrium swelling rate, which decreased from 0.27 to 0.24 at 0.5 and 1 % additives.

A more significant effect on the formation of dense molecular bonds was exerted by adding CNTs into the composition, and the index of the volume equilibrium swelling rate decreased from 0.27 to 0.22 at 0.05 % CNTs and to 0.21 at 0.1 % CNTs in the enamel composition.

The results of studies on the example of modifiers introduction into the paint material showed that nanomodification leads to the formation of denser mesh structures of coatings, which explain the increase in their physical and mechanical properties (adhesion strength, hardness, etc.) (Tables 1, 2) [3, 18, 19].

Scanning of various surface areas of specimens of nanostructured paint coatings, before chemical action on them, on the atomic force microscope showed that the surface becomes smoother nanometer roughness decreases from 50–60 nm (Fig. 2*a*) to 20–30 nm (Figs. 2*b*, *c*) when modified with bismuth oxide and carbon nanotubes. Moreover, a more significant reduction of protrusions is observed in CNT-modified coatings.

At the same time, at the joint introduction of bismuth oxide nanoparticles and carbon nanotubes, the number and size of protrusions are minimized and the Ra parameter decreases to 10–15 nm (Fig. 2*d*), which indicates a strengthening effect of the joint introduction and, consequently, hardening of the

coating by reducing the size of depressions and pores [3].

Thus, microstructural analysis allowed us to prove the existence of the optimal content of nanoadditives to enhance the quality parameters of protective paint coatings.

4. Conclusion

According to the results of this study it was found that by using nanoscale materials it is possible to produce effective nanostructured protective coatings capable of reliably protecting metal surfaces operating in a variety of aggressive chemical environments. It is most effective to apply nanostructured coatings when adding CNT-based compositions and bismuth oxide nanoparticles. It is more preferable to use acrylic paint materials to obtain chemoresistant nanostructured protective coatings. Thus, adding CNTs and bismuth oxide, the resulting coating has high adhesive strength (more than 3 MPa at cohesive detachment character up to 50% and higher), and also increased chemical resistance that is expressed in decrease of coating equilibrium swelling rate (from 0.27 to 0.21), preservation of specimen weight and its hardness (2H-H) caused by chemical media exposure. The increase in chemical resistance of such coatings is justified by the fact that they have a more hardened mesh structure with a minimum size of recesses and micropores in the surface.


Fig. 2. AFM-images of nanomodified coatings: a – without additives, b – BO 1 %, c – composition with CNTs 0.1 %, d – BO 1 % + composition with CNTs 0.1 %

5. Supplementary Material

A number of the data presented in this study are openly available at [https://gos_att.bstu.ru/shared/ attachments/272578].

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7. Conflict of interest

The authors declare no conflict of interest.

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Electron beam lithography using SiO₂ as a sensitive layer

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Abstract: In this paper, we study the capabilities and some features of direct electron-beam lithography using a layer of silicon dioxide SiO₂ (grown by thermal oxidation) as a resist sensitive to the action of the electron beam and a developing composition based on an aqueous solution of dilute buffered hydrofluoric acid. Additional factors influencing the lithography result (the existence of an initial period of exposure effect enhancement) are found. To explain this feature, | a hypothesis about the mechanism of the influence of the electric charge introduced into the SiO₂ layer (during exposure) on the process of further development of the latent image is proposed. As a measure eliminating the manifestations of contamination phenomena, an approach using a sacrificial copper layer applied during the exposure period is proposed. A rationale for choosing the metal of the sacrificial layer is given based on experimental observations and a hypothesis about the possible chemical composition of contamination spots in the exposed areas. The parameters of the direct lithography process on SiO₂ known from the literature are clarified. The nonlinear nature of the effect of the electron beam on the silicon dioxide layer is found and simple empirical dependencies that allow a quantitative description of the result of the lithography process for the case of large-scale structures are proposed. It is shown that even when using a sacrificial copper layer, it is possible to achieve a lithographic process resolution of no worse than 30 nm.

Keywords: electron beam lithography; grayscale lithography; inorganic resists; contamination; charging effect.

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Электронно-лучевая литография с использованием SiO₂ в качестве чувствительного слоя

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Аннотация: Изучены возможности и некоторые особенности прямой электронно-лучевой литографии с использованием слоя диоксида кремния SiO₂ (выращенного термическим окислением) в качестве резиста, чувствительного к действию электронного луча, и проявляющего состава на основе водного раствора разбавленной буферизованной плавиковой кислоты. Найдены дополнительные факторы, влияющие на результат литографии (существование первоначального периода усиления эффекта экспонирования). Для объяснения данной особенности предложена гипотеза о механизме влияния внедренного в слой SiO₂ (в процессе экспонирования) электрического заряда на процесс дальнейшего проявления скрытого изображения. В качестве меры, устраняющей проявления контаминационных явлений, предложен подход с использованием жертвенного слоя меди, наносимого на период проведения экспозиции. Приведено обоснование выбора металла жертвенного слоя на основе экспериментальных наблюдений и гипотезы о возможном химическом составе контаминационных пятен в экспонированных областях. Уточнены известные из литературы параметры процесса прямой литографии на SiO₂. Найден нелинейный характер эффекта воздействия электронного луча на слой диоксида кремния,

и предложены простые эмпирические зависимости, позволяющие количественно описать результат процесса литографии для случая крупномасштабных структур. Показано, что даже при использовании жертвенного слоя меди возможно достижение разрешения литографического процесса не хуже 30 нм.

Ключевые слова: электронно-лучевая литография; полутоновая литография; неорганические резисты; контаминация; эффект зарядки.

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1. Introduction

Direct electron beam lithography on thermally grown silicon dioxide films has been known for a long time. The relevance of such studies is related, among other things, to the fact that silicon dioxide is often included in various micro- and nanodevices. However, most of such studies were conducted using high-energy electron beams [1-8]. An interesting feature of this process is high lithography resolution. The works [1, 5–7] describe the process of direct electron beam lithography on SiO₂ at an electron energy of 300 keV and show the achieved half-step resolution of 7.5 nm on a free SiO₂ membrane on Si_3N_4 [1] and 5.4 nm in the work [7] (also on a free membrane). The papers [3, 4, 8, 9] describe the application of direct lithography on SiO₂/Si/SiO₂ layers with exposure to electrons with an energy of 50 keV to create elements with sizes of less than 10 nm [3, 9]. In the paper [10], the process of direct electron beam lithography on SiO2 was used to create structures of field-effect transistors based on silicon nanowires (electron energy during exposure is 30 keV). Among the papers in which the study of electron beam lithography was carried out using lowenergy electrons (units of kiloelectron volts), the paper [11] can be mentioned. One of the discovered of using electron beams with advantages comparatively low energies is the higher sensitivity of SiO₂ to their impact. However, this paper did not evaluate the capabilities of direct lithography on SiO₂ in terms of resolution. The characteristics of electron beam lithography (and in particular the resolution) on SiO₂ films as a resist are of interest, since it is precisely for electron beams with comparatively low energies that an alternative mechanism for the formation of latent images can be proposed, potentially allowing for a significant increase in the dose sensitivity of the lithography process.

An alternative mechanism for the formation of latent images is the well-known phenomenon of charging dielectrics irradiated by an electron beam. This phenomenon is usually considered as a factor that interferes with the exposure process in electronbeam lithography and in the study of samples in a scanning electron microscope. However, there are works that show the fundamental possibility of using this phenomenon to form microstructures [12, 13]. Thus, the paper [12] experimentally shows the effect of an electric field created in a SiO₂ layer (using quartz glass as an example) on the rate of its dissolution in hydrofluoric acid. Thus, the presence of a local electric charge in the SiO₂ dielectric layer (formed under the action of an electron beam) can lead to a change in the local etching rate of the dielectric film. This mechanism is of interest because the expected maximum dose sensitivity of the lithography process is much higher than that usually observed for SiO₂ films, and can be compared with the sensitivity of resists with the so-called chemical enhancement (i.e., on the order of units of $\mu C \cdot cm^{-2}$). This value can be estimated using a simple model of a flat capacitor. Of course, the estimate obtained on the basis of such a model will only be approximate. Thus, the paper [12] presents the characteristic electric field strength, at which the effect of changing the etching rate of SiO₂ is observed (the first hundreds of $V \cdot \mu m^{-1}$). Also, knowing the value of the dielectric constant of SiO2, it is possible to calculate the specific charge density on the plates in the flat capacitor model using the known formula (1):

$$q = \frac{Q}{S} = \varepsilon \varepsilon_0 E, \qquad (1)$$

where S is the plate area; Q is the total charge on the plates; q is the specific charge on the plates; ε and ε_0 are the relative permittivity of the material and the permittivity of vacuum, respectively; E is the strength of the electric field created by the charges in the dielectric volume.

In reality, one can certainly expect the influence of a particular spatial distribution of charges both in the dielectric volume and in the solution layer directly wetting the charged dielectric (double electric layer), at least for the cases of small-sized structures. For this reason, more accurate calculations of real distributions will require taking into account

the spatial distribution of charges in the volumes of the contacting phases. If we take a typical value of the dielectric permittivity of SiO₂ in the range of 3.7-3.9, such an estimate gives a charge density of 3.3-3.5 μ C·cm⁻² at an electric field strength of 1000 V· μ m⁻¹ (a value close in order to the dielectric strength of silicon dioxide). The obtained value of the specific charge will be a minimum estimate of the dose required to implement the described lithography mechanism. Of course, the real value may differ significantly from this rough estimate due to a number of factors: incomplete use of the charge transferred by the electron beam (charge runoff, reflection and generation of secondary electrons), the structure of the oxide layer, the composition and conditions of development, etc. However, even from a preliminary rough estimate, one can conclude that there are prospects for a significant improvement in the dose characteristics of SiO2 and materials based on it as a resist for electron beam lithography. It is also worth mentioning the paper [13], in which the authors present the results of experiments on the formation of graphene-like microstructures on SiO₂ films (obtained by thermal oxidation) after their exposure to an electron beam. According to the data presented in this paper, sensitivity at the level of hundreds of $\mu C \cdot cm^{-2}$ or better was achieved. The authors of this paper particularly note that the possibility of the mechanism of inducing the growth of graphene-like structures due to the phenomenon of contamination in the described experiments was excluded, and thus, the most probable mechanism of latent image formation is precisely the local charging of the SiO₂ layer. In general, it can be noted that despite the fact that the process of electron-beam lithography on SiO_2 has been studied for a very long time, many details of the processes taking place are still unknown. Moreover, some characteristics of the process are still unknown (in particular, the resolution at low electron energies).

The main goal of the presented work is to identify the main factors influencing the characteristics of the process of direct electron-beam lithography on SiO_2 films at electron energies within 10 keV.

2. Materials and Methods

2.1. Source materials and reagents

All experiments on electron-beam lithography described in this work were carried out on SiO_2 films with a thickness of 100–130 nm and 4.0 μ m, which

were grown by thermal oxidation on substrates made of single-crystal silicon with the orientation < 100 >.

The exposure of SiO_2 films was carried out on an electron-beam lithography of the E-Line series by Raith.

Aqueous solutions of dilute hydrofluoric acid with a volume ratio of components HF (47 % by weight) : NH_4F (40 % by weight) : H_2O (distillate) equal to 1 : 6 : 93 were used as the developer.

2.2. Film application and property determination methods

The metal films were deposited by magnetron sputtering on a 208HR Cressington setup. The nanostructures formed during lithography were studied by atomic force microscopy (AFM) on an NT-MDT Ntegra Prima AFM and transmission electron microscopy (TEM) on a Jeol JEM-2100 Plus TEM.

Numerical modeling of the electron penetration depth in the broad beam approximation for 130 nm and 4 μ m thick SiO₂ films with a 12 nm thick protective copper coating was performed in CASINO version 2.48.

3. Results and Discussion

3.1. Exposure of SiO₂ films without additional preparation

In the first series of experiments, silicon wafers were used after oxidation without any additional treatment, except for cleaning in solvents (rinsing in acetone and isopropanol). In these experiments, SiO₂ films (100-130 nm thick) were exposed to an electron beam with subsequent development in a solution of dilute buffered hydrofluoric acid. Samples of the exposed SiO₂ film were studied using an AFM and an optical microscope before and after the development process. For such samples, darkening of the SiO₂ film color was observed in the exposed areas (starting with doses of several $\mu C \cdot cm^{-2}$). In addition, characteristic changes were observed in the nature of the surface relief of the film in the exposed areas after development. The appearance of the relief after development in many cases can be described as a "sponge" protruding above the surface surrounded by a uniformly etched oxide film. These changes in the relief can be explained by incomplete masking of the SiO₂ surface (due to numerous defects in such "masking"). In this case, the "pores" of such a spongy structure can extend below the level of the surrounding unexposed oxide. Another feature of

exposed structures on such samples is the frequently observed blurring of the exposure zone due to the formation of electrically charged areas inside the oxide film and the distortion of the electron trajectory during exposure. Observation of the above-described spongy structures with high surface roughness clearly indicates the presence of the so-called contamination of the oxide surface during electron beam exposure. This phenomenon radically worsens the quality of direct electron beam lithography on SiO2, and for exposure doses of tens of $mC \cdot cm^{-2}$ and higher makes such lithography completely impossible without taking special measures. The influence of this factor on the resolution of the direct electron beam lithography process on SiO₂ films is noted in the previously mentioned works, for example [1, 2, 11]. The phenomenon itself has been known and studied for a long time, since it often interferes with the electron microscopy process [14]. The generally for the accepted mechanism formation of contaminant deposits is the decomposition of adsorbed organic compounds (e.g., hydrocarbons from the lubricant of a pump system). In terms of the composition of the decomposition products, there are different opinions – from polymer compounds [15] to various carbon films [16–19]. Despite the fact that the question of the nature of contaminant deposits has a long history, there is still no complete understanding of the mechanism of their formation, as well as their composition and structure, despite examples of the successful application of this phenomenon for the formation of microstructures [20].

common method of Α combating this phenomenon is to treat the surface of the exposed SiO₂ film in oxygen plasma. This is what the authors of [11] used. However, this approach has certain drawbacks associated with the relatively harsh physical impact on the oxide film in oxygen plasma. In addition to the chemical effect of oxygen plasma on contamination traces, a process of reactive ion sputtering of the oxide film material is possible, which in principle can affect the characteristics of the lithography process (for example, the residual roughness of the film and the resolution of the lithography process).

During the described experiments, it was noted that the contamination phenomenon is especially strong at low electron energies (the first few keV). It is also worth noting the extreme chemical stability of contamination spots in the exposure zones – they did not disappear even when exposed to a mixture of concentrated nitric and sulfuric acids when heated to $80 \,^{\circ}$ C for several minutes. It is noteworthy in connection with the fact that such a mixture of acids is used in the processes of nitration of aromatic hydrocarbons and oxidation of graphite. For this reason, it can be assumed that the nature of the resulting contamination spots is not associated with simple adsorption and/or decomposition to carbon residue under the action of an electron beam of traces of organic impurities that may be present in very small quantities in the vacuum chamber during sample exposure.

