ABSTRACT

of dissertation of Artykova Zhadyra Kuanyshovna on the theme
"Development of technology for the production of composite polymer stabilizers for regulating the rheological properties of drilling fluids"
for the degree of Doctor of Philosophy (PhD) in the specialty
6D072100 – "Chemical technology of organic substances"

The relevance of the theme. In recent decades, polymer composite stabilizers have been widely used in the oil and gas industry, in particular in deep well drilling. Currently, the use of polymer stabilizers is increasing, and new types and modifications of polymers with high performance qualities are being developed. This should ensure the necessary requirements for drilling fluids used in drilling wells, as well as for opening productive formations. Polymer reagents are mainly used to increase the efficiency of drilling mud in a highly mineralized environment. For these purposes, polyelectrolytes are used, presented by foreign companies, which are purchased for foreign currency. In this regard, the task is to develop a technology for obtaining composite polymer stabilizers to regulate the rheological properties of drilling fluids resistant to high temperatures and highly mineralized environments. In this work, the possibilities of regulating the rheological properties of drilling fluids by introducing a sulfogroup into the macromolecular chain of a polymer in order to obtain composite polymer stabilizers are considered.

The purpose of the work is to study is to develop of technology for the production of composite polymer stabilizers for regulating the rheological properties of drilling fluids

The research objectives.

– preparation of a composite polymer stabilizer SANVSA-1 for drilling mud by copolymerization of acrylonitrile and vinylsulfonic acid and its modification;

– hydrolysis of polyacrylonitrile with different molecular weights in order to obtain composite polymer stabilizers SANVSA-2 and SANVSA-3 and their modification;

– investigation of the physico-chemical properties of synthesized composite polymers of the SANVSA series and their aqueous solutions;

– investigation of the effect of the obtained composite polymers of the SANVSA series on the rheological, filtration and technological properties of clay solutions of Darbaza bentonite clay;

– development of technology for the production of composite polymer stabilizers of drilling fluids resistant to saline media and high temperatures;

– conducting field tests of the obtained composite polymer stabilizers;

– mathematical optimization of the main parameters of the process of obtaining composite polymers and the economic efficiency of their use in the drilling of oil and gas wells.

Methods and objects of research. The objects of research are acrylonitrile, polyacrylonitrile, gossypol resin, sodium hydroxide, vinyl sulfonic acid, butyl methacrylate, potassium persulfate, sodium bisulfite, sodium thiosulfate, bentonite clay and the resulting composite polymer stabilizers: SANVSA-1, SANVSA-2,

SANVSA-3 and SANBMA. Research methods. The identification of the obtained polymer stabilizers was performed using the INCA Energy X-ray energy-dispersed microanalyzer (Oxford Instruments), IR spectroscopy on the Shimadzu IR Prestige-21 infrared Fourier spectrometer, the ISM-6490LV electron liquid microscope (IED), and the Polymer RPE-1M rotary viscometer.1. The properties of drilling fluids obtained on the basis of polymer reagents were studied by measuring viscosity, static shear stress, crust thickness, water yield and density.

The main provisions for the defense:

– copolymerization of acrylonitrile and vinylsulfonic acid in a monomer ratio of 80:20, in a pH=3-6 medium, for 2.0-2.5 hours, at a temperature of 20-35°C, followed by hydrolysis with sodium hydroxide at a temperature of 95-98°C, for 2.0-2.5 hours, followed by modification of fatty acids of gossypol resin, for 0.5-1.0 hours, at a temperature of – 60-70°C;

– hydrolysis of polyacrylonitrile with different molecular weights of 4-6% sodium hydroxide and 4% sulfuric acid at a temperature of 95-98°C for 2.0-2.5 hours with modification in pH=4-6 for 30-40 minutes with fatty acids of gossypol resin or formalin and sodium thiosulfate;

– results of rheological, filtration and technological properties for stabilization of 15% drilling fluid of Darbaza bentonite clay in the presence of SANVSA-2 and SANVSA-3 – 0.5% and SANVSA-1 – 0.25%;

– the optimal stabilization concentration of 15% suspensions of Darbaza bentonite clay SANVSA-2 and SANVSA-3 is 0.5% and SANVSA–1 is 0.25%, SANVSA-2 is resistant to a saline environment at temperatures of 180-200°C and concentrations of 20% NaCI, 2% $CaCI_2$;

– technology for producing composite polymer stabilizers of heat-resistant drilling fluids in a saline environment, the stabilizer includes 15% Darbaza bentonite clay and SANVSA series, productivity is 7475 tons/year;

– the results of field tests of composite polymer stabilizers obtained;

– the results of mathematical processing of experimental data and calculation of the economic efficiency of the technology for obtaining composite polymer stabilizers for drilling fluids.

The main research results:

– new composite polymer stabilizer SANVSA-1 was obtained by copolymerization of acrylonitrile and vinylsulfonic acid at a monomer ratio of 80:20, pH=3-6, for 2.0-2.5 hours, at a temperature of 20-35°C, followed by hydrolysis of the copolymer using sodium hydroxide at a temperature of