## ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD)
in the specialty “8D07101 - Petrochemistry”

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## DEVELOPMENT OF ANTICORROSION COATINGS FOR OIL FIELD EQUIPMENT

The dissertation work is devoted to the development of anti-corrosion coatings on metal surfaces to protect equipment at oil refineries.

**The relevance of thesis**

Today's metal corrosion problems cause significant economic damage. Corrosion protection of oilfield equipment is especially important because the climatic conditions of oil production are harsh. Paint and varnish coatings are most widely used to protect metal structures from atmospheric corrosion. The creation of environmentally friendly, energy- and resource-saving technological processes for metal surface treatment has become possible due to the development of fundamentally new chemical conversion coatings. One of the most common methods of protecting metal structures from corrosion is the application of anti-corrosion coatings. These include various chemical coatings, paints, varnishes and electrochemical galvanic coatings. Currently, corrosion protection by coatings ranks first among all corrosion protection methods in terms of the area of application. The processes of deposition anticorrosive phosphate and zirconium oxide coatings find wide application in the industry for the decision of various technical problems, which is due to the unique functional properties of these coatings, such as high bond strength with a metal substrate, high adsorption capacity; high anti-friction and extrusive properties and low electrical conductivity.

The main disadvantages of existing solutions of phosphating are the content of toxic nickel ions, ion nitrite, etc.; high energy intensity, due to high operating temperatures of processes 70-90 °C; the release of hydrogen, which prevents the formation of dense deposition, high sludge formation. In addition, for the implementation of modern phosphating technologies, complex equipment is necessary, and the processes themselves require strict control, since the properties of the formed coatings depend heavily on such parameters as free and total acidity, temperature, concentration of accelerators, etc. The most promising substances that would allow reducing the number of stages, stabilizing phosphating processes, increasing the overvoltage of hydrogen evolution, and reduce the temperature can be ecologically safe organic nitrogen compounds. It should be noted that there are no domestic developments using such technologies.

In recent years nanostructured ceramic adhesion coatings have been increasingly used as an alternative to adhesion phosphate layers in world practice. Advantages of new methods are their lower energy intensity and manufacturability in comparison with phosphating processes. Solutions for these coatings do not require heating, do

not require such strict control parameters, easy to use, form much less slurry and more environmentally friendly. Potential consumers of nanostructured ceramic adhesion and adhesive phosphate coatings are chemical, metallurgical, machine-building and oil-producing industries. In this regard, the development of new methods for applying adhesive phosphate and zirconium oxide coatings is an **actual** scientific and applied task.

**The purpose of the work** is the development of new import-substituting methods for applying adhesive nanostructured ceramic and phosphate coatings under paint and varnish coatings (LCP) for the purpose of use in the petrochemical, machine- and instrument engineering industries.

**The objects of research are** adhesive phosphate coatings on the surface of steel and brass samples, nanostructured zirconium oxide coatings on the surface of steel samples.

**Subject of study are** is the process of formation of phosphate and zirconium oxide anticorrosive protective coatings on the surface of steel and brass samples.

**Research methods are** the methods of generating solutions, tensor algebra and analytical methods of solving the system of nonlinear, second-order partial differential equations and numerical methods for back-ray tracing methods were used.

Protective and corrosion characteristics of phosphate and ceramic coatings were determined by voltammetry and Akimov's visual method. Electrochemical studies of corrosion resistance were carried out on a Gamry Reference and Autolab potentiostat. Corrosion tests were carried out in a salt fog chamber (Ascott S450iP). The properties of the developed coatings were investigated using a set of physicochemical methods: scanning electron microscopy (SEM), metallographic microscopy, spectroscopic ellipsometer, LK-1 Goniometer, PosiTestAT digital adhesion meter; XPS spectra were recorded using a special CLAM100 camera mounted on an HB100 Auger microscope (Vacuum Generators), GB.

**The novelty of the work**

The dissertation presents the following original results:

1. An electrochemical method for determining the corrosion resistance of phosphate coatings on iron and brass samples based on the value of the characteristic maximum current (A) in the cathode region of cyclic volt-ampere curves is proposed, which makes it possible to differentiate the selection of solutions and conditions for phosphating. A patent for a utility model has been received.

2. The composition of a phosphating solution for the production of phosphate coatings on iron samples (based on the Majef salt with the addition of hydroxylamine) has been developed using minimal concentrations of salts of heavy metals such as copper, nickel, zinc, chromium, which has a negative impact on the environment.

3. Phosphating solutions based on rust converters have been developed using organic nitro compounds (nitrophenol, m-nitrobenzosulfonate sodium) as accelerators, which make it possible to obtain corrosion coatings with corrosion resistance up to 330 c according to the Akimov method, which significantly exceeds the corrosion resistance of coatings compared with known phosphate coatings. It has

been shown that phosphate coatings deposited from a Phosphomet solution using nitrophenol with a concentration of 5 g/l as an accelerator at a deposition temperature of 40 °C and a deposition time of 10 minutes have the greatest corrosion resistance.