3.2. Elimination of SiO₂ contamination of films exposed to metal coatings

To avoid the influence of contamination, further experiments were carried out on samples with SiO₂ films, onto which thin (about 10-15 nm) layers of various metals (copper, platinum, tungsten) were applied by magnetron sputtering. The main idea of this approach is to remove contamination spots formed during exposure before development together with the underlying sacrificial layer of metal. The choice of metal films as protective coatings is also due to the fact that they are able to effectively eliminate the manifestations of the charge accumulated by the dielectric oxide layer under the action of the electron beam (the "charging" effect). The main conclusion from the experiments with various metal coatings is that the efficiency of eliminating the influence of contamination spots depends on the nature of the metal used. Thus, for tungsten, contamination spots had significantly greater chemical resistance than in the case of copper or platinum. This conclusion was made from experiments in which the tungsten film was etched in a mixture of aqueous solutions of H₂O₂ and NH₃ after exposure - strong contamination spots on the tungsten were almost not affected by this mixture, despite the fact that the original tungsten film was completely removed in less than 5 min. In addition, these spots also had significant mechanical resistance to abrasion, which follows from the observation of their preservation even after intensive wiping of the sample with a cotton swab moistened with acetone (the original tungsten film is mostly removed from the surface of the sample under similar conditions). In the case of copper and platinum films, no fundamental difference in the chemical resistance of the films in the contamination zones compared to the unirradiated areas was observed. Thus, copper films are completely removed together with contamination spots in solutions of dilute nitric acid in a few minutes. The set of observations made during the experiments allows us to suggest that the nature of contamination on different materials may be different

(at least there are two alternatives). For SiO₂ and tungsten, the nature of contamination spots can be associated with the formation of very thin layers of carbides (or other carbon-containing, carbide-like compounds) of the corresponding element. Some carbides (such as SiC and W_xC) are known for their chemical resistance and that is why they can work as a mask during the development process. Metals such as copper and platinum do not form stable carbides, for this reason the nature and properties of contamination spots for them will be different than for materials based on carbide-forming elements.

3.3. Determination of the dose dependence of the depth of structures formed in the SiO_2 layer using direct electron beam lithography

For experiments on determining the dose dependence of the depth of structures formed in the SiO₂ layer using the direct electron beam lithography method, samples with SiO₂ films on single-crystal silicon wafers (with an oxide thickness from 100 nm to 4 µm, obtained by thermal oxidation of the silicon substrate with the < 100 > orientation) and a metal layer (copper or platinum, 10-15 nm thick) deposited on the oxide were used. Such layers were chosen as protective sacrificial layers because they demonstrated the effectiveness of protection against contamination and the charging phenomenon. Figure 1 shows images of the surface relief of a developed sample with an example of contamination (without a protective sacrificial copper layer) and with a protective coating (*Ra* is the average roughness).

A diluted buffered hydrofluoric acid solution with a volume ratio of HF (47 % by weight) : NH_4F

(40 % by weight) : H₂O (distillate) components equal to 1:6:93 (similar to that used in [11]) was used as a developer. The development time was from 3 to 10 min, the temperature was 21 °C. Thus, the conditions of the experiments carried out allow us to compare the results obtained in this work with the results described in the paper [11]. It can be noted that the qualitatively obtained results are in agreement with the data of [11] – an increase in the depth of structures in the dose range up to the first hundreds of $mC \cdot cm^{-2}$ and then reaching a constant value. A significant, although expected, difference is a decrease in the dose sensitivity of the process by approximately 2-3 times compared to the data of [11]. This decrease is expressed in a less sharp dependence of the depth of the obtained structures on the exposure dose, and a shift in the dose of the output at a constant (maximum) depth towards higher dose values. In addition, in contrast to work [11], the maximum sensitivity to the action of the electron beam occurred at high values of electron energy -in the range of 3-6 keV. All these results, at least at a qualitative level, are quite expected, since they are obviously associated with the shielding effect of the protective metal layer. However, compared with the data of work [11], the results obtained in this work allow us to make a significant clarification - the initial section of the dose dependence of the depth of the structures on the exposure dose is not linear, but more complex. In general, the dependence of the depth of the formed structures observed in our experiments can be described quite accurately by the following empirical S-shaped dependence (2):

$$h(D) = h_{\text{sat}} \frac{D^n}{D^n + D_{h/2}^n},$$
 (2)



Fig. 1. Surface relief of exposed and developed samples (according to AFM data): a – without using a 12 nm protective copper layer at the exposure stage (in the exposed region Ra = 2.5-3.8 nm); b – with a protective layer (in the exposed region Ra = 1.7 nm). The average value of the SiOa surface roughness after development in unexposed regions Ra = 0.3-0.7 nm

The average value of the SiO₂ surface roughness after development in unexposed regions Ra = 0.3-0.7 nm

where h_{sat} is a factor that specifies the maximum (for a given electron energy and development conditions) depth of the structures being formed, i.e. a depth limitation for the case of obviously large exposure doses (the "saturation" region); *D* is the exposure dose; $D_{h/2}$ is the dose corresponding to half of the maximum depth of the structures; *n* is an empirical factor that determines the degree of nonlinearity of the given dependence.

For the case of small exposure doses, this dependence can be simplified to a power dependence of the form (3):

$$h(D) = k D^n, \tag{3}$$

where k is the coefficient of proportionality, it is obvious that at $D \ll D_{h/2}$, $k \to h_{sat} / D_{h/2}^n$. This type of dependence can be useful, for example, for cases of high electron energies in the beam, when the value of $D_{h/2}$ is large and the applied exposure doses are obviously lower than this value. According to the experimental results, all the specified parameters show a dependence on the presence of a protective the development laver and on conditions. The experiments also show that they depend to a much lesser extent on the thickness of the SiO₂ layer (practically only in the form of a dependence on the duration of time between exposure and development).

From the given dependences (experiment and approximation), it is evident that there is an initial section of the dependence corresponding to a weak increase in depth with increasing dose and a section of reaching an almost constant value. Accordingly, the steepness of the dose dependence in the sections before "saturation" is not constant, but has a maximum in the region of average values of exposure doses. Based on this result, it can be assumed that this feature can be used to improve the dose sensitivity of the process, at least in some cases, for direct electron-beam lithography on SiO_2 , by additional uniform exposure of the entire sample area with an electron beam – before or after exposure of the structures themselves.

Also, within the framework of this work, studies on the dependences of the depth of the structures obtained during lithography on exposure doses on much thicker SiO₂ films (4 μ m) were conducted. In the course of these studies, it was found that the general nature of the dependence of the depth of the structures after development has the same character as on thin (130 nm) SiO₂ films (Fig. 2).

However, the quantitative ratios for a 4 μ m oxide film are somewhat different from those for 100–130 nm oxide films for electron energies greater than 6 keV. In addition, an important feature was discovered for 4 μ m films: if the film was developed not within the next 4 hours after exposure, but after 3 days, the depth of the structures formed during development was significantly greater (Fig. 3).

In other words, processes that increase the average rate of its etching in a dilute solution of buffered hydrofluoric acid (at least in the first 3 days) occur in SiO₂ exposed to an electron beam, when stored at room temperature. For thin SiO₂ films (130 nm), a similar phenomenon of increasing the exposure efficiency after holding the samples (before the development of the latent image of the structures) was observed only for low electron energies (1.5 keV) and to a significantly lesser extent (Fig. 4).



Fig. 2. Dependences of the depth of structures formed in the oxide during 3 min of development (less than 4 hours after exposure) in a solution of diluted buffered hydrofluoric acid on the exposure dose. The initial thickness of the SiO₂ layer in the graph on the left is 130 nm, on the right – 4 μ m (in all cases, a protective copper coating with a thickness of 12 nm was used during exposure)



Fig. 3. Dependences of the depth of structures formed in SiO₂ (4 μm thick) during 3 min of development, for cases of development immediately (less than 4 hours) and 3 days after exposure (in all cases, a protective coating of 12 nm copper was used during exposure)

It is worth noting that for the indicated cases (for SiO₂ films with a thickness of 130 nm and 4 μ m, with a protective copper coating of 12 nm), numerical modeling was carried out in the broad beam approximation, which showed that the distributions of specific energy losses by electrons (per unit volume) in a silicon dioxide layer under the same protective copper layer are practically independent of the thickness of the SiO₂ layer (Fig. 5).

This simulation result is consistent with the experiments for oxide films of different thicknesses and also indicates the need to expand and refine the model used to describe the processes occurring during irradiation of the oxide layer by an electron beam. At the same time, a comparison of the simulation results and experimental data confirms the conclusions of the paper [11] on the determining role of the electron penetration depth, for cases of low



Fig. 4. Dependences of the depth of structures formed in SiO₂ (130 nm thick) after 3 min of development, for cases of development immediately (less than 4 hours), after 3 days and after 6 days after exposure (in all cases, a protective coating of 12 nm copper was used during exposure)



Fig. 5. Distributions of specific energy losses by electrons according to modeling (in the same relative values on all graphs) by the volume of the SiO₂ layer (taking into account the influence of the overlying protective layer of 12 nm copper) depending on the depth of the corresponding layer: a -for a SiO₂ layer of 130 nm; $b - 4 \mu$ m





energies, to the maximum depth of the structures formed during development (parameter h_{sat} in the equation of the S-shaped dependence given above). Thus, for electron energies up to 2 keV, no significant difference is observed in the depth of the structures formed for either 3 min of development or 10 min of development (Fig. 6).

This fact is easily explained if we take into account that for low electron energies, the area of their impact on the oxide layer is limited in depth. With further etching of the underlying layers, there will be no additional difference in the amount of dissolved oxide. Reaching the maximum depth of the structures for large exposure doses in the experiments described in this paper is also consistent with the observations of [11] on the existence of a maximum value of the acceleration factor for the etching of the exposed oxide. For the etching rate measured in the described experiments (about 7.1 nm·min⁻¹ for SiO₂ in the above solution of diluted buffered hydrofluoric acid at 21 °C), the acceleration factor reaches a value of about 2.9 and higher, which indicates a sufficiently high efficiency of oxide protection from contamination by the copper layer.

All parameters of the approximating dependences of the depth of the formed structures on the exposure dose (structures in the form of homogeneous areas) presented in the graphs in this paper are given in Table 1.

Thickness Electron		Exposure time (dash – less than	Development	Parameters of the approximating dependence for the depth of structures				
of SiO ₂	energy, kev	4 h), 24 h	time, min	h _{sat}	$D_{h/2}$, mC·cm ⁻²	п		
1	2	3	4	5	6	7		
130 nm	1.5	_	3	18.6	108	1.82		
130 nm	2.0	_	3	28.5	164	2.15		
130 nm	3.0	_	3	64.6	139	2.13		
130 nm	4.0	_	3	57.3	111	2.85		
130 nm	5.0	_	3	63.7	134	2.91		
130 nm	6.0	_	3	65.5	140	2.99		
130 nm	7.0	_	3	66.8	236	2.54		
130 nm	10.0	_	3	k	= 0.00143	1.71		
130 nm	1.5	3	3	23.4	99	1.67		
130 nm	1.5	6	3	21.4	86	1.83		
130 nm	5.0	3	3	65.2	135	2.91		
130 nm	5.0	6	3	66.3	138	2.90		
130 nm	10.0	3	3	k	= 0.00220	1.65		
130 nm	10.0	6	3	k	= 0.00238	1.63		
4,0 µm	1.5	_	3	14.2	84	1.90		
4,0 µm	2.0	_	3	35.5	80	1.90		
4,0 µm	2.5	_	3	45.9	85	2.11		

Table 1. Parameters of approximating dependences of the depth of formed structures on the exposure dose

					00	illinualion Tuble T
1	2	3	4	5	6	7
4,0 µm	3.0	_	3	48.2	84	2.33
4,0 µm	4.0	_	3	48.1	98	2.54
4,0 µm	5.0	_	3	54.7	130	2.30
4,0 µm	6.0	_	3	89.7	260	1.92
4,0 µm	7.0	_	3	147	526	1.80
4,0 µm	8.0	_	3	k = 0	0.00408	1.59
4,0 µm	10.0	_	3	k = 0	0.00757	1.43
4,0 µm	1.5	_	10	24.0	157	1.45
4,0 µm	2.0	_	10	37.4	97	1.57
4,0 µm	2.5	_	10	62.2	93	1.65
4,0 µm	3.0	_	10	83.3	88	1.72
4,0 µm	4.0	_	10	134	114	1.95
4,0 µm	5.0	_	10	152	135	2.12
4,0 µm	6.0	_	10	203	188	2.08
4,0 µm	7.0	_	10	190	225	2.07
4,0 µm	8.0	_	10	k =	0.0487	1.40
4,0 µm	10.0	_	10	k =	0.0137	1.53
4,0 µm	1.5	3	3	22.0	103	1.67
4,0 µm	5	3	3	81.6	158	2.05
4,0 µm	10	3	3	k =	0.0170	1.40

Continuation Table 1

3.4. Determination of the resolving power of direct electron beam lithography on SiO₂ using an electron beam with low electron energies

One of the objectives of this work was to determine the resolving power of direct electronbeam lithography on SiO₂ using an electron beam with low (within 10 keV) electron energies. These experiments were performed on samples with a SiO_2 layer thickness of about 130 nm and an additional copper layer of 12 nm (magnetron sputtering). To test the resolving power of the process, sets of structures in the form of parallel lines and dot arrays with different periods were used. The exposure parameters were: electron energy of 10 keV at doses from 30 to 480 nC·cm⁻¹ for structures in the form of parallel and intersecting lines and from 0.075 to 1.2 pC for a dot array. After exposure, the copper layer was removed using a dilute (about 20 wt. %) nitric acid solution (etching for 3 min). The actual development of the latent image was carried out in an aqueous solution of diluted buffered hydrofluoric acid with a volume ratio of the initial components HF (aqueous solution 47 % by weight): NH_4F (aqueous solution 40 % by

weight) : H_2O equal to 1 : 6 : 93. The test structures obtained after the development of the latent image were studied using atomic force microscopy methods (Figs. 7, 8).

In addition, for some of the structures obtained in the described process, TEM-images (Fig. 9) of their cross sections shown in the figure below were obtained. These images allow a more accurate assessment of the characteristics of the described lithography process.

The obtained images of the structures (Figs. 7–10) allow us to say that the resolution of the described lithography process is in all cases no worse than 30 nm (in half-step resolution for a set of lines). Figure 9 shows the profile for widely spaced parallel lines, and Fig. 10 shows the profiles for lines with a period of 60 nm (the densest arrangement, at which the proximity effect is not yet noticeably evident). The TEM (the most accurate characteristic of the resolution) and AFM (a more rapid assessment, since it does not require special sample preparation) data provide a consistent assessment of the resolution of the described lithographic process.



Fig. 7. AFM-images of developed structures in the form of parallel and intersecting lines (with a period of 60 nm) obtained by exposing (linear dose 480 nC·cm⁻¹) a 130 nm SiO₂ film (12 nm protective Cu layer) and developing for 3 min in dilute buffered hydrofluoric acid



Fig. 8. AFM-images of developed structures in the form of an array of dots (with a period of 60 nm) obtained by exposing (dose 1.2 pC per dot) a 130 nm SiO₂ film (12 nm protective Cu layer) and developing for 3 min in dilute buffered hydrofluoric acid



Fig. 9. TEM-images of cross-section of parallel line structures (period 120 nm). SiO₂ layer initial thickness 130 nm (Cu protective layer 12 nm) developed for 3 min in dilute buffered hydrofluoric acid (linear dose 480 nC·cm⁻¹)



Fig. 10. TEM-images of cross-section of parallel line structures (period 60 nm). SiO₂ layer initial thickness 130 nm (Cu protective layer 12 nm) developed for 3 min in dilute buffered hydrofluoric acid (linear dose 480 nC·cm⁻¹)

The following assessment criteria were used: the line profile according to the TEM data and the relief data of the structures from AFM (based on the coincidence of the oxide levels at the tops of the ridges between the line depressions and the level in the unexposed area of the SiO_2 film). When forming nanostructures in the form of individual dots, a resolution of no worse than 25 nm (according to the width of the transverse profile at half the depth) was achieved.

