ABSTRACT

For the thesis «To develop corrosion preventive compounds on the basis of technical gossypol and polyolefins to protect the gathering system pipelines of oil» by Yessentayeva Ayzhan Amangeldievna, submitted for the degree of Doctor of Philosophy (PhD) in specialty 6D072100 – «Chemical technology of organic substances»

Relevance of the research topic. Currently, large volumes of metal consumption and operating conditions of oil and gas field equipment in a sharply continental climate make the problem of increasing the durability of the equipment one of the main ones determining the growth rates and technical and economic efficiency of oil extraction, collection and preparation. Corrosion of oilfield equipment, in particular, pipelines of downhole production collection systems during its transportation from producing wells to measuring installations and further to the installation of complex oil treatment is the object of attention of scientists and production workers. I must say that in this case, the destruction of the metal of the pipeline is a consequence of processes occurring under the influence of atmospheric corrosion and corrosion in underground conditions. The main losses from corrosion are premature failure of internal oil pipelines, metal structures, the cost of manufacturing which in some cases significantly exceeds the cost of the metal used. Another equally important problem is the implementation of a set of measures to combat corrosion, the solution of which is also very costly. In today's conditions, insulation with polymer materials occupies a large place among various options of anticorrosive coatings for protecting oil pipelines and equipment from corrosion. However, the production of most polymer materials is based on imported raw materials. It should be noted that to date, the petrochemical industry in our country has developed rather poorly. Only in recent years, the Atyrau region has been producing up to 180 thousand tons of aromatic hydrocarbons (benzene, paraxylene), in addition, lines for the production of polyethylene and polypropylene based on its own raw materials (associated gases) have been launched. Moreover, the production of coatings for pipelines of smaller diameter, that is, internal ones, which are pipelines of the oil collection and treatment system, have distinctive features. It is not advisable to use polymer ready-made films, which are used when laying trunk oil pipelines. The production of most composite anticorrosive materials is based on polymer materials, solvents, binders, various fillers.

The above suggests that the problem of efficient processing of secondary resources to obtain competitive products is relevant for all industrially developed countries. The need to solve the problem in this dissertation work is due to modern requirements for solving the problem of finding affordable raw materials for producing efficient and cheap composite materials, developing a coating technology to protect oilfield equipment of the oil collection system from corrosion under atmospheric corrosion of both ground and pipelines operated in underground conditions.

In the dissertation work, the problems of obtaining new materials for anticorrosive protection of oilfield equipment and waste disposal are solved comprehensively through the use of by-products of fat-and-oil production - cotton soapstocks, which are formed both at large and at mini-plants for processing cotton oil. In addition, the composition of the coating also includes polyethylene terephthalate (plastic). To obtain anticorrosive coatings, in addition to soapstocks and polymer materials, various fillers are also used: polyethylene terephthalate, guzapaya, mineral fillers and a number of other components based on local raw materials to obtain new effective materials.

In recent decades, the task of developing new materials has been solved by modifying the basic grades of already existing large-tonnage polymers, since the modification of known polymers, the creation of polymer composite materials is one of the priority and economically justified directions for the development of technology for the production of modern equipment in the oil and gas industry. Composite materials, including those based on polymer compounds, have a number of significant advantages, they often manage to increase the modulus of elasticity, strength, thermal and chemical stability, resistance to burning, reduce the gas permeability of the material and other qualities. At the same time, modern economic conditions dictate the need for the production of materials that also have sufficient availability and cheapness. Achieving an optimal ratio between the cost and effective characteristics of a polymer composite material is achieved through the use of affordable and inexpensive fillers, as well as various industrial wastes, the use of which allows not only to reduce the cost of production, but also to eliminate their negative impact on the environment.

Thus, a set of measures to fulfill the tasks set in this dissertation work using economically available raw materials, as well as a set of experimental studies using modern physico-chemical methods for analyzing raw materials and target compositions contributed to the successful completion of the work and the achievement of the goal. The above is to say that the results obtained during the performance of the dissertation work are relevant for the oil and gas complex of Kazakhstan.

The purpose and objectives of the research. The purpose of this dissertation is to obtain anticorrosive coatings based on polymers, soapstock and technical gossypol and some fillers for oil pipelines of the oil collection system.

To achieve the goal, the following tasks were performed:

-to analyze the problems of corrosion protection of oilfield equipment of the oil collection system in conditions of atmospheric and underground corrosion;

-select objects, research methods and provide the material base of research;

-obtaining and studying the properties of mixed compositions based on polyolefins, gossypol, its derivatives and some fillers;

-preparation of antibacterial compositions using technical gossypol as a stabilizer;

- development of technology for obtaining an anticorrosive composition based on polyethylene terephthalate, soapstock and fillers;

- preparation of composite compositions to protect oil pipelines of the oil collection system from corrosion;

-to conduct pilot tests of new compositions of composite anticorrosive coatings for oil pipelines of the oil collection system and calculate their economic efficiency.