4. A new solution for applying zirconium oxide coatings on a steel base containing hexafluorocyrconic acid, molybdenum and tungsten ions has been developed. The optimal composition of precipitation of zirconium oxide coatings on steel is Zr (IV) - 1.5 g/l; Mo(VI) – 0.05 g/l; W(VI) – 0.05 g/l. Optimal conditions for deposition of zirconium oxide coatings on steel - pH - 4.5–5.5; solution temperature - 40-45°C; precipitation temperature - 5 min.; drying temperature - 60-70°C; drying temperature - 10 min.

5. Corrosion resistance tests using the Akimov method and in the salt mist chamber showed that the proposed zirconium oxide coatings meet the requirements for adhesive layers for paint coatings (LCP) in terms of protective ability, since the width of corrosion penetration from the incision site in these cases does not exceed 2.0 mm after 185 hours of testing.

6. According to the results of the X-ray photoelectron spectroscopy (XPS), it is shown in which compounds iron, zirconium, molybdenum and tungsten are included in the coating. The wide oxygen peak can be interpreted as a mixture of iron, zirconium and molybdenum oxides. Iron is present in the form of $Fe_2O_3$ oxide. The energy peak position for zirconium corresponds to $ZrO_2$ oxide. Molybdenum is present in the form of $MoO_3$ oxide (232.8 eV), and tungsten in the form of $WO_3$ oxide (35.9 eV).

7. The corrosion resistance of the developed zirconium oxide coatings on the steel surface significantly exceeds the corrosion resistance of the foreign analogue Interlox 5705. The corrosion resistance of the zirconium oxide coating developed by us is 35 s. (Akimov method), and the corrosion resistance of Interlox 5705 is 18 s.

**Scientific provisions for the defense**

1. An electrochemical method has been developed for determining the corrosion resistance of phosphate coatings on brass and iron samples based on the maximum current value on the cathode portion of cyclic volt-ampere curves, making it possible to differentiate the selection of solutions and conditions for carrying out phosphating.

2. Optimal conditions for the chemical phosphating of brass and iron using the electrochemical method by removing cyclic voltage curves have been determined.

3. The composition of a phosphating solution based on the Majef salt and hydroxylamine has been developed to obtain phosphate coatings on iron samples, which eliminates the use of salts of heavy metals such as copper, nickel, zinc, chromium, which does not have a negative impact on the environment. Phosphating solutions based on rust converters have been developed using organic nitro compounds as accelerators, which make it possible to obtain low-temperature coatings with high corrosion resistance

4. For the first time, optimal conditions for the application of zirconium oxide coatings used as adsorption layers for paint coatings have been developed from solutions containing hexafluorocyrconic acid, nickel and molybdenum salts to a steel base.

**Practical and theoretical significance of the scientific results**

The results of the dissertation expanded the known knowledge in the fields of anticorrosive phosphate and zirconium oxide coatings. The development of a new electrochemical method for the formation of anticorrosive coatings is a contribution to fundamental and applied electrochemistry. Advantages of the proposed development are: low energy intensity, since coatings are applied at a temperature of 25-30°C; high process ability, since it is not necessary to strictly control the parameters of the solution and the phosphating process itself; no hydrogen evolution, which promotes good adhesion of phosphates to the metal surface; absence of slime and negative impact on the environment; reduction in the cost and time of formation of phosphate coating. Research into the formation of nano-sized ceramic coatings will make it possible to replace energy-intensive and environmentally hazardous chromating and phosphating processes, which are widely used in oil refineries.

**Reliability and validity of the results**

The high scientific level of the research carried out and the validity of the results are confirmed by scientific publications both in Kazakhstan and in journals abroad, as well as by testing the results at international conferences and symposia.

**The author's personal contribution** Obtaining anti-corrosion coatings in the object of research, searching in literature sources of scientific research works on coatings with high corrosion resistance and analysis of studies, writing of theoretical and experimental parts of the dissertation, execution of the experimental part of the work, generalization and interpretation of the obtained experimental data and conclusions were carried out by the author independently.

**Publications**

According to materials presented in the dissertation, in the dissertation 12 publications have been published in total: 5 articles in journals indexed in Web of Knowledge (Thomson Reuters, USA) and Scopus (Elsevier, Netherlands); 1 article in journals recommended by the Ministry of Science and Higher Education of the Republic of Kazakhstan; 5 publications in collections of international scientific conferences. According to the results of the work in co-authorship, 1 positive decision was also received on the application (a patent for a utility model).

**Approbation of the dissertation**

The main results of the dissertation were presented and discussed at seminars of the Faculty of Chemistry and Chemical Technologies of Al-Farabi Kazakh National University and at the following international conferences:

- International Conference dedicated to the 100th anniversary of the D.I. Mendeleev RCTU, "Surface Treatment and Corrosion Protection", September 23, 2021, Moscow, Russia;
- XI International Beremzhanov Congress on Chemistry and Chemical Technology, November 19-20, 2021, Almaty.
- VI International Russian-Kazakh Scientific and Practical Conference "Chemical technologies of functional materials", June 15-16, 2020, Almaty;

**Volume and structure thesis**

The dissertation work consists of an introduction, 3 chapters, general conclusions and a list of sources used. The dissertation is presented on 118 pages, contains 12 tables, 75 figures. The list of references contains 119 sources.