4. Conclusion

The effects of contamination and charging during exposure of SiO_2 films to an electron beam are particularly pronounced when using relatively low electron energies, especially in the range of keV units. The nature of contamination has a clear

dependence on the composition of the upper layers. A correlation between the ability of the elements constituting the upper layers to form stable carbides and the chemical stability of contamination spots has been noted. These phenomena, which have a strong effect on the process of developing a latent image, can be effectively eliminated even by thin (10–15 nm) sacrificial layers of metals that do not form stable carbides (for example, copper or platinum).

The dose dependences of the depth of developed structures for the process of direct electron beam lithography on SiO₂ have an S-shape with an area of greatest growth at average dose values and subsequent reaching the maximum depth value. Based on the described dose dependence, it is possible to propose a method for increasing the effective sensitivity of the described lithography process by additional uniform exposure of the SiO₂ layer to the electron beam. The characteristic (primarily for thick SiO₂ films) increase in the depth of structures during the first 3 days after exposure suggests the presence of several mechanisms or stages of the process of forming latent images in the SiO₂ layer. Experimental data clearly indicate the presence of processes occurring in the "activated" areas of SiO₂ after the electron beam has ceased to act. As a hypothesis explaining the mechanism of these processes at a qualitative level, it is possible to propose the process of draining volume charges from the exposed areas.

The issue of the dependence of the depth of structures on the time elapsed since the moment of exposure is of great interest, since it has previously been almost never considered in the literature and requires further more detailed study from the point of view of establishing the mechanisms of the processes occurring in SiO₂ films, both during and after their exposure to electrons. This information, together with the temperature dependence (an estimate of the activation energy of processes in the film after exposure) can provide valuable information on the kinetics of the processes taking place.

The resolution (not worse than 30 nm) achieved in the described processes of electron-beam lithography on SiO_2 as a sensitive layer allows us to talk about the possibility of their application in the production of certain nanostructures, in particular nanopores.

5. Supplementary Material

The data is contained in the paper or additional material located at: https://disk.yandex.ru/d/ c5M2GacXmpkGJg

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7. Conflict of interest

The authors declare no conflict of interest.

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Theoretical investigation of the interaction mechanism of trialkylamine derivatives with the copper phthalocyanine surface

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Abstract: The paper presents a theoretical study of the sorption mechanisms of tripropylamine, triisopropylamine, triisopropylamines, and tetrapropylammonium chloride on the surface of copper phthalocyanine containing a metal atom, using density functional theory. The critical points of QTAIM, IRI, and charge distributions in sorbate-sorbent complexes were analyzed to investigate the interaction mechanism between the sorbate molecule and the surface. It was found that trialkylamines exhibit a higher binding energy with the surface than trialkylaminoalcohols due to their lower interaction energy with the solvent. In all cases, the binding of sorbate molecules to the surface is primarily driven by electrostatic and dispersion interactions; however, the presence of bonds with orbital overlap significantly enhances the stability of the complexes. The complex with the quaternary ammonium salt is the most stable due to a combination of electrostatic and orbital interactions. In the complex with a quaternary ammonium cation, significant polarization of the surface toward the crystal interior is observed, which may increase the interaction energy between molecules in the surface layers and reduce the solubility of modified particles in polar solvents. In all complexes with orbital overlap, the $3d_{2}$ -orbitals of the copper atom contribute from the surface side.

Keywords: copper phthalocyanine; DFT; adsorption; trialkylamines; QTAIM; IRI; surface modification.

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Теоретическое изучение механизма взаимодействия производных триалкиламинов с поверхностью фталоцианина меди

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Аннотация: Проведено теоретическое исследование механизмов сорбции трипропиламина, триизопропиламина, тригидроксипропиламинов и хлорида тетрапропиламмония на поверхности фталоцианина меди, включающей атом металла на уровне теории функционала плотности. В качестве инструментов изучения механизма взаимодействия молекулы сорбата с поверхностью использовались критические точки QTAIM, IRI и распределения зарядов в комплексах сорбат-сорбент. Определено, что триалкиламины имеют более высокую энергию связи с поверхностью, чем триалкиламиноспирты, за счет меньшей энергии взаимодействия с растворителем. Во всех случаях связь молекул сорбата с поверхностью в основном имеет электростатический и дисперсионный механизм, однако присутствие связей с перекрытием орбиталей существенно увеличивает стабильность комплексов. Комплекс с солью четвертичного аммониевого основания является самым стабильным за счет сочетания электростатического и орбитального механизмов. В комплексе с четвертичным аммониевым катионом наблюдается существенная поляризация поверхности по направлению вглубь кристалла, что может увеличивать энергию взаимодействия между молекулами в приповерхностных слоях и уменьшать растворимость модифицированных таким образом частиц в полярных растворителях. Во всех комплексах с перекрытием орбиталей со стороны поверхности участвует 3*d*₂ -орбитали атома меди.

Ключевые слова: фталоцианин меди; DFT; адсорбция; триалкиламины; QTAIM; IRI; модификация поверхности.

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1. Introduction

Surface modification of pigments is widely used to impart specific characteristics, including surface morphology, crystalline structure and particle size, optical properties, and the rheological characteristics of coatings and paints (CPs) formulated with these pigments [1].

Among the most commonly used surface modifiers are various surfactants (SAs) [2–5], high-molecular-weight substances [3–5], silicon oxide [3–4], as well as chemical functionalization of the surface, such as sulfo groups [6].

For pigments used in liquid CP formulations, the primary property determining pigment affinity for the binder is the oleophilic-hydrophilic balance of the surface. The higher the surface affinity, the easier the pigment disperses and the more stable the CPs formed with it are against sedimentation. When using acrylic, polyurethane, and other water-based coatings, efforts are made to increase surface hydrophilicity, whereas for alkyd coatings, oleophilicity is preferred.

Copper phthalocyanine (phthalocyanine blue pigment) is one of the most widely used organic pigments and is commonly used in CPs with alkyd binders. Although its surface is primarily oleophilic, it contains regions capable of adsorbing water molecules and other polar substances [7–8]. This can lead to difficulties in obtaining stable suspensions in alkyd binders when moisture impurities are present in the pigment itself or in auxiliary substances [9]. These regions can be shielded by adsorbing surfactants onto them. The most promising surfactants for this purpose include trialkylamines, quaternary ammonium bases, and their derivatives [10].

This study focuses on investigating the interaction mechanism of trialkylamines and some of their derivatives with the surface of copper phthalocyanine containing a metal atom, as this is the only part of the surface requiring shielding of hydrophilic sites [11]. Understanding the fundamental principles of the interaction mechanism between surfactants and the pigment surface will aid in selecting the optimal modifier for specific applications and producing materials with the desired properties.

The selected surfactants must perform well in both alkyd and aqueous environments (e.g., wet pigment or flash paste production). Surfactants are generally water-soluble, and their adsorption from an aqueous medium is of particular interest because if they adsorb well from water, they will also adsorb well from an alkyd medium and onto dry pigment. Therefore, this study will focus on the adsorption mechanism of surfactants from an aqueous medium onto the pigment surface. The structure of copper phthalocyanine was assumed to correspond to the β -modification, as this is the most commonly used form in pigment applications.

2. Materials and Methods

For this study, trialkylamines and their derivatives with a three-carbon chain length were selected, as tripropylamine is the first in the series of unbranched trialkylamines that adsorbs onto the copper phthalocyanine surface with a negative Gibbs free energy [11]. The structural formulas of the studied surfactants are as follows:

- Tripropylamine



- Tris(2-hydroxypropyl)amine



- Tetrapropylammoniumchloride



For hydroxypropylamines, two adsorption configurations were considered: with hydroxyl groups oriented toward and away from the surface.

For tetrapropylammonium chloride, hydrolysis of the molecule into a cation and chloride ion is possible:

$$\operatorname{TetPACl}^{K_1} \operatorname{TetPA}^+ + \operatorname{Cl}^-.$$
(1)

Since tetrapropylammonium chloride is a salt of a strong acid and a weak base, the resulting cation recombines with a water molecule to form tetrapropylammonium hydroxide:

$$TetPA^{+} + H_2O \Leftrightarrow TetPAOH + H^{+}.$$
 (2)

The overall reaction (1), (2) can be expressed as:

$$\text{TetPACl} + \text{H}_2\text{O} \Leftrightarrow \text{TetPAOH} + \text{H}^+ + \text{Cl}^-.$$
(3)

At the same time, tetrapropylammonium hydroxide itself undergoes hydrolysis:

$$TetPAOH \Leftrightarrow TetPA^{+} + OH^{-}.$$
(4)

Thus, in aqueous solution, tetrapropylammonium can exist in three forms: chloride, hydroxide, and cationic. Their concentrations can be estimated using the dissociation constants of chloride and hydroxide (K_1 and K_2). While these values are not available for tetrapropylammonium, they are known for the structurally and chemically similar tetrabutylammonium: $K_1 = 0.24$; $K_2 = 0.011 \text{ mol} \cdot \text{L}^{-1}$ at 298 K [12]. The equilibrium constant for the overall reaction (3) is given by:

$$K = \frac{C_{\text{TetAOH}} \times C_{\text{H}^{+}} \times C_{\text{CI}^{-}}}{C_{\text{TetACI}} \times C_{\text{H}_{2}\text{O}}} = \frac{K_{1}}{K_{2}} \frac{10^{-14}}{C_{\text{H}_{2}\text{O}}} =$$

= 3.93×10⁻¹⁵ mol·L⁻¹ (298 K), (5)

indicating a very low final concentration of hydroxide.

Additionally, this can be demonstrated by assuming an initial tetrapropylammonium chloride concentration of up to 5 % by mass (which is typically the maximum surfactant concentration in industrial processes involving organic pigments), corresponding to a molar concentration of 0.225 mol·L⁻¹. Solving the equilibrium and mass balance equations simultaneously, the results are presented in Fig. 1.

Under these conditions, the concentration of tetrapropylammonium hydroxide does not exceed $4 \cdot 10^{-7}$ mol·L⁻¹. Therefore, only the adsorption of the chloride and cation species was considered in further analysis.

The copper phthalocyanine surface was modeled using a cluster consisting of four molecules. The cluster geometry was based on experimental data for the β -crystal modification [13], with all nonhydrogen atoms fixed during geometry optimization to maintain consistency with the crystal lattice structure. The optimization process involved adjusting the position of the sorbate molecule relative to the surface, along with its internal coordinates.





To model the adsorption process, a two-layer ONIOM scheme [14] was employed. The surfactant molecules and the two nearest copper phthalocyanine molecules were treated with a high-level method, while the remaining two molecules were modeled using a low-level method. The extended tight-binding (XTB2) method [15] was used for the low-level calculations, while density functional theory (DFT) was employed for the high-level calculations. Specifically, the r²SCAN-3c composite method [16] was used for geometry optimization, and single-point energy calculations were performed using the ω B97x/def2-SVPD method [17–19].

The solvent was modeled using the continuum ALPB approach [20]. All geometry optimizations and wavefunction calculations were conducted using the ORCA 6 software package [21].

To determine the interaction mechanisms within the sorbate-sorbent complexes, the following approaches were used:

- Bader's Atoms in Molecules (QTAIM) theory [22, 23];

- Interaction Region Indicator (IRI) [24];

- Charge distribution analysis using the Hirshfeld [25], Bader (AIM) [22], and CHELPG [26] methods.

All calculations related to the interaction mechanism were performed using the Multiwfn software package [27], based on molecular orbitals obtained from single-point calculations.

QTAIM analysis allows for the identification of critical points corresponding to the maximum electron density at the boundary between two atomic basins, known as bond critical points (BCPs, type (3, -1)). The presence of these points confirms the existence of a bond between two atoms. The nature and characteristics of this bond can be assessed by evaluating key parameters at the BCP, including:

- Electron density (ρ_{BCP});

- Electron localization function (ELF_{BCP}) [28];

- Localized orbital locator (LOL_{BCP}) [29];

- The product of the second Hessian eigenvalue sign and electron density $(sign(\lambda_2) \times \rho_{BCP})$ [24];

– Lagrangian kinetic energy density (G_{BCP}) and potential energy density (V_{BCP}).

For hydrogen bonds, the bond energy $(kJ \cdot mol^{-1})$ can be estimated from the electron density using the equation [30]:

 $E_H \approx -933.33 \,\rho_{\rm BCP} + 3.11.$ (6)

 ELF_{BCP} and LOL_{BCP} values close to 1 (0.8–1.0) indicate covalent bonding, while values below 0.5 suggest non-covalent interactions.

A negative sign(λ_2)× ρ_{BCP} value confirms a bonding interaction, with its magnitude reflecting bond strength. A $\rho_{BCP} \approx 0$ value near zero is characteristic of van der Waals interactions [24]. Hydrogen bonds exhibit ρ_{BCP} values of approximately 0.02–0.05 for classical, 0.05–0.09 for strong, and 0.09–0.12 for very strong interactions [31]. Halogen, pnictogen, and other donor-acceptor non-covalent bonds have a broader ρ_{BCP} range (0.004–0.12), but within a specific bond type, ρ_{BCP} and bond energy are typically linearly correlated [32, 33].

Reference [32] categorizes non-covalent interactions based on the $(|V|/G)_{BCP}$ ratio:

 $-(|V|/G)_{BCP} < 1$ as ρ_{BCP} increases, interactions resemble ionic (closed-shell) bonds;

 $-1 < (|V|/G)_{BCP} < 2$ – intermediate bonds;

 $-2 < (|V|/G)_{BCP}$ – as ρ_{BCP} increases, interactions resemble covalent (shared-shell) bonds.

A comprehensive analysis of donor-acceptor interactions in [33] provides correlation equations for bond energy as a function of ρ_{BCP} for three bond types:

$$E_B \approx -2768 \,\rho_{\rm BCP} + 2.1;$$
 (7)

- Intermediate

$$E_B \approx -1487 \,\rho_{\rm BCP} + 6.5;$$
 (8)

- Shared-shell

$$E_B \approx -857 \rho_{\rm BCP} - 0.4.$$
 (9)

As seen from equations (7) - (9), hydrogen bonds, which are described by equation (6), are closer to shared-shell interactions, meaning they tend to form molecular orbitals in the space between bonded nuclei.

Only the critical points connecting the sorbate molecule to the copper phthalocyanine cluster were analyzed.

The contributions of individual orbitals to bond formation were also assessed using a localized molecular orbital (LMO) decomposition at the critical point. The Pipek-Mezey localization method with Mulliken population analysis was used in this study [34, 35].

The IRI index highlights regions of attractive or repulsive interactions. In these regions, the IRI parameter, calculated using equation (10), approaches zero, while the $sign(\lambda_2) \times \rho(r)$ value indicates interaction strength and direction.

$$\operatorname{IRI}(r) = \frac{|\nabla \rho(r)|}{\rho(r)^{1.1}}.$$
 (10)

Charge distribution analysis helps evaluate electrostatic interactions between the surface and the sorbed molecule. Charges were computed for the high-level region from the wavefunction obtained using the ω B97x/def2-SVPD method. The atomic charges were determined for the surface copper atom interacting with the sorbate, nitrogen and chlorine atoms (for tetrapropylammonium chloride), and the molecular fragments forming the sorbate-sorbent complex:

- Frag. 1 - subsurface copper phthalocyanine molecule;

- Frag. 2 - copper phthalocyanine molecule in direct contact with the sorbate;

- Frag. 3 - sorbate molecule.

Additionally, for all sorbate-sorbent complexes, formation energy was evaluated at the r^2 SCAN-3c theoretical level.

Visualizations were created using the VMD software [36].

3. Results and Discussion

The description of the obtained complexes and their formation energies are presented in Table 1, and their structures are shown in Fig. 2. Tetrapropylammonium chloride has the highest binding energy to the surface. The tetrapropylammonium cation and both isomers of tripropylamine have approximately three times lower binding energy. Amino alcohols exhibit the weakest interaction with the surface among the studied surfactants, which can be explained by the hydrophilic OH groups increasing their interaction energy with the solvent. This, in turn, makes adsorption onto the pigment surface less favorable.

