ANNOTATION

of the dissertation submitted for the degree of Doctor of Philosophy (PhD)
in the educational program "6D060600 – Chemistry"
by Yeldana Bakhytzhan
on the topic:

" Synthesis of chemisorption and nanocomposite polymer coatings on steel with high anticorrosive properties"

General work description

The dissertation is devoted to creating and improving of methods for the synthesis of new chemisorption, polymer, and polymer-nanocomposite coatings on the surface of metals to protect the surface of mild steel from corrosion. In the course of scientific work, new inhibitors with high inhibitory efficiency were proposed, optimal conditions for the synthesis of polymer, polymer-nanocomposite coatings with high anti-corrosion properties on the surfaces of mild steel was determined, and the protective mechanism of the synthesized coatings was studied. The anti-corrosion properties of new polymer nanocomposite coatings were determined by modern electrochemical and physicochemical methods.

Relevance of the research topic

Corrosion is a process in which a metal interacts with its environment, including air, water, acids, alkalis, salts, and various solvents, causing chemical or electrochemical reactions. From the point of view of thermodynamics, the corrosion of metals is a spontaneous process. During the corrosion process, metallic materials can corrode and lose their original physical and mechanical functions. As is known, metal materials occupy a leading position as industrial raw materials and are the basis of industry. They are widely used in various industries such as aerospace, automotive, shipbuilding, and pipeline transport. A variety of engineering materials can corrode, from microelectronics to materials for orthopedic implants, from civil infrastructure to household items. The presence of metal corrosion causes serious harm to healthcare safety, and human health, huge economic costs, and waste of resources. Economic losses from corrosion amount to about 3-5% of the gross domestic product of all countries of the world and show an increasing trend every year, which significantly exceeds losses from various accidents. Corrosion is one of the main challenges and threats to society and the economy. Nowadays, people's quality of life mainly depends on the use of materials, and rapid changes in social factors require greater attention to corrosion prevention and reduction.

Corrosion is a serious problem in industrialized countries. Before designing any industry, it is important to consider the effects of corrosion on equipment and the environment. Several unsolved corrosion problems are hindering engineering progress in many industries.

The problem of corrosion resistance is relevant every year in industrialized countries with large reserves of metals, the USA, Australia, and China. Corrosion problems cost approximately US$2.5 trillion, equivalent to 3.4% of global GWP.

Several countries are conducting studies on the costs associated with metal corrosion. In 1949, US spending was $5.5 billion, or 12.1% of GWP, but over time, spending increased 12-fold to $70 billion in 1978. In 1998 and 2016, it was $276 billion and $1.1 trillion, respectively. If we look at the data presented, it is established that the cost of costs associated with corrosion will increase with technological progress.

Kazakhstan is a leading country with sufficient metal reserves. Therefore, it is important to explore new ways to protect steel from corrosion to reduce the country's costs.

Goal of the research work.

The goal of the thesis is the synthesis of highly effective chemisorption and polymer nanocomposite coatings that protect mild steel from corrosion.

Tasks set to achieve the work goal:

1. To synthesize heterofunctional organic compounds and investigate their protective effect on mild steel in acidic and chloride media using gravimetric and electrochemical methods.

2. To determine the protection mechanism of effective inhibitors based on the analysis of adsorption characteristics, electrochemical parameters, and surface morphology of their interaction with the steel surface.

3. To optimize the conditions for the electrochemical synthesis of POA and POA/metal oxide coatings on the surface of mild steel.

4. To study the anticorrosive properties of the synthesized polymer, copolymer, and polymer nanocomposite coatings using linear voltammetry and electrochemical impedance spectroscopy (EIS).

5. To investigate the morphological features and elemental composition of the polymer, copolymer, and polymer nanocomposite coatings synthesized on St3 grade steel using scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDAX), and to determine the formation and anticorrosion protection mechanisms of POA/metal oxide-based polymer nanocomposites.

Objects of research. Steel grade st3, heterocyclic inhibitors containing nitrogen and oxygen, as well as polymer, copolymer, polymer nanocomposite coatings.

Subject of study. Protective effect of chemisorption and polymer nanocomposite coatings on the surface of CT3 steel, corrosion potential, corrosion rate, current density.

Research methods.

Gravimetry, Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), linear voltammetry (LSV), chronoamperometry (CA), scanning electron microscopy (SEM), and energy dispersive analysis (EDAX).

Supply of equipment.

Autolab 302N potentiostat/galvanostat is equipped with the following modules: RDE, FRA 32M, Bio-Logic SP300 and VSP300 potentiostat/galvanostat, SEM Philips XL-30 FEG scanning electron microscope, Axio inversion microscope. Vert A1 (Germany), electron probe microanalyzer “Superprore 733”, Jeol (*10000).

The scientific novelty of the work:

Currently, nanocomposite polymer coatings are used to protect metals from corrosion. There are many works in the literature on this topic, but the mechanism of formation of the polymer coating is not clearly explained. In this work, polymer and copolymer nanocomposite coatings of a new composition were synthesized using an electrochemical method and their corrosion properties in aggressive environments were studied. In addition, the formation mechanism and protection mechanism of the nanocomposite were determined.

Another novelty of the work is the study of the protective properties of substances synthesized for the first time at the Department of Chemistry and Technology of Organic Substances, Natural Compounds and Polymers of KazNU. al-Farabi Faculty of Chemistry. The synthesis of a number of studied organic compounds was carried out based on of available primary reagents using a simple reaction scheme.