Objects of research. The main objects of research are anticorrosive compositions based on technical gossypol, polyolefins and fillers for pipelines of the oil collection system.

Subject of research. Conducting research on the production of anticorrosive composite materials to protect oil collection system pipelines from corrosion in commercial conditions. Study and justification of the influence of aggressive media on the resistance of coatings in the conditions of atmospheric and underground corrosion.

Methods of research. The experimental research base of this dissertation work includes physical, physico-chemical, chemical research methods, thanks to which the properties of the initial components were evaluated to obtain anticorrosive compositions, obtained anticorrosive compositions. In the experimental part of the work, the following methods were used: dispersion analysis, mechanical tests, rheological tests, tests of incised samples, optical microscopy, obtaining a mixture in an extruder, the use of infrared, NMR and UV spectroscopy. The combined use of these methods allowed us to obtain complementary information about the objects under study. Thus, the reliability of the results obtained is ensured by the use of modern methods of analysis, mathematical processing of the results, laboratory and field tests.

Scientific novelty of the study:

- the fundamental possibility of creating technologies for the production of anticorrosive coatings for the protection of oil pipelines of the oil collection system using technical gossypol, polyolefins and fillers has been proved and substantiated;

- the ability of technical gossypol, both in free form and as part of cotton soapstock, to exhibit the properties of an inhibitor of polyolefin oxidation, a polymer stabilizer is shown. The introduction of soapstock and gossypol into the composition of low-density polyethylene inhibits the oxidation of the polymer, the resulting anticorrosive compositions become more stable;

- it was found that the protective effect of an antibacterial composition based on technical gossypol and its derivatives significantly suppresses the vital activity of sulfate-reducing (SVB) bacteria at a concentration of 25-30%. The degree of suppression of SVB during corrosion of the oil pipeline is 50-60% with an exposure time of 10 hours and 65-80%, respectively, with an exposure time of 20 hours.

- on the basis of physico-chemical research methods, an assumption has been made about the course of chemical processes in the composition of an anticorrosive

composition. The structure of the obtained anticorrosive composite was established by IR, UV and NMR (PMR) methods. It is shown that during the preparation of the composite, the chemical interaction occurs due to hydrogen bonds at the place of the carbonyl groups of savylene and hydroxyl groups of gossypol molecules at the place of carbon atoms at the 7.7' position.

- It was found that savylene, carbon black, soapstock and guzapaya as part of the anticorrosive coating increase adhesion to the steel surface of the pipeline at concentrations of 30-35%.

Practical significance. The practical significance of the results obtained is due to the significant potential market for new products - protective coatings of pipelines. The development of technologies for obtaining modern multifunctional coatings using local raw materials and industrial waste for anticorrosive protection of oil pipelines, equipment for oil collection and treatment systems, taking into account operating conditions, is of great practical importance for the oil and gas industry of Kazakhstan.

Connection of the research with the plan of the scientific programs. The dissertation work was carried out the in South Kazakhstan University of M. Auezov and the Department of «Oil Refining and Petrochemistry» scientific research work SB-16-03-05 «Development of technology for obtaining combined coatings to protect refinery equipment and pipelines from corrosion» (2015-2020), and the agreement $N_{9}199$, program and target financing «Development of technologies for obtaining new effective materials for the oil and gas industry from waste oil and fat industry».

Basic findings for the defence:

1) Obtaining and studying the properties of mixed compositions based on polyolefins, gossypol, its derivatives and some fillers;

2) Preparation of antibacterial compositions using technical gossypol as a stabilizer;

3) Development of technology for obtaining an anticorrosive composition based on polyethylene terephthalate, soapstock and fillers;

4) Composite compositions to protect oil pipelines from corrosion;

5)Corrosion of the discharge pipe of the oil collection system in atmospheric and underground conditions, technological scheme for obtaining a composite coating;

6) The economic efficiency of the anticorrosive coating and the results of field tests of anticorrosive compositions.

Publications. The key points, results and conclusions of the thesis were presented in 13 publications, of which: in international peer-reviewed scientific journals, including 1 in a publication with a percentile of at least 25 according to the Scopus database; 3 articles in journals recommended by the Committee for Quality Assurance in Education and Science MES RK; 6 articles in materials of international conferences near and far abroad; 1 article in the journal "Bulletin of Science of South Kazakhstan"; 2 utility model patents.

The structure and volume of the thesis. The thesis is presented in 133 pages of computer text, includes 16 tables and 34 figures. This thesis consists of an introduction, 3 chapters, conclusion, list of references and appendices.