For the (3, -1) critical points, the values of electron density, ELF_{BCP} and LOL_{BCP}, *G*_{BCP} and *V*_{BCP} energy densities were calculated, along with the estimated bond energies assuming hydrogen bonding (2) and using generalized formulas for weak interactions (3) – (5). All values a represented in Table 2.

The $(|V|/G)_{BCP}$ values indicate that nearly all intermolecular interactions in the studied complexes are predominantly electrostatic in nature. This conclusion is further supported by the low ELF and LOL values at the critical points. Only four bonds, found in complexes 1, 2, 5, and 7, exhibit $(|V|/G)_{BCP} \ge 1$, all of which involve the interaction between a surface copper atom and an atom within the surfactant molecule. Comparing the complex numbers with their formation energies from Table 1 reveals that the complexes containing a BCP with $(|V|/G)_{BCP} \ge 1$ have higher binding energies than those without such interactions (except for the complex with the cation).

Complex No.	Sorbate type and its location	Sorption energy	Cu-N distance between the sorbate and the surface, Å
1	tripropylamine	-48.03	3.235
2	triisopropylamine	-48.52	4.252
3	tris-(1-hydroxypropyl)amine, OH towards the surface	-30.08	4.772
4	tris-(1-hydroxypropyl)amine, OH away from the surface	-33.20	3.729
5	tris-(2-hydroxypropyl)amine, OH towards the surface	-46.18	4.131
6	tris-(2-hydroxypropyl)amine, OH away from the surface	-39.00	3.719
7	tetrapropylammonium chloride	-158.09	5.946
8	tetrapropylammonium cation	-50.59	5.707

 Table 1. The formation energy of sorbate-sorbent complexes of the studied surfactants with a copper phthalocyanine cluster



Fig. 2. The structure of sorbate-sorbent complexes of the studied surfactants with a copper phthalocyanine cluster is shown, with critical points (3, -1) for intermolecular interactions between the sorbate and the surface, and pathways connecting them to the points (3, -3)

Complex No.	Interacting atoms	The distance between atoms, Å	ρвср	$(V /G)_{\rm BCP}$	ELF _{BCP}	LOLBCP	E_H	E_B
1	2	3	4	5	6	7	8	9
	C66-H135	2.701	0.00757	0.81	0.0268	0.1426	-3.95	-18.84
	N77-H121	3.178	0.00342	0.71	0.0080	0.0829	-0.09	-7.38
	С79-Н133	2.705	0.00678	0.75	0.0187	0.1216	-3.22	-16.66
1	N75-H121	3.229	0.00292	0.67	0.0068	0.0766	0.39	-5.98
1	N75-H119	2.718	0.00756	0.86	0.0251	0.1384	-3.95	-18.84
	Cu114-N115	3.235	0.00806	1.00	0.0293	0.1483	-4.41	-5.41
	N74-H125	2.730	0.00768	0.85	0.0250	0.1381	-4.05	-19.15
	N72-H132	2.690	0.00719	0.90	0.0240	0.1357	-3.60	-17.81
	С79-Н135	3.014	0.00471	0.69	0.0138	0.1062	-1.29	-10.94
	N77-H121	2.814	0.00638	0.81	0.0191	0.1227	-2.85	-15.56
	Cu114-H119	2.527	0.01125	1.10	0.0407	0.1710	-7.39	-10.13
2	N76-H121	2.746	0.00703	0.84	0.0225	0.1321	-3.45	-17.35
	С59-Н133	3.287	0.00258	0.66	0.0064	0.0749	0.71	-5.03
	N70-H131	3,439	0.00173	0.63	0.0034	0.0555	1.50	-2.68
	N74-H143	2.875	0.00614	0.82	0.0185	0.1210	-2.62	-14.89
	N71-H143	3.452	0.00159	0.60	0.0031	0.0535	1.63	-2.30
	N77-0126	3 006	0.00837	0.84	0.0193	0 1233	-4 70	-21.06
	N75-0125	3.143	0.00685	0.82	0.0149	0.1097	-3.28	-16.86
3	Cu114-O127	3.162	0.00724	0.90	0.0176	0.1181	-3.64	-17.93
-	N74-0127	3 200	0.00682	0 79	0.0152	0 1108	-3.26	-16 78
	C67-H139	3 143	0.00354	0.74	0.0086	0.0857	-0.20	-7 71
	N70-H147	3 355	0.00189	0.64	0.0039	0.0595	1 35	-3.12
	N71-H131	2 615	0.00871	0.90	0.02892	0 14738	-5.02	-22.02
	Cu114-N115	3 729	0.00330	0.70	0.01062	0.09429	0.03	-7.02
4	N76-H133	2.513	0.01060	0.94	0.04046	0.17055	-6.78	-27.24
	C80-H132	2.630	0.00835	0.79	0.02321	0.13375	-4.68	-21.00
	N71-H142	2.865	0.00486	0.82	0.01419	0.10742	-1.43	-11.37
	Cu114-H131	2.615	0.00965	1.00	0.03282	0.15574	-5.89	-7.76
	N73-0126	3.730	0.00238	0.66	0.00504	0.06684	0.89	-4.49
	N76-H132	2.567	0.00947	0.91	0.03561	0.16141	-5.73	-24.12
5	N74-H133	2.730	0.00718	0.88	0.02505	0.13839	-3.59	-17.77
	C63-H145	2.929	0.00483	0.77	0.01591	0.11312	-1.40	-11.28
	С65-Н139	3.688	0.00120	0.56	0.00285	0.05141	1.99	-1.23
	C69-O127	3.858	0.00189	0.64	0.00437	0.06260	1.34	-3.14
	C78-H144	2.884	0.00532	0.72	0.01646	0.11483	-1.86	-12.63
	N77-H135	2.769	0.00652	0.85	0.02155	0.12947	-2.97	-15.94
	Cu114-N115	3.719	0.00360	0.69	0.01272	0.10237	-0.25	-7.87
	N74-N115	3.723	0.00356	0.68	0.01300	0.10341	-0.21	-7.75
6	C80-H136	2 584	0.00886	0.83	0.03023	0 15026	-5.16	-22.43
	C67-H141	2 935	0.00545	0.76	0.01752	0 11809	-1.97	-12.98
	C81-H134	2 654	0.00772	0.80	0.02334	0 13410	-4 09	-19 27
	C65-H138	2.989	0.00505	0.74	0.01620	0.11402	-1.61	-11 89
	Cl140-Cu114	3 133	0.01350	1 19	0.05466	0 19402	_9.49	_13.46
7	H143-N70	3 025	0.00420	0 74	0.01152	0.09773	-0.81	_9 52
	H150-C67	3.133	0.00334	0.72	0.00986	0.09111	0.00	-7.13

Table 2. Characteristics of BCP binding the sorbent molecule and the surface

Journal of Advanced Materials and Technologies. 2025. Vol. 10, No.	2
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						Com	inualioi	i Tuble
1	2	3	4	5	6	7	8	9
	H133-C81	2.813	0.00624	0.71	0.01767	0.11849	-2.72	-15.18
	H126-C61	2.766	0.00614	0.76	0.01781	0.11891	-2.62	-14.91
7	N72-H120	2.629	0.00772	0.89	0.02805	0.14545	-4.10	-19.28
/	H127-C69	3.040	0.00499	0.72	0.01698	0.11649	-1.55	-11.72
	H148-H101	2.579	0.00278	0.62	0.00635	0.07440	0.52	-5.59
	H121-C84	2.996	0.00492	0.69	0.01777	0.11889	-1.49	-11.53
	N73-H146	3.160	0.00322	0.74	0.00752	0.08039	0.10	-6.82
	Cu114-H147	2.746	0.00731	0.91	0.02333	0.13410	-3.71	-18.13
	C81-H127	2.692	0.00745	0.79	0.02173	0.12991	-3.85	-18.53
	C61-H129	2.912	0.00542	0.71	0.01657	0.11516	-1.95	-12.91
8	N72-H121	2.612	0.00823	0.90	0.03131	0.15263	-4.58	-20.69
	C69-C130	2.886	0.00634	0.76	0.02167	0.12981	-2.81	-15.45
	C89-H120	3.015	0.00463	0.72	0.01685	0.11611	-1.21	-10.72
	H101-H142	2.640	0.00338	0.63	0.00946	0.08939	-0.04	-7.25
	H109-H142	3.328	0.00060	0.43	0.00119	0.03427	2.55	0.45







Fig. 3. LMO involved in interactions with $(|V|/G)_{BCP} \ge 1$, isosurface at 0.1 a.u.

Letus take a closer look at the interactions where $(|V|/G)_{BCP} \ge 1$. Since these interactions are of an intermediate type, possessing both orbital and electrostatic contributions, it is useful to examine the orbitals involved in their formation. Figure 3 presents the contributions of localized molecular orbitals (LMOs) to the BCP of these interactions, displaying orbitals with contributions exceeding 10 %.

As shown in Figure 3, in all of the presented interactions, the copper atom's $3d_{z^2}$ -orbital is involved from the surface side, which can be recognized by its characteristic shape. The contribution from this orbital remains constant at around 25 %.

On the sorbate side, in two cases, the molecular orbitals of the C–H bond are involved in the interaction (complexes 2 and 5). In complex 5, a reorientation of the copper $3d_{z^2}$ -orbital (LMO 315) occurs toward the sorbate molecular orbital (LMO 260). It is also worth noting that the interaction involves the C–H bond of the methylene group adjacent to the nitrogen atom, which is the most polarized.

In complexes 1 and 7, two orbitals are involved from the sorbate side. In complex 1, these are the lone electron pair of the nitrogen atom (LMO 121, 25.35 %) and the molecular orbital of the N–C bond (LMO 279, 16.47 %). In complex 7, these are the porbital (LMO 352, 30.17 %) and the sp-orbital (LMO 350, 21.77 %) of the chlorine atom (atomic orbital decomposition coefficients > 0.4 for the 3s and $3p_v$ electrons).

In complexes 4 and 6, the interaction involving the nitrogen lone pair is also present, but it is much weaker than in complex 1 and is based solely on the electrostatic mechanism. This is likely due to the distance factor; at r = 3.2 Å (complex 1), overlap with the copper $3d_{z^2}$ -orbitals is still possible, while at r = 3.7 Å (complexes 4 and 6), it is no longer possible. The critical distance for the overlap of copper $3d_{z^2}$ -orbitals and C–H molecular orbitals is around 2.6 Å (for complex 8, r = 2.746 Å and $(|V|/G)_{BCP} = 0.91$).

Thus, the presence of orbital interactions positively affects the stability of the sorbate-sorbent complexes, but it does not explain the high adsorption energy of tetra-n-propylammonium chloride, which is characteristic of chemisorption. However, the highest value of $\rho_{BCP} = 0.0135$ indicates a weak non-covalent interaction, which is further supported by the ELF_{BCP} and LOL_{BCP} values.

The sums of the E_H and E_B values for a single complex do not match the calculated adsorption energy. ΣE_H always gives a lower value, while ΣE_B gives an overestimated value, except for complex 7. The lower value of ΣE_H can be explained by the fact that most interactions are far from those with a shared shell. The overestimated value of ΣE_B can be explained by the influence of the solvent, as equations (3) – (5) were derived for the gas phase.

The results of the IRI calculations for the investigated complexes are shown in Fig. 4.

For complexes 1–2 and 7–8, all peak values in the binding region are within $\rho \approx 0$ to 0.01 a.u., as shown in Table 2. For complexes with amino alcohols (3–6), additional peaks are observed in the regions $\rho \approx 0.02$ a.u. (complexes with hydroxyl groups oriented toward the pigment surface) and $\rho \approx 0.017$ a.u. (complexes with hydroxyl groups oriented away from the pigment surface). To understand what these interactions are, let us construct a 3D map of the IRI parameter for one of these complexes (Fig. 5).

As seen in Figure 5, these peaks correspond to intramolecular H···OH bonds, so the corresponding critical points (3, -1) did not appear in the table for intermolecular interactions.

The presence of sufficiently extensive binding regions with $\rho \approx 0$ to 0.01 near nonpolar groups (Fig. 5) indicates the significant role of dispersion forces in the formation of sorbate-sorbent complexes.

The charges for the fragments, as well as the copper atom on the surface, and the nitrogen and chlorine atoms of the sorbate, are presented in Table 3.

For all the complexes of tertiary amines and amino alcohols, a similar pattern is observed. There is a slight polarization of the surface (using the Hirshfeld and AIM methods), with the subsurface molecule becoming positively charged and the surface negatively charged. Meanwhile, the sorbate molecule acquires a small negative charge (Hirshfeld and CHELPG methods) or remains neutral (AIM). When looking at the fragment charges, only the CHELPG method shows a small electrostatic interaction between the sorbate and the surface. Considering the centers of positive and negative charges – the copper atom on the surface and the nitrogen atom of the sorbate - attraction is possible in all cases (AIM shows almost quantitative charges of Cu^{-} and N^{-}), but the distance between these centers is quite large (see Table 1), which hinders effective interaction.



Fig. 4. IRI for sorbate-sorbent complexes



Fig. 5. Isosurface IRI = 1 for complex 5; *1* is the region of intramolecular hydrogen bonds in the sorbate molecule, 2 is the region of weak intermolecular interactions

For the tetra-n-propylammonium chloride complex, surface polarization is observed only when using the CHELPG method. It is noted that the occupancy of nitrogen and copper atoms is reduced compared to the average value for complexes 1–6, which, together with the shorter Cu–Cl distance compared to Cu–N, makes the electrostatic interaction between the chlorine atom and the surface more significant than that between the nitrogen atom and the surface in previous complexes.

For the tetra-n-propylammonium cation complex, the strongest surface polarization is observed. Both the Hirshfeld and CHELPG methods show charge transfer from the cation to the pigment

		Hi	rshfeld	l meth	od			C	HELPC	6 meth	od				AIM n	nethod	1	
Complex No	Frag 1	Frag 2	Frag 3	Cu114	N115	CI	Frag 1	Frag 2	Frag 3	Cu114	N115	CI	Frag 1	Frag 2	Frag 3	Cu114	N115	CI
1	0.17	-0.10	-0.07	0.36	-0.09	_	0.09	0.13	-0.22	0.66	-0.65	_	0.18	-0.19	0.01	1.04	-1.14	_
2	0.21	-0.12	-0.09	0.34	-0.10	_	0.13	0.09	-0.22	0.71	-0.98	_	0.22	-0.22	0.00	0.99	-1.16	_
3	0.21	-0.17	-0.03	0.35	-0.11	_	0.12	0.06	-0.19	0.65	-0.76	_	0.22	-0.21	-0.01	1.01	-1.18	_
4	0.25	-0.15	-0.10	0.34	-0.10	_	0.17	0.07	-0.24	0.67	-0.98	_	0.26	-0.26	0.00	1.00	-1.18	_
5	0.13	-0.08	-0.06	0.35	-0.11	_	0.06	0.11	-0.17	0.68	-0.73	_	0.14	-0.15	0.01	1.01	-1.12	_
6	0.19	-0.08	-0.11	0.35	-0.10	_	0.11	0.12	-0.23	0.70	-0.86	_	0.19	-0.19	0.00	1.02	-1.12	_
7	0.00	-0.01	0.01	0.38	0.10	-0.66	-0.08	0.20	-0.13	0.71	-0.27	-0.82	0.00	-0.04	0.03	1.10	-1.09	-0.89
8	0.59	-0.40	0.81	0.26	0.10	_	0.55	-0.21	0.65	0.59	-0.06	_	0.61	-0.57	0.96	0.89	-1.10	_

Table 3. Charge distribution in sorbate-sorbent complexes

surface. Based on the charges on fragments 2 and 3, substantial interaction is expected, and from the absence of orbital overlap bonds in this complex, it can be concluded that this interaction contributes significantly to the adsorption energy. Significant polarization directed into the surface may also increase the stability of copper phthalocyanine crystals through electrostatic interactions between the molecules. This effect can occur during the adsorption of any cations, but only cations whose interaction energy with the solvent is small enough to make adsorption favorable will effectively adsorb. This effect can be used to stabilize (reduce the solubility of) crystals in polar solvents.