Theoretical significance of the work.

The results of the dissertation research are of great importance in the context of the development of the theoretical foundations of electrochemistry, especially in terms of obtaining protective coatings that prevent metal corrosion. The contribution of this research to the field of electrochemistry is the development of new reliable materials with superior protective properties, which in turn can have a positive impact on various industries where metal corrosion is an important problem.

Practical significance of the work.

One of the issues of interest to the metallurgical industry is corrosion protection. To keep metal structures in a safe condition, it is important to know the corrosion mechanism, factors influencing the corrosion of metals, the interaction of metals with the environment, and the properties of metals in various environments.

Several methods are used to protect metals from corrosion. In recent years, one of the most important areas of electrochemistry has been the synthesis of conductive polymer coatings on metal surfaces. The advantage of polymer, copolymer, and nanocomposite polymer coatings over paints is that they do not contain toxic substances harmful to the environment. In addition, polymer, copolymer, and nanocomposite polymer coatings act as a physical and electronic barrier on the metal surface.

Adsorption of nanocomposite polymer coatings on active areas of the surface of a metal coating inhibits the process of metal dissolution and leads to the formation of a uniform protective coating.

Despite continuous research in this field in recent years, the number of papers describing the electropolymerization mechanism is very few, and there are not even studies showing the electropolymerization of polyanisidine. Therefore, in this work, in addition to obtaining polymer coatings and studying their anti-corrosion properties, the mechanism of the electroplating process is considered. In turn, these studies provide fundamental results in the field of corrosion.

Main questions proposed for defense:

1.The heterofunctional compounds — O-acetoxy-bis(O-propionitrile)triethanolamine, N-benzyl-O-acetoxy-bis(O-propionitrile)triethanolammonium chloride, and N-(β-ethoxypropionitrile)-N,N-bis(2-hydroxyethylethoxy) fatty amide — used for the first time as corrosion inhibitors, demonstrate significantly higher inhibitory activity compared to existing analogues such as triethanolamine and alkyl- or benzylammonium derivatives. Their protective efficiency increases proportionally with concentration and ranges from 70% to 99%.

2. The protective mechanism of the synthesized inhibitors — O-acetoxy-bis(O-propionitrile)triethanolamine, N-benzyl-O-acetoxy-bis(O-propionitrile)triethanolammonium chloride, and N-(β-ethoxypropionitrile)-N,N-bis(2-hydroxyethylethoxy) fatty amide — is attributed to their ability to irreversibly chemisorb onto the steel surface, forming a stable monomolecular layer, which is described by the Temkin adsorption isotherm.

3. The incorporation of metal oxides (SiO_2, MoO_3) into the poly(o-anisidine) (POA) polymer matrix increases the resistance of the resulting coatings by 2–4 times (R, kΩ), while correspondingly reducing the corrosion current density by 2–4 times (j, A·cm²), compared to the POA coatings without oxide inclusions.

4. The electrochemical polymerization of o-anisidine, proceeding via a cation-radical mechanism in the presence of metal oxide nanoparticles (SiO_2, MoO_3), leads to the formation of a nanocomposite coating with a denser structure and enhanced anticorrosive performance due to the barrier effect of the oxide fillers, compared to poly(o-anisidine) (POA) coatings without such inclusions.

Personal contribution of the author. The author independently searched and analyzed scientific literature, practical and theoretical parts of the dissertation work, processed, analyzed, reviewed, summarized and published the research results presented in the dissertation in the form of a scientific article in the role of the main author.

Work overview.

The main conclusions and results of the dissertation were presented orally and discussed at the following international and national conferences:

1. Electrochemistry conference – 2019, Istanbul, Turkey, 2019.
2. Republican scientific and practical conference with the participation of foreign professors and young scientists on the topic “Current problems of analytical chemistry”, Uzbekistan, Tashkent, 2023.
3. Mediterranean Geosciences Union -2023, Istanbul, Turkey, 2023.
4. MedGU-2024, Barcelona, Spain, 2024.

Connection of work with the plan of state scientific programs.

The dissertation work was carried out by the research plan of the Department of Analytical, Colloidal Chemistry and Technology of Rare Elements of al-Farabi KazNU and within the framework of the projects “Center for Physico-Chemical Research and Methods of Analysis”.

As part of government grant funding projects:

1) IRN AR0513457 “Inhibitory and polymer nanocomposite protection of industrial metals from corrosion”, 2018-2020, (junior researcher);

2) IRN AP15473133 “Electrochemical synthesis of polymer nanocomposite coatings with high anti-corrosion properties on the surface of steel”, 2022-2024. (project manager).

Publications:

The results of the dissertation work were reflected in 13 scientific papers, including:

- 2 scientific articles, according to the Web of Science Clarivate Analytics information database, the impact factor is not equal to zero, or published in international publications included in the Scopus information database (1 - 89%, Q1, 2 - 35%, Q4).

- 4 articles were published in publications recommended by the Committee for Control in the Field of Education and Science of the Republic of Kazakhstan.

- 7 theses were published in collections of theses and materials of international and state conferences, including 5 theses published in materials of foreign conferences.

Structure and scope of work. The dissertation consists of a list of definitions and notations, introduction, literature review, experimental part, discussion of the results obtained, conclusion and list of references. The text of the work is printed on 121 pages and includes a bibliography consisting of 120 sources, 22 tables and 76 figures.