4. Conclusion

Tertiary alkylamines generally have higher binding energy with the copper phthalocyanine surface in the aqueous phase than tertiary alkylamino alcohols due to their lower interaction energy with the solvent. The binding of sorbate molecules to the surface mainly involves electrostatic and dispersion mechanisms. However, the presence of bonds with orbital overlap significantly increases the stability of the complexes. Therefore, it can be concluded that for effective surfactant adsorption on the copper phthalocyanine surface, it is necessary to ensure the overlap of sorbate molecule orbitals with the $3d_{z^2}$ orbitals of the copper atom on the surface. The complex with a quaternary ammonium salt is the most stable due to the combination of electrostatic

and orbital interaction mechanisms. In the complex

with the charged particle – the quaternary ammonium cation – there is significant surface polarization directed deep into the crystal, which may increase the interaction energy between pigment molecules in the subsurface layers and reduce the solubility of the modified particles in polar solvents.

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6. Conflict of interest

The authors declare no conflict of interest.

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Sorption dynamics of organic dyes from aqueous solutions using activated carbon derived from peach modified with carbon nanotubes

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Abstract: This study synthesized nanocomposite activated carbon (AC) from plant raw materials (peach production waste), modified with carbon nanotubes (CNTs). The first stage in obtaining all samples involved hydrothermal carbonization (HTC) of peach pomace in an aqueous environment with the addition of a specific amount of CNTs, after which the biomass was gradually carbonized and activated using an alkali (KOH) in an inert atmosphere. The aim of the study was to evaluate the effect of CNTs on the structure and physicochemical and functional properties of the nanocomposite AC. It was established that the carbon obtained from the initial mixture containing 0.05 wt. % CNTs showed a specific surface area according to the BET model of 2876 m²·g⁻¹ and a total pore volume of 1.643 cm³·g⁻¹. It is presumed that the interaction of the biomass with the nanotubes occurs at sites on the surfaces of the samples after HTC, where functional groups are located. The sample with 0.05 wt. % CNTs exhibited minimal I_D/I_G and d_{100} values, indicating a higher order of the carbon structure. For all carbons, the sorption capacity relative to synthetic dyes – malachite green (MG) and Congo red (CR) – was determined. A general correlation was found between the changes in the I_D/I_G and d_{100} values and the activity of the AC samples. The AC with 0.05 wt. % CNTs demonstrated the highest capacity for both dyes in static mode: 2987 mg·g⁻¹ for MG and 1201 mg·g⁻¹ for CR, respectively. For this particular sample, an assessment of the sorption kinetics was conducted.

Keywords: activated carbon; biochar; carbon nanotubes; peach processing waste; synthetic dyes; Congo red; malachite green; adsorption dynamics; kinetics.

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Динамика сорбции органических красителей из водных растворов активированным углем из персика, модифицированного углеродными нанотрубками

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Аннотация: В работе синтезировали нанокомпозиционный активированный уголь (АУ) из растительного сырья (отходов производства персика), модифицированного углеродными нанотрубками (УНТ). Первой стадией получения всех образцов была гидротермальная карбонизация (ГТК) персиковых выжимок в водной среде

с добавлением определенного количества УНТ, после чего биомассу поэтапно карбонизировали и активировали с помощью щелочи (КОН) в инертной среде. Цель работы – оценка влияния УНТ на структуру и физикохимические и функциональные свойства нанокомпозиционного АУ. Установлено, что уголь, полученный из исходной смеси, содержащей 0,05 мас. % УНТ, показывает величину удельной поверхности по модели БЭТ, равную 2876 м²/г, и общий объем пор – 1,643 см³/г. Предположительно, взаимодействие биомассы с нанотрубками происходит на участках поверхности образцов после ГТК, где расположены функциональные группы. Образец с 0,05 мас. % УНТ показывает минимальные значения I_D/I_G и d_{100} , что говорит о более высокой упорядоченности углеродной структуры. Для всех углей определяли сорбционную способность по отношению к синтетическим красителям – малахитовый зеленый (МЗ) и конго красный (КК). Обнаружена общая корреляция характера изменения показателей I_D/I_G и d_{100} с активностью образцов АУ. Наибольшую емкость по обоим красителям в статическом режиме показал АУ с 0,05 мас. % УНТ: 2987 и 1201 мг/г для МЗ и КК соответственно. Для указанного образца проведена оценка кинетики сорбции в динамическом режиме. По результатам экспериментальных и теоретических исследований определены такие важные показатели поглощения, как константы скорости сорбции и коэффициенты диффузии.

Ключевые слова: активированный уголь; биоуголь; углеродные нанотрубки; отходы переработки персика; синтетические красители; конго красный; малахитовый зеленый; динамика адсорбции; кинетика.

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1. Introduction

Global consumption of clean freshwater is increasing annually. However, its quality is noticeably declining. This is partly related to the problem of discharging untreated wastewater [1, 2]. More than 100,000 types of synthetic dyes are used in the textile, paint, paper, leather, and printing industries [3]. The discharge of wastewater from industrial enterprises leads to the accumulation of pollutants and has a negative impact on the environment [4, 5]. Malachite green (MG) is a common organic cationic dye used in chemical processes, the textile industry, as a medical disinfectant, and so on. Congo red (CR) is an azo dye, an acid-base indicator, and is used in histology and microscopic studies for staining fungal cell walls. Furthermore, adsorption is one of the most effective methods used for the removal of MG and CR [6, 7].

The choice of adsorbent is fundamental to the successful development, effectiveness, and implementation of the adsorption process. Activated carbon from plant material can compete with traditional coals due to its exceptional properties: high porosity, large surface area, and the presence of functional groups. Various methods of producing biochar are known, including hydrothermal carbonization (HTC), pyrolysis, and gasification [8, 9].

To enhance the adsorption capacity of biochar, modification of target waste is carried out to create active centers (functional groups) on its surface, which can effectively retain dyes under suitable conditions. Various methods of modification are known, including the use of acids, bases, surfactants, esterification, and the process of grafted copolymerization, resulting in the formation of different functional groups on the material's surface (hydroxyl, carboxylate, amide, amino, and ester groups). Waste from bananas, coconuts, apricots, peaches, etc., can be used as precursors for biochar production for wastewater treatment [10–12]. Peaches are consumed in nearly all parts of the world due to their unique flavor and aroma. The peach processing industry discards many parts of the fruit, including the pit and skin, referred to as "peach waste," which is rich in hemicellulose, lignin, and cellulose compounds, making these products valuable for the production of effective biochar [13].

The authors [12] synthesized biochar from the cladodes of the cactus Opuntia ficus-indica. Modification of the biochar using NaOH resulted in increased surface basicity. The maximum adsorption capacities based on the Langmuir model were found to be 1341, 49, and 44 mg \cdot g⁻¹ for MG, Cu²⁺ and Ni²⁺, respectively.

The sorption capacity of biochar derived from date palm leaves [14] reached values of 334 mg·g⁻¹ for MG. In the study [15], biochar obtained from banana peels was functionalized using microwave pyrolysis. It was established that the maximum adsorption capacity for MG reached 2297.83 mg·g⁻¹ with a contact time of 120 min. The mechanism of dye adsorption for MG included hydrophobic interactions, the formation of hydrogen bonds, π - π interactions, and ion exchange.

The adsorption of Congo red (CR) was conducted using activated biochar from *Haematoxylum*

campechianum waste obtained through pyrolysis. The maximum adsorption capacity, determined using the Langmuir adsorption isotherm model, was found to be 114.8 mg·g⁻¹ at 300.15 K, pH = 5.4, and an activated biochar dose of 1.0 g·L⁻¹ [16]. Biochar from *Medulla Tetrapanacis* modified with K₂CO₃showed an adsorption capacity for CR of 584.17 mg·g⁻¹ [17]. The adsorption capacity of the biochar from rice husks for CR amounted to 42.918 mg·g⁻¹, with equilibrium adsorption occurring after 120 min. The process of CR adsorption on biochar took place through physical adsorption and chemisorption, involving hydrogen bonds, electrostatic interactions, and π - π interactions [18].

Another method for enhancing the sorption activity of biochars is the creation of composites with carbon structures (such as carbon nanotubes (CNTs), graphene, etc.), metal oxides, and others [19, 20]. A method has been developed for obtaining CNTbiochar nanocomposites using a surfactant derived from hickory chips and sugarcane bagasse [21]. In one study [22], biochar was synthesized from potato peeling waste (utilizing various activation technologies) followed by modification with CNTs.

The objective of this work is to study the organic dyes (MG and CR) adsorption dynamics on a nanocomposite material – activated carbon (AC) derived from peach pomace, modified with CNTs. To achieve the research goal, samples of composite biochars with varying mass percentages of CNTs were synthesized, their physicochemical properties were determined, and the kinetics of malachite green sorption in a dynamic mode were assessed.

2. Methods and Materials

2.1. Preparation of activated carbon modified with carbon nanotubes

Biochar was obtained through HTC in an aqueous environment from biomass generated from peach pomace, which was first dried and ground. "Taunit-M" nanotubes The carbon (LLC "NanoTechCenter", Tambov) were added in dry form (0.01, 0.05, 0.1, 0.5, 1 wt. %) to the powdered peach material, and the resulting mixture was further mechanically ground. The dispersed bulk material was placed in a stainless steel autoclave, and distilled water was added. The mass ratio of "bulk material: water" was 1:3. The mixture was processed in the autoclave at a temperature of 180°C for 12 hours. The obtained HTC biochar was filtered and washed with water to remove by-products of the reaction and dried to a constant residual mass at 90 °C. The material was then subjected to thermal carbonization at 150, 350, and 700 °C (for 1 hour at each temperature) in an inert argon environment (with a flow rate of $1.4 \text{ L} \cdot \text{min}^{-1}$). To obtain activated carbon, the carbonized samples were mixed with an alkali (KOH) in a mass ratio of 1:6, then treated in an argon atmosphere at 400 and 750 °C (for 1 hour at each temperature). The resulting material was washed with distilled water until a neutral pH (~7) was reached. It was then soaked in concentrated hydrochloric acid for 24 hours. Afterward, it was washed again until a neutral pH was achieved. The washed material was dried at 90 °C until a constant mass was obtained.

The obtained experimental samples of composite activated carbon were stored in airtight plastic containers.

2.2. Adsorption test

2.2.1. Static conditions

To preliminarily assess the sorption capacity of the developed materials toward organic dyes MG and CR, studies were conducted under limited-volume conditions with the following fixed parameters: initial dye model solution concentration – 1500 mg·L⁻¹, pH = 6, sorbent weight – 0.01 g, contact time – 30 min. The optical density of the synthetic dye solutions was measured using a PE-5400V spectrophotometer (Ekros, St. Petersburg, Russia) at wavelengths λ (MG) = 810 nm and λ (CR) = 625 nm.

2.2.2. Dynamic conditions

Kinetic studies under dynamic conditions were carried out using an experimental setup (Fig. 1). A 100 mL stock solution of MG and CR with a concentration of 1500 mg·L⁻¹ was delivered by a peristaltic pump (3) into a sorption cell (1) containing the sorbent (mass 0.03 g) and circulated back to the original reservoir (R). A parallel circuit was used to deliver the solution to a cuvette located in the spectrophotometer (2).

2.3. Analytical methods

The morphology of the materials was examined using scanning electron microscopy (SEM) with a TESCAN Vega III microscope (Czech Republic).



Fig. 1. Laboratory setup for dynamic sorption (R - reservoir with the initial solution; 1 - sorption cell; 2 - spectrophotometer, 3 - peristaltic pump)

To qualitatively identify functional groups, FTIR spectra of the samples were recorded in attenuated total reflectance (ATR) mode using a Jasco FT/IR 6700 spectrometer (Jasco International Co., Ltd., Japan) in the wavenumber range of 500 to 4000 cm⁻¹. Structural features of the samples were determined based on Raman spectra, recorded with a DXR Raman Microscope (Thermo Scientific Instruments Group, Waltham, USA) using a laser excitation wavelength of $\lambda = 532$ nm. The phase composition of the materials was determined from X-ray diffraction (XRD) patterns obtained using a Thermo Scientific ARL Equinox 1000 diffractometer (TechTrend Science Co., Ltd., Taiwan).

To evaluate the thermal stability of the samples, simultaneous thermal analysis was performed recording thermogravimetric (TG) curves and differential scanning calorimetry (DSC) curves simultaneously – using a NETZSCH STA 449 F3 Jupiter instrument (NETZSCH-Feinmahltechnik GmbH, Selb, Germany) under an air atmosphere with a heating rate of 10 K·min⁻¹. The specific surface area and porous structure parameters were determined using a high-precision surface area and pore size analyzer TOP 200 (Altamira Instruments, USA). The specific surface area (S_{BET}) was calculated using the Brunauer-Emmett-Teller (BET) theory, and the total pore volume (V_{total}) was determined by the Barrett-Joyner-Halenda (BJH) method.

3. Results and Discussion

3.1. Evaluation of physicochemical properties

SEM-images of the biochars (Fig. 2a-e) show that all materials, regardless of treatment method, possess a rough, irregular, and variably porous structure. The morphology of the samples subjected to HTC treatment (Fig. 2a) is mainly represented by elongated grains (fibers) and microspheres. It was found that the introduction of CNTs during the hydrothermal carbonization stage results in a reduction in the diameter of the microspheres – from a size range of 200–250 nm to 100–200 nm (for HTC biochar modified with CNTs).

The modified HTC biochar (Fig. 2b, c) contains CNTs and catalyst particles with an average diameter of approximately 35 nm. According to the obtained images, the nanotubes are uniformly distributed within the carbon matrix derived from peach biomass and are directly encapsulated in the biochar microspheres. The sample of activated carbon modified with CNTs is characterized by inclusions up to 10 nm in diameter and the presence of bridges between the material grains. It is presumed that during the alkaline activation process, partial destruction of the CNT graphene structure occurred, resulting in the formation of connecting "bridges" between granules and an increase in surface defects due to the formation of grooves.



(e)

Thus, the incorporation of CNTs into the biochar, regardless of the processing stage, led to changes in the surface morphology and grain size of the structural elements of the biochar. This suggests the formation of a more favorable porous architecture in the activated carbon for the removal of toxic pollutants from aqueous media.

Fig. 2. SEM-images of raw HTC biochar (*a*), HTC biochar with 0.05 wt. % CNTs (*b*, *c*), and activated carbon (AC) with 0.05 wt. % CNTs (*d*, *e*)

To assess material changes under different processing conditions, IR-spectra were analyzed for the following samples: the original (HTC) and modified (HTC/CNT_0.01 et al.) materials after hydrothermal carbonization; the original carbonized coal (CC) and modified (CC/CNT_0.01 et al.) after thermal carbonization; and the original activated

carbon (AC) and modified (AC/CNT_0.01 et al.) after alkaline activation.

The IR-spectrum of the material obtained via HTC treatment of the raw material (without CNTs) (Fig. 3*a*) shows characteristic peaks attributed to:

- Stretching vibrations of O-H bonds in hydroxyl groups and/or water molecules (broad peak centered at 3423 cm^{-1});

- Asymmetric (2957 and 2922 cm^{-1}) and symmetric (2865 cm^{-1}) stretching vibrations of C–H bonds in alkyl groups;

- Stretching vibrations of C=O bonds in carboxyl groups (1710 cm⁻¹) and in carbonyl groups conjugated with two aromatic rings (1627 cm⁻¹);

– Various vibration modes of oxygen-containing groups in cellulose fragments (group of peaks within the broad band of $1000-1500 \text{ cm}^{-1}$).

The addition of CNTs to the biomaterial does not qualitatively alter the chemical composition of the HTC products. A slight decrease in the intensity of all absorption bands is observed, which may be due to the chemical inertness of CNTs.

carbonization (Fig. During *3b*), thermal decomposition removes most of the oxygencontaining functional groups. As a result, only the peaks at 3423 and 1627 cm⁻¹ remain relatively intense in the IR-spectra. The former is likely due to adsorbed moisture, and the latter to the relatively high stability of the carbonyl bond conjugated with two aromatic rings. The intensities of peaks indicating the presence of alkyl groups and cellulose fragments are significantly lower compared to the spectra of HTCtreated samples. There is no qualitative difference in the composition of CNT-modified materials at this stage.

After alkaline activation (Fig. 3c), no significant changes are observed in the IR-spectra of the samples. However, it should be noted that the activated sample with the highest CNTs content has the most "depleted" composition, as its IR spectrum lacks peaks corresponding to alkyl and oxygencontaining groups in the 1000–1500 cm⁻¹ region.

Based on scanning electron microscopy data, it can be assumed that the bonding between the nanotubes and the biomass-derived matrix during composite formation occurs at the sites originally occupied by functional groups. This likely explains the observed changes in the IR spectral characteristics.

All of the analyzed samples exhibit prominent D (~1350 cm⁻¹) and G (~1590 cm⁻¹) bands in their Raman spectra. The intensity ratio of these peaks (I_D/I_G) is commonly used to assess the degree of graphitization in carbon materials, where a higher I_D/I_G value indicates a greater level of structural disorder or defects in the sample [23, 24].







Fig. 4. Raman spectra of biochar samples

No significant differences are observed among the Raman spectra of the analyzed samples (Fig. 4). However, calculations show that as the CNTs content increases up to 0.05 wt. %, the I_D/I_G ratio initially decreases and then increases. Notably, the sample with 1 wt. % CNTs has a slightly lower I_D/I_G ratio than the sample containing 0.5 wt. % CNTs (see Table 1).

The non-uniform trend in the defectiveness index with increasing CNTs content is likely due to differences in the composite morphology and the varying resistance of the components to alkaline treatment at high temperatures.

The X-ray diffractograms of the analyzed samples exhibit a qualitatively similar features (Fig. 5). They show a broad halo with a peak at 2θ around 12° , which is characteristic of amorphous porous carbon materials[25], and a wide peak at 2θ around 43° , which corresponds to the crystallographic plane (100) of graphite [26].



Fig. 5. XRD-patterns of biochar samples

 Table 1. Influence of CNTs content

 on the structural characteristics of the samples

Mass fraction of CNTs, wt. %	0	0.01	0.05	0.1	0.5	1
I_D/I_G	1.054	1.021	0.985	1.053	1.060	1.043
$d_{100},$ Å	2.114	2.111	2.101	2.111	2.117	2.101

The interplanar spacings (d_{100}) , calculated using the Wulff–Bragg equation, are presented in Table 1.

It can be observed that the trend in the d_{100} values correlates with the changes in the I_D/I_G ratio. The increase in structural defects may be attributed not only to the destruction of the surface or graphene layers of the components but also to the presence of an amorphous phase within the material. Particles of this phase can potentially block pores and reduce the sorption capacity.





Kadum A.H.K., Burakova I.V., Badin D.A., Rybakova S.O., Timirgaliev A.N. et al.

According to thermogravimetric analysis (TGA) (Fig. 6), all samples exhibit relatively homogeneous chemical composition due to the effective decomposition of low-molecular-weight organic components and the removal of volatile functional groups during the carbonization and alkaline activation stages. The TG curves display a single prominent weight-loss region, which corresponds to a peak in the DSC curve.

The addition of CNTs contributes to a slight increase in the thermal stability of the resulting composites. However, the sample with the highest CNTs content shows the greatest initial mass loss on the TG curve compared to the other composites, likely due to its specific structural characteristics.

Particularly noteworthy is the correlation between the DSC analysis results and the data from Raman spectroscopy and X-ray diffraction. Samples that showed a decrease in structural defects (lower I_D/I_G values) also exhibited a lower exothermic effect during thermo-oxidative degradation compared to the unmodified material (without CNTs). The most intense DSC peak is observed for the sample with 0.5 wt. % CNTs, which also exhibits the highest I_D/I_G and d_{100} values.

According to the data presented in Table 2, the sample containing 0.05 wt. % CNTs demonstrates the highest specific surface area and specific micropore volume. As shown earlier, this material also has the lowest I_D/I_G and d_{100} values.

The decrease in surface area and porosity parameters with increasing defectiveness can be explained by the adverse effect of amorphous phase inclusions on the sorbent's characteristics. As the CNTs content exceeds a certain threshold, it promotes the formation of amorphous phase particles that block the pores.

Table 2. Specific surface area and specific micropore volume of the base activated carbon and composite sorbents with varying CNTs content

No.	Mass fraction of CNTs in the composite, wt. %	$S_{\text{BET}},$ $\text{m}^2 \cdot \text{g}^{-1}$	$V_{\text{total}}, \\ \text{cm}^3 \cdot \text{g}^{-1}$
1	_	2945	1.703
2	0.01	2700	1.456
3	0.05	2876	1.643
4	0.1	2757	1.601
5	0.5	2690	1.570
6	1	2057	0.653

3.2. Determination of adsorption capacity

3.2.1. Comparative testing of samples under static conditions

The results of the liquid-phase adsorption studies of organic dyes on the developed materials under static conditions are presented in Fig. 7.

According to Fig. 7, the sample containing 0.05 wt. % CNTs exhibits the highest adsorption capacity, with its capacity being 25 % greater than that of the base activated carbon without CNTs. Further increases in the CNTs content do not result in a positive effect and are therefore not advisable. It is worth noting that the variation in the sorption activity of the composites toward organic dyes generally correlates with the Raman spectroscopy and X-ray diffraction data.

3.2.2. Adsorption dynamics

The experimental kinetic curves for the adsorption of MG and CR dyes under dynamic conditions are shown in Fig. 8*a*. For MG removal using the nanocomposite, equilibrium in the sorption system is reached within 30 min, while for CR it is achieved within 10 min. The studied sorbent demonstrates a high adsorption rate during the initial period (up to 10 min).

Table 3 shows the models equations used in this work to describe the mechanism of dye adsorption. Tables 4 and 5 below present the results of the mathematical analysis of the experimental data using diffusion and chemical kinetic models.

The dependence describing intraparticle diffusion (Fig. 8*b*) exhibits a multilinear curve.



Fig. 7. Comparative adsorption capacity of peach-derived activated carbons for MG and CR dyes

Kadum A.H.K., Burakova I.V., Badin D.A., Rybakova S.O., Timirgaliev A.N. et al.


Fig. 8. Kinetic curves of MG and CR dye adsorption (*a*) and kinetic models: *b* – Intraparticle diffusion; *c* – Boyd; *d* – Pseudo-first-order; *e* – Pseudo-second-order; *f* – Elovich model

Since the approximating line does not pass through the origin, there is a boundary diffusion layer effect; diffusion is not the rate-limiting step, and the diffusion process is overlapped by a surface adsorption stage [20]. These observations are characteristic for both dyes. The diffusion rate for MG is several times higher than for CR (for example, $k_{id1} = 3519.5 \text{ mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5}$ vs. $k_{id1} =$

= 537.41 mg·g⁻¹·min^{-0.5}). For the Boyd's model, the kinetic data were processed for F < 0.85, i.e., in the initial period of adsorption. The correlation of experimental data using Boyd's equation (Fig. 8*c*) further confirms the influence of intraparticle diffusion on the adsorption rate, making it possible to calculate the effective diffusion coefficient (Table 5) [27].

Model	Equation
Pseudo-first-order model	$\lg(Q_e - Q_t) = \lg(Q_e) - \frac{k_1 t}{k_1 t}$
Pseudo-second-order model	$\frac{t}{t} = \frac{1}{1} + \frac{1}{t}t$
Elovich model	$Q_t k_2 Q_e^2 Q_e$ $Q_t = -\ln(\alpha\beta) + -\ln(t)$
Intraparticle diffusion model	$\mathcal{Q}_{t} = k_{id} t^{0.5} + c;$
Boyd	$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{n=\infty} \frac{1}{n^2} \exp(-\operatorname{Bt} n^2);$
	$B = \frac{D\pi^2}{r_0^2}$

Table 3. Kinetic model equations* [20, 27]

* t – adsorption time, min; Q_e – adsorption capacity at equilibrium, mg·g⁻¹; Q_t – adsorption capacity at time t, mg·g⁻¹; k_1 – rate constant for pseudo-first-order adsorption, min⁻¹; k_2 – rate constant for pseudo-second-order adsorption, g·mg⁻¹·min⁻¹; k_{id} – intraparticle diffusion coefficient, mg·g⁻¹·min^{-0.5}; c – boundary layer thickness (constant), mg·g⁻¹; α – initial adsorption rate, mg·g⁻¹·min⁻¹; β – desorption constant reflecting surface coverage and activation energy of chemisorption, g·mg⁻¹; F – fractional attainment of equilibrium; B – kinetic coefficient, min⁻¹; D – effective diffusion coefficient, m²·s⁻¹; r_0 – average radius of sorbent particle, μ m; Bt – dimensionless parameter.

Table 4. Parameters	of chemical	kinetics	of dye	sorption
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	Experimental	Pseu	do-first o	rder	Pse	udo-second ord	er	Ele	ovich	
Dies	adsorption capacity, $mg g^{-1}$	$Q_{e}, \\ \mathrm{mg} \cdot \mathrm{g}^{-1}$	$k_1,$ min ⁻¹	R^2	$Q_{e}, \\ \mathrm{mg} \cdot \mathrm{g}^{-1}$	$k_2,$ $g \cdot mg^{-1} \cdot min^{-1}$	R^2	α , mg·g ⁻¹ ·min ⁻¹	$\beta, g \cdot mg^{-1}$	R^2
MG	2987	995.86	0.0854	0.9794	3333.3	0.00015	0.9982	532439.5	0.0038	0.9885
CR	1201	441.88	0.0884	0.9773	1250	0.00043	0.9998	22967.7	0.0074	0.9133

Table 5. Parameters of diffusion kinetic models for dye adsorption

Internal diffusion									Boyd			
Dies	k _{id1}	k _{id2}	k _{id3}	C_1	<i>C</i> ₂	<i>C</i> ₃		R^2		R	$D \cdot 10^{-5} \text{ m}^2 \text{s}^{-1}$	R^2
	mg	$g^{-1} \cdot min^{-0.3}$	5		$mg \cdot g^{-1}$			Λ		D	D^{10} , III S	Λ
MG	3519.5	190.68	73.463	2213.1	1996.8	2501.6	0.9794	0.9552	0.9241	0.1184	0.004	0.9699
CR	537.41	63.574	16.722	117.4	842.07	1087.5	0.9853	0.9654	0.9162	0.2091	0.007	0.9805

If the experimental results are well approximated by the pseudo-second-order equation, the reaction between the adsorbate and functional groups occurs strictly stoichiometrically (one molecule occupies one adsorption site) [20]. For both dyes, the data show a strong correlation with this model, with $R^2 = 0.9998$ and $R^2 = 0.9982$ (Fig. 8e; Table 4). The rate constants are k_2 (MG) = 0.00015 g·mg⁻¹·min⁻¹ and k_2 (CR) = = 0.00043 g·mg⁻¹·min⁻¹.

Kadum A.H.K., Burakova I.V., Badin D.A., Rybakova S.O., Timirgaliev A.N. et al.

4. Conclusion

This study developed a method for producing an effective sorbent nanocomposite based on activated carbon derived from peach pomace, modified with carbon nanotubes. The composite material was prepared by HTC of the raw biochar with varying mass fractions of CNTs, followed by thermal treatment and alkaline activation. Characterization confirmed the presence of CNTs on the surface and within the structure of the biochar granules. The material containing 0.05 wt. % CNTs showed the most ordered carbon structure and exhibited the highest porosity among all samples. Kinetic studies under dynamic conditions determined the adsorption capacity of the nanocomposite with 0.05 wt. % CNTs for MG and CR, as well as the equilibrium sorption times: $MG - 2987 \text{ mg} \cdot \text{g}^{-1}$ in 30 min, and $CR - 1201 \text{ mg} \cdot \text{g}^{-1}$ in 10 min. It was established that the adsorption process for both dyes proceeds via a mixed diffusion regime, with the diffusion of MG molecules occurring 6.5 times faster than that of CR.

5. Funding

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6. Conflict of interest

The authors declare no conflict of interest.

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Reviews

Materials for energy and environment, next-generation photovoltaics, and green technologies

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Design of carbon dioxide sorbents in the context of the potential energy landscape

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Abstract: This article explores a modern approach to the design of carbon dioxide (CO_2) sorbents based on the concept of the potential energy landscape (PEL). The authors analyze the relationship between PEL characteristics and CO_2 sorption efficiency. The article demonstrates how the manipulation of PEL parameters enables the development of optimized materials with desired sorption properties. The article examines the influence of the depth and distribution of energy minima on the selectivity, capacity, and kinetics of CO_2 sorption. Various strategies for modifying the PEL, including surface functionalization and the targeted introduction of defects, to achieve the desired sorption characteristics are highlighted. Examples of different types of sorbents, such as MOFs, zeolites, and activated carbons, designed within the framework of the PEL concept are presented. Potential applications of the developed sorbents in carbon capture and storage technologies, as well as the synthesis of chemically valuable products have been considered. This review will be of interest to materials science and energy specialists involved in the development of new sorption materials.

Keywords: carbon dioxide; molecular modeling; sorption; quantum chemistry; potential energy landscape.

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Проектирование сорбентов диоксида углерода в рамках концепции ландшафта потенциальной энергии

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Аннотация: Рассмотрен современный подход к проектированию сорбентов диоксида углерода (CO₂) на основе концепции ландшафта потенциальной энергии (ЛПЭ). Приведен анализ взаимосвязи между характеристиками ЛПЭ и эффективностью сорбции CO₂. Показано, как изменение параметров ЛПЭ позволяет разрабатывать оптимизированные материалы с требуемыми сорбционными свойствами. Исследовано влияние глубины и распределения энергетических минимумов на селективность, емкость и кинетику сорбции CO₂. Обсуждаются различные стратегии изменения ЛПЭ, включая функционализацию поверхности, целенаправленное введение дефектов для достижения желаемых сорбционных характеристик. Приведены примеры различных типов сорбентов, таких как МОF, цеолиты, активированные угли, проектирование которых осуществлялось в рамках концепции ЛПЭ. Рассмотрены потенциальные применения разработанных сорбентов в технологиях улавливания, хранения углерода, а также синтез химически ценных продуктов. Обзор представляет интерес для специалистов в области материаловедения и энергетики, занимающихся разработкой новых сорбционных материалов.

Ключевые слова: диоксид углерода; молекулярное моделирование; сорбция; квантовая химия; ландшафт потенциальной энергии.

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1. Introduction

With the ever increasing concentration of carbon dioxide (CO_2) in the atmosphere and the associated alarming climatic changes - global warming and suppression of certain ecological systems - the development of effective methods for CO₂ capture is increasingly urgent task becoming an [1]. The chemical and physicochemical properties of this sorbate make the problem of CO₂ fixation complex. It should be noted that CO₂ has an extremely lowenergy chemical structure, which determines its phenomenal thermodynamic stability. It cannot be efficiently decomposed into its simple constituents, solid carbon and molecular oxygen. CO₂ does not react chemically with other low-energy substances [1]. For example, even the most energetically successful chemical interactions of CO_2 (with water and amines) are reversible. The enthalpic increase of the Gibbs free energy only partially compensates for the entropic prohibition against reducing the conformational freedom of the sorbed gas molecules [2].

Plants and some bacteria use CO_2 to produce glucose, which is further converted to cellulose for cell walls, starch as a form of chemical energy storage, and proteins and lipids for the daily functioning of living things. The thermodynamic potential of CO_2 physisorption is also estimated to be mediocre. Because of the lack of dipole moment of this gas molecule, its electrostatic attraction to the particles of potential sorbents (Lewis bases or nanometer pore walls) is not strong enough. While effective binding of CO_2 is in principle hardly possible, many materials show a reasonably satisfactory sorption capacity [2, 3].

Currently, promising approaches include CO_2 adsorption by solid sorbents and absorption by liquid sorbents [4]. In particular, porous materials [5] stand out due to their ability to utilize their high surface area. In order to obtain the maximum practical benefit from this group of materials, it is necessary to optimize the diameters of the available pores as well as their volumes [5, 6]. In turn, liquid sorbents can be competitive in terms of their performance as they have similar intermolecular interaction energies in sorbent-sorbent and sorbent-sorbate pairs. The resulting favorable enthalpic factor should numerically exceed the unfavorable entropic factor. The latter is always unfavorable in gas sorption applications due to the increase in the order of the system, i.e. the suppression of the degrees of freedom of the bound sorbate [7]. In this case, the absolute efficiency and rating of any test sorbent is determined by its ability to selectively bind CO_2 and by the kinetics of sorption and desorption.

The aim of this review was to consider the basic principles of rational design of CO_2 sorbents on the basis of the potential energy landscape (PEL) concept. The review provides examples of satisfactory theoretical realizations of this approach to obtain more functional materials. The PEL describes the dependence of the potential energy of a system on its internal coordinates, where the system under study consists of a certain number of atoms or molecules that define fundamentally important properties of the material.

2. The concept of potential energy landscape

The concept of PEL provides a powerful tool for rational design of sorbents with given properties [8–12]. Within the PEL concept, all possible values of the potential energy of a system (or other suitable thermodynamic potential) are unified by a single mathematical function depending on a set of internal coordinates of the system (Fig. 1).



Fig. 1. Model PEL calculated for a small area
of an arbitrary CO₂ sorbent: *x*, *y* are arbitrarily chosen linear directions on a multidimensional surface;
"Energy" is the total potential energy of the system;
"The PEL" is the potential energy landscape

The concept of PEL is close in meaning to the concept of phase space, with the difference that PEL does not operate with instantaneous values of atomic momentum when a point within the space is given. Both PEL and phase space are mathematical models and have no material analogs. The multidimensionality of the PEL does not allow one to visualize all its surfaces simultaneously, but suggests mechanisms for analyzing the PEL by means of differential analysis for multidimensional functions.

The PEL concept is applied to analyze systems having many possible states with different stability. In the context of molecular modeling, the PEL makes it possible to:

- Determine the geometry of molecules: Minima on the PEL correspond to the most stable conformations of molecules;

- Study mechanisms of chemical reactions: A reaction pathway on the PEL corresponds to a transition from one minimum (reactants) to another (products) through a saddle point (transition state). The height of the barrier between minima determines the activation energy of the reaction;

– Analyze molecular dynamics: PEL allows to simulate the movement of atoms in a molecule and to study transitions between different conformations.

Theoretical methods for studying the PEL of material or working system include any а mathematical algorithm that supports the physically relevant evolution of the system geometry, i.e. the change of its internal variables in the direction of a systematic decrease of the total energy of the z-matrix. These include classical and ab initio molecular dynamics, Monte Carlo Metropolis, iterative algorithms for minimizing the forces acting on each atom in the system, and algorithms for finding the global minimum of energy with a stochastic component, such as the periodic kinetic energy injection method [13–16]. The most valuable information provided by the latter is the list of lowenergy stationary points. The obtained minima of the potential energy of the system are uniquely characterized in terms of total energy and geometrical parameters (z-matrix of the structure). The total energy depends on the Hamiltonian applied to the model system. It is useful to express this quantity in terms of the detected global minimum belonging to the PEL. Among the most relevant groups of model Hamiltonians, we would like to highlight the following three, which are characterized below.

First, we deal with the molecular-mechanical Hamiltonians. In standard applications they represent the integral potential energy by the sum of independent equations for the interatomic Coulomb $(\sim R^{-12})$ and London $(\sim R^{-6})$ forces and the interelectronic repulsion forces ($\sim R^{-12}$). If covalent bonds are present in the system, bond, valence plane angle and valence dihedral angle equations must be defined [17–19]. These equations specify a harmonic or more complex dependence of the energy of the system on its actual deviation from the initially given equilibrium value. Such interaction potentials do not imply the breaking and forming of covalent bonds, but adequately reproduce the thermal motion of atoms at sufficiently high temperatures and pressures [20-23]. Molecular mechanical potentials are still actively used in biophysical and materials science research projects [24], including the design of sorption materials for CO₂.

Second, Density Functional Theory (DFT) provides the optimal balance between the accuracy of capturing the electronic structure of the material and the cost of the computational cycle. DFT is ubiquitously used in materials science problems, including the analysis of possibilities for improvement of previously known sorbents [14, 25-28]. The screening of possible directions for improving the properties of the base material is performed by testing the PEL for each structural modification option in terms of thermodynamic potentials. In particular, PEL scans are often performed along the assumed coordinates of the chemisorption reaction and physisorption process to identify activation barriers and preferred sorption centers in the case of functionalized materials.

Third, semiempirical Hamiltonians – both derived from Hartree-Fock theory and based on simplified Density Functional Theory - provide a rather comfortable balance between the size of the system and the duration of the numerical calculation It seems possible to improve the [29–32]. computational performance by more than three orders of magnitude compared to Hartree-Fock and most DFT methods. Unfortunately, none of the semiempirical methods solve the problem of increasing the computational cost by three orders of magnitude while increasing the problem size by only a factor of two [30]. Because of the relatively low computational cost, semiempirical Hamiltonians are particularly important for the study of PEL, which requires extensive initial scans to qualitatively understand the shape of the landscape [30, 33–35].

Certain PEL properties can be obtained or verified by experimental physical methods [36–40], such as structural analysis (XRD, AFM), spectroscopy (FTIR, Raman, NMR) and, to a large extent, modern electron microscopy (REM, SEM, TEM). The measurement of the heat of adsorption by chemical calorimetry techniques allows determining the binding energy of CO_2 to the sorbent. On the other hand, by measuring adsorption isotherms, adsorption capacity and adsorption kinetics can be determined to better parameterize and confirm the main patterns on the PEL. A combination of theoretical and experimental methods is the most relevant philosophy of modern materials science. In this case, the more resource-intensive part is delegated to molecular modeling methods.

3. Results and Discussion

The development of more efficient materials for primary CO₂ sorption is being actively pursued worldwide. While some technologies have already been implemented in industry, e.g. amine scrubbing [40], many still need to be improved and made more competitive [38–41]. However, the largest group of methods is of purely academic interest [21, 24, 42–45]. The main reason for this situation is the excessive cost of the proposed materials. Systematic research on the PEL characteristics of economically inefficient materials can pave the way for their cheaper production.

Let us consider some currently used and promising carbon dioxide sorbents to which the concept of potential energy landscape has been applied.

3.1. Using inorganic compounds

According to the principle of chemistry of inorganic compounds, the reactions of carbonate formation can be a basic solution. For example, strong bases – hydroxides of calcium, sodium, potassium, lithium – have good CO_2 sorption parameters. Calcium and iron oxides are also worth mentioning [1, 46]. A PEL study using a combination

of global minimum search and molecular dynamics simulations for an alkaline earth metal salt with a weakly coordinating anion showed that calcium tetrakis (pentafluorophenyl)-borate traps 5.5 CO_2 molecules per calcium atom, while barium tetrakis (pentafluorophenyl)-borate traps 3.6 CO_2 molecules per calcium atom [46]. Iron oxide reacts with CO₂ and moisture to form iron carbonate, effectively removing CO₂ from the environment. This is widely used as an absorber in food packaging and industrial applications.

3.2. Using organic compounds

Among the organic sorbents, ionic liquids should be mentioned [7]. This term covers a large group of solvents with a very wide temperature range of the liquid state. Due to the liquid aggregate state of the sorbent, gas absorption occurs with its entire volume (Fig. 2). Many ionic liquids form hydrogen bonds of varying strength with one of the oxygen atoms of CO₂. Thus, the sorbent and the sorbate develop an affinity between them [23, 47-50]. Lanyun Wang et al. performed molecular dynamics calculations for hybrid systems containing ionic liquids, metal cations and CO₂, which showed that in [Bmim][BF₄]-MBF₄, the Na⁺ ion has the least tendency to aggregate and form an M⁺ layer, making it difficult for CO₂ to contact the anion. In addition, Na⁺ has the strongest attraction to the $[BF_4]^-$ anion, which favours the of [Bmim][BF₄] expansion the space and consequently an increase in the number of CO₂ molecules absorbed. This is in agreement with the experimental data. On the other hand, the addition of other metal cations weakens the ability of the [Ac]⁻ anion to chemically bind to CO₂, which is the main reason for the decrease in the absorption capacity of the system [23].



Fig. 2. Phosphonium and sulfonium ionic liquids with aprotonic heterocyclic anions for CO₂ chemisorption. Reproduced from the author's open-access source [51]

The authors of this article have investigated the mechanism of carbon dioxide sorption by sulfonium and phosphonium ionic liquids (Fig. 2) through the formation of intermediate products – ylides. To evaluate the efficiency of sorbents, electronic properties were calculated, charge transfer was studied, and geometrical parameters of compounds were estimated [51].

3.3. Using liquid membranes

 CO_2 is separated from other gases by liquid membranes, which are thin layers of liquid. Liquid membranes selectively allow CO₂ to pass through while retaining other gases due to the different binding strengths of different gases. The liquid layer can be sandwiched between two gas-permeable membranes or deposited on a porous substrate [52–54]. Hao Dong et al. investigated the CO_2/H_2 sorption selectivity of graphene oxide based membranes with different ionic liquids. PEL calculation by density functional theory method and binding energy determination explained the preferential permeation of CO₂ over H₂ and the anomalously high values for graphene oxide with C₄mimBF₄ ionic liquid [52]. Compared to traditional gas separation methods such as cryogenic distillation, liquid membranes require less energy. In addition, membrane systems are generally more compact than other gas separation technologies. In a supported liquid membrane, the liquid phase is retained in the pores of the porous substrate. In an emulsion membrane, the liquid phase is dispersed as an emulsion in another liquid. This technology is used in natural gas purification, CO₂ capture from flue gas waste and separation of gases such as CO₂, H₂S and N_2 in the petrochemical industry [42, 55–58]. Guangyao Yu et al. studied the reduction reaction of carbon dioxide on graphene substrate doped with magnesium, nickel and nitrogen. The PEL calculation and the resulting charges, electronic state densities and Gibbs energies confirmed the assumption that both magnesium and nickel centres are jointly involved in the reaction [55]. The study of the PEL of a sorbent in direct contact with the pollutant gas is the most obvious application of the PEL concept. The same applies without reservation to the solution of competitive absorption problems. The knowledge of the parameters of the corresponding PEL dramatically changes the speed of the design of a new material. although it requires experimental verification.

3.4. Development of polymeric membranes

PEL can be of great support for the synthesis of polymeric membranes in which the most successful structural patterns are purposefully combined to accelerate CO_2 absorption kinetics and increase sorbent capacity. Understanding the activation barriers of the process and the specificity of steric factors makes it possible to design the most promising new sorbents.

3.5. CO₂ capture using biological systems

Microalgae such as chlorella and spirulina are capable of absorbing CO_2 during photosynthesis [59]. This is an environmentally friendly and sustainable way to capture CO_2 , which can be used to produce biofuels and other valuable products. Some enzymes, such as carboanhydrase, can catalyze the hydration reaction of CO_2 , converting it into bicarbonate. This approach can be used to create biological CO_2 capture systems [59].

3.6. PEL study to evaluate the efficiency of CO₂ sorption

In the context of gas sorption by a solid or liquid material, the PEL determines the interaction of a CO₂ molecule with the sorbent surface [60-63]. In cases where CO_2 is fixed by the entire volume of the sorbent, the difficulty of PEL analysis increases significantly because of the number of landscape dimensions involved. For example, the minima on the PEL correspond to stable states of the sorbed molecule. and the depth of the minimum characterizes the energy of its binding to the sorbate. A sorbent can have different types of active centers with different CO_2 binding energies. This is shown on the PEL as multiple minima of different depths. The barriers on the PEL determine the kinetics of sorption and desorption and indicate the relative simplicity or complexity of activation of these processes. A comparison of the activation barriers present on the PELs allows the researcher to understand the microscopic scenario in which the physical and chemical processes induced in the system will unfold [15, 27, 28, 64, 65]. Note that each PEL contains information about a large number of behavioral scenarios, but only the lowest energy scenarios are projected in the real world. In systems confined at high temperatures and pressures, the probabilities of high-energy and low-energy scenarios are balanced as the limiting role of activation barriers on PELs is offset [66-68].

Sorbent	Coordination centers	Distance between adsorption center and CO ₂ , nm	Enthalpy of the formation, $kJ \cdot mol^{-1}$	Bindingenergy, kJ·mol ⁻¹	Source			
Study of geometrical parameters								
[emim][TfO]	$C(CO_2)-O(TfO)$	0.235		29.8	[14]			
[emim][Tf2N]	$O(CO_2)-H(emim)$	0.236		23.3	[14]			
amino-functionalized	$C(CO_2)-N(FG)$	0.137	+9.36		[16]			
graphene (FG)	$C(CO_{2})$	0 254		19	[39]			
CH2-COO	$C(CO_2)=0$	0.289		9	[39]			
$-CH_2-NH-CO-CH_2-$	$C(CO_2)=0$	0.295		8	[39]			
$-CH_2-N(CO)_2-C_6H_3-$	$C(CO_2)=0$	0.275		10	[39]			
-Сп2-О-Сп2-	$C(CO_2)=0$	0.318		4.4	[30]			
$-C_{6}H_{4}-O-C_{6}H_{4}-O_{6}H_{4}-O_{6}H_{4}-O_{6}H_{6}+O_{6}H_{6}+O_{6}H_{6}+O_{6}H_{6}+O_{$	$C(CO_2) = 0$	0.203		73	[30]			
$-CH_2-SI-(OCH_3)_3$	$C(CO_2)=0$	0.293		1.5	[39]			
	$O(CO_2)-H$	0.231		14	[39]			
IBA	О(СО ₂)–Н	0.267		6.7	[39]			
IBP	О(СО ₂)–Н	0.324		3.7	[39]			
BMPYRR	О(СО ₂)-Н	0.262		9.3	[39]			
indezolido	Stua	ly of chemical reaction	i path		[15]			
1.2.4 trianalida	$C(CO_2)-N$		-68		[15]			
1,2,4-triazolide	$C(CO_2)-N$		-46		[15]			
	$C(CO_2)-N$		-40		[15]			
3-trifluoromethyl-	$C(CO_2)-N$		-0		[15]			
[P2224][BENZIM]	$C(CO_2) = C(P2224)$	0.157	-132		[27]			
[P66614][BENZIM]	$C(CO_2) = C(P_{2224})$	0.158	-129		[27]			
[P2224][2MTRENZIM]	$C(CO_2) = C(100014)$	0.159	-71		[27]			
[P66614]	$C(CO_2) = C(P_{2224})$	0.158	-127		[27]			
[2MTBENZIM]	$C(CO_2) - C(F00014)$	0.120	12/		[27]			
tetraethylammonium	$C(CO_2)-$	0.152	-23		[28]			
1,2,3-	N(triazolide)							
triazolide	Stud	u ofmologularoonform	ations					
Dialkylcarbonates(DAC)	$C(CO_{2}) = O(DAC)$	0 246	-11.6 (D8C)		[25]			
[Bmim][BF4]	$C(CO_2) = O(DAC)$	0.2.10	11.0 (200)		[23]			
[Bmim][BF4]–[Li][BF4]					[23]			
[Bmim][BF4]–					[23]			
[Na][BF4]	anion/	anion –						
[Bmim][BF4]–[K][BF4]	cation/metal-CO ₂ .	$CO_2 < cation - CO_2$			[23]			
[Bmim][Ac]		0.02 0.000 0.02			[23]			
[Bmim][Ac]=[Na][Ac]					[23]			
[Bmim][Ac]–[K][Ac]					[23]			
[Ca][TFPB]	O(CO ₂)–Ca	0.22	-8		[46]			
[Ba][TFPB]	O(CO ₂)–Ba	0.30	-7.8		[46]			
C ₁ mimBF ₄	< <i></i> /			1.01	[52]			
C ₄ mimBF ₄				1.32	[52]			
C ₈ mimBF ₄				1.54	[52]			
C ₄ mimPF ₆				1.34	[52]			
C ₄ mimOTf				1.44	[52]			
C4mimNTf2				1.82	[52]			

Table 1. Relationship between PEL characteristics and CO_2 sorption efficiency

Table 1 shows the relationships between some parameters characterizing the CO₂ sorption efficiency and the PEL for a number of sorbents studied. Geometric parameters, chemical reaction pathways, and molecular conformation studies were considered as options for applying the PEL concept. The following descriptors were selected for analysis: distance between interacting centers, enthalpy of formation, and binding energy. The distance between interacting centers is an important parameter that reflects the force of attraction between the particles. The bond length determined by this distance indicates the nature of the interaction - electrostatic or covalent - and is inversely proportional to the bond strength: the smaller the distance, the stronger the bond. The distances for the sorbents shown in Table 1 range from 0.137 nm between CO₂ carbon and nitrogen of functionalized graphene, corresponding to a covalent bond, to 0.324 nm between CO2 oxygen and tetrabutylphosphonium hydrogen of (TBP), corresponding to an electrostatic interaction. The enthalpy of formation, whose negative value indicates the exothermic character of the process, is also an important factor that often favors sorption. For amine-functionalized graphene, the enthalpy of addition of the CO2 molecule is positive, $+9.36 \text{ kJ} \cdot \text{mol}^{-1}$. This indicates a lower stability of the obtained compound compared to the starting materials. A negative enthalpy of formation, as in $[P2224][BENZIM] -132 kJ \cdot mol^{-1},$ [P66614] [BENZIM] -129 kJ·mol⁻¹ and others, indicates the stability of the formed product. Finally, the binding energy, which characterizes the strength of the interaction between the elements of the system, is directly correlated with the bond strength and corresponds to the depth of the potential well on the PEL.

The PEL of a sorbent is determined by its chemical composition and surface structure. The key factors affecting the PEL are as follows. The chemical nature of the adsorption centers determines the intermolecular interactions between the sorbent and the sorbate. The introduction of *functional groups* capable of interacting specifically with CO₂ can increase the binding energy and selectivity of adsorption (Fig. 3). For example, amine, hydroxyl, and carboxyl groups exhibit relatively strong electrostatic interaction with the bound gas molecules [69–71]. This increases the enthalpic gain in absorption and adsorption applications by liquid and solid porous materials. The porosity and specific surface area of the sorbent have a positive effect on its CO2 sorption capacity. At the same time, such





sorbent characteristics can worsen the sorption and desorption kinetics. The manifestation of this effect should be expected in case of the presence of "pockets" in the porous sorbent sample, which are difficult to access for sorbate particles. The correct design of hierarchical porous structures is the primary task in the application of the PEL concept. A developed porous structure with a large specific surface area provides a large number of sorption centers and, consequently, a high sorption capacity of the material [5, 71–75].

Achieving a perfect match between the pore diameter of the synthesized material and the effective diameter of the CO2 molecule is considered a challenge for current chemical nanotechnology. Visible success in the controlled production of pores with a strictly required diameter could fundamentally change the situation with the adsorption of greenhouse gases. These gases are (in order of their negative impact on the planet's atmosphere) water vapor, CO₂, methane, ozone, and nitrous oxide. It is not difficult to see the similarity in the size of the molecules of the most harmful greenhouse gases. Having a cheap way to synthesize a material of random chemical composition with a significant number of pores with an effective diameter of about 0.5 nm could take the current state of this field of research to a new level. Even if such a nanomaterial does not provide the desired selectivity towards dinitrogen and dioxygen, it would easily capture harmful emissions from industries.

Currently, it is believed that efficient adsorption of CO_2 requires micropores (less than 2 nm), which provide a sufficiently strong interaction with CO_2 .

In turn, mesopores, 2-50 nm, satisfy the requirement for rapid transport of CO₂ molecules to the adsorption centers. Surface morphology, such as defects and roughness, can influence the availability of adsorption centers and adsorption kinetics [77–80].

3.7. Development of sorbents by functional groupsgrafting

The introduction of functional groups into the sorbent surface is one of the most effective ways to modify the PEL towards its affinity for CO₂. As Lewis bases, amines form chemical bonds with CO₂, resulting in significant chemisorption energy. Nevertheless, the reaction of amine-functionalized material with CO₂ is reversible [16]. In the development of new sorbents, it is important to consider the sorption energy, as CO₂ desorption and sorbent regeneration are still required [81–84].

Hydroxyl groups only form hydrogen bonds with CO_2 . This ensures moderate gas adsorption energy and consequently cheaper desorption. Carboxyl groups, on the other hand, are also capable of forming hydrogen bonds with CO_2 and can participate in ionic interactions that are sufficiently strong by the standards of physisorption processes. The PEL directly reflects these non-covalent interactions and makes the search for optimal structural parameters more rational. Further grafting of the sorbent has minor effects to the PEL.

3.8. The use of porous materials

It should be reiterated that, in addition to the presence of molecular fragments with the properties of Lewis bases in the sorbent composition [16], the hierarchical porous structure should be considered as an independent factor stimulating the sorption capacity. When located in a very narrow pore, the CO_2 molecule is attracted by the London forces simultaneously to all its walls. Because of this, the enthalpy of adsorption more than doubles compared to the above mentioned two-nanometer pores. The developed porous structure with high specific surface area is an important factor for efficient CO_2 adsorption.

Activated carbons possess the high specific surface area and relatively adjustable porous structure desired by researchers. Such carbon materials are highly reactive, i.e., they can be easily functionalized with carboxyl, hydroxyl, or amine groups [85, 86]. For example, the previously well-studied oxidized graphite and graphene samples, which also preferentially contain sp^2 -hybridized carbon atoms, can be applied [86]. Activated carbon definitely represents a suitable starting platform for the improvement of CO₂ sorbents. The PEL concept assists in comparing the thermodynamic effect in the case of different types of grafting of the initial carbon material.

3.9. The use of zeolites

Zeolites are crystalline aluminosilicates that also have a fairly ordered porous structure [87–90]. The pore size and chemical composition of zeolites can be varied to a certain extent by chemical methods to optimize the adsorption properties [89, 90]. The thermodynamic stability of this group of sorption materials promotes their large-scale application in environmental technologies [91–93].

3.10. Metal-organic frameworks

Similarly, metal-organic frameworks (MOFs) represent a new class of porous materials with high specific surface area and tunable structure [71]. The research interest in MOFs in the context of CO_2 sorption is primarily due to their structural diversity and suitable pore sizes [94-97]. More importantly, it seems uncomplicated to use MOF active centers to intercalate additional sorption active centers. A fullfledged study of the PEL of MOFs has still not been carried out, despite many localized problems in this field solved using DFT [98, 99]. PEL is crucial to understand the limiting capacities of MOF structures with respect to greenhouse gases. The practical difficulty in analyzing the PEL for different MOF structures is that the unit cell size of these periodic structures is too large [71] to allow a full PEL sampling by DFT methods with a plane-wave basis set.

3.11. Composite materials

The design of composite materials combining the properties of different components with individual adsorption properties can achieve synergetic effects and improve the adsorption performance of the new product [16, 76, 100–102]. Carbon-based composites have attracted paramount attention in this context because carbon chemistry is extremely diverse and the techniques for its realization are not badly documented as of today. The incorporation of metal oxide nanoparticles into the carbon matrix allows to increase the binding energy of the thus obtained new sorbent material with CO₂. Improved MOF-based composite materials can

be obtained in a similar manner [71, 103, 104]. Combinations of MOFs with polymers show improved mechanical properties and thermodynamic stability of the sorbent. The flexible polymer chains are able to partially penetrate the MOF pores because of the matching size. Thus, more perfect atom packing variants are achieved. At the same time, the polymer contains groups important for CO₂ sorption, and the obtained material can be considered for gas binding. The combined effect of the combination of micropores and functional groups can be quite large in the context of practical applications of the composite material.

3.12. Nanotubes and zeolites

By combining carbon nanotubes with various substances, sorbents with high adsorption capacities and good regenerability can be created [60, 66]. In turn, zeolites allow to achieve high selectivity for CO_2 , but only under the condition of proper selection of the pore hierarchy, which thermodynamically favor the retention of this gas. Note that the size of pores and the variation of their diameters in materials based on silicon compounds, in most cases is significantly larger compared to carbon materials. In turn, the preparation of zeolites for adsorption tasks is often cheaper and can be a more relevant solution for large industrial applications.

3.13. Electrochemical adsorption of carbon dioxide

A recent workable method of electrochemical CO_2 capture, in which a charged carbon cathode is the adsorbent, has been proven by the authors of this review using molecular modeling [105] (Fig. 4).



Fig. 4. One of the measurements of the PEL, the linear distance between the CO_2 carbon atom and the carbon atom of the positively charged graphite layer, characterizing the electrochemical chemisorption of CO_2 on the graphite cathode. Reproduced from the author's source [105] with permission from Elsevier. Copyright Elsevier 2024

The point is that when voltage is applied to the cathode, the carbon structure constituting it receives additional π -filled orbitals. Due to this, the carbon partially acquires the chemical properties of nitrogen. A nucleophilic addition reaction occurs with the formation of a covalent bond carbon (sorbent)-carbon (CO₂) [106].

According to the calculated PEL plots, this bond kinetically stable up until the cathode is is disconnected from the current source [105]. The developed sorbent can be used in solid state. Thus, a more significant chemisorption energy is added to the physisorption energy due to the London interaction with the pore walls. A reformulation of the method in which the nano-organized carbon (graphene, nanotube, graphite) is dispersed in some suitable solvent that supports exfoliation is probably also possible [16]. Since electrochemical adsorption relies on an electrical energy source rather than a chemical one, as more traditional methods of CO₂ capture, its implementation and scaling appear to be more efficient [105].

The PEL modifications presented in this work are summarized in Table 2.

4. Conclusion

We have reviewed all relevant chemical compounds and materials that can be expected to improve CO₂ sorbents and noted the applicability of the PEL concept to the given objectives. All the discussed promising materials should be categorized into three groups. The first includes amine scrubbing technology related solutions in which the chemisorption centers are the same amino group cleaved to a liquid carrier, for example, an ionic liquid cation [102]. The second group includes solid porous materials with complex hierarchical pore structure based on carbon, silicon or MOF [99, 107]. The third group includes combinations of structural fragments belonging to the first and second groups recombined into a single material. For example, an extensive surface of activated carbon, decorated with amino groups [16], solves the problem of sorbent volatility in the case of classical amine scrubbing [40].

The PEL concept is a powerful tool for the rational design of porous CO_2 sorbents. Further development in this area involves systematizing the design of new materials with specific properties. Using nanotechnologies and composite materials opens up broad opportunities for creating highly efficient CO_2 sorbents. Applying more precise quantum-chemical methods and developing new experimental techniques will allow to more accurately reveal the types of CO_2 -sorbent interactions depending on the sorption's specificity and purpose [16].

Table 2. Strategie	s for changing	the potential	energy	landscape
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Type of PEL changing	Source			
Modification of the sorbent surface				
Grafting amino groups onto the graphene surface changes the PEL and creates active centers for interaction with sorbate molecules. Quantum-chemical calculations, including calculation of electron density distribution, electrostatic potential and thermodynamic potentials, allow to study the interaction of sorbate with the modified surface	[16], [85]			
In order to study the mechanism of sorption during cellulose modification to produce a polyionic liquid, both experimental studies and molecular dynamics calculations were carried out. Modeling allowed to establish the key role of anion in the sorption process and to reveal the peculiarities of interaction of each element in the system	[38]			
Functionalization of ionic liquid cations by amino groups for CO_2 sorption. The sorption capacities of the new compounds were determined by calculating thermodynamic potentials	[76], [102]			
Modification of fullerene C-60 by grafting amino groups yields a non-volatile compound promising for CO ₂ sorption. Quantum chemical calculations including charge distribution, dipole moment and HOMO-LUMO energy analyses, as well as calculation of the Gibbs energy change (Δ G) upon interaction with CO ₂ are used to evaluate the sorption capacity of the modified fullerene				
Introduction of defects				
The incorporation of magnesium, nickel and nitrogen into the carbon matrix, as well as the calculation of Gibbs energy, allowed the identification of the centers involved in the electroreduction of CO_2	[55]			
Nickel and nitrogen atoms were deposited on a carbon carrier. Thermodynamic potentials were calculated for the modified system. The study shows that Ni plays an important role in CO ₂ activation, providing a low energy barrier for Ni–C bond formation and facilitating further CO ₂ reduction	[56]			
Charge transfer to the sorbent				
Modification of the sorbent surface by introducing additional negative charge changes the PEL. In the case of graphene, the negative charge is responsible for lowering the energy barrier and reducing the thermal effect of the reaction, which contributes to the increase of its sorption properties	[105], [106]			

modeling study of substances and materials. Incorporating it into the working program of a materials research group makes it possible to consider potential energy as a physical property at the atomic level. Meanwhile, although experimental research on materials allows for the acquisition of indirect energy descriptors, it cannot compare to the spatial resolution of the microscopic results provided. Even the interpretation of new types of electron microscopy relies to some extent on the PEL modeling. As convincingly demonstrated in this review, the specific features of PELs can be correlated with macroscopic properties of materials or processes.

The PEL concept can be used to develop carbon dioxide sorbents for various industries that emit CO_2 or require CO_2 capture. Currently, fossil fuel-fired thermal power plants, cement and metallurgical plants, oil refineries, and chemical plants are the main producers of carbon dioxide [1–3, 18, 24, 53].

Technological optimization of sorption and desorption process parameters will allow for increased efficiency and cost-effectiveness of the CO_2 capture process in the future. Currently, our expert opinion leans toward microporous silicon and carbon materials, along with MOFs that have the right elemental composition to trigger electrostatic interaction between the sorbent and the sorbate [98, 99]. When discussing competing materials science solutions, it should be understood that the winning technology is almost always the cheapest. Developing commercially successful methods for obtaining narrow pores with small diameter variation should be prioritized.

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7. Conflict of interest

The authors declare no conflict of interest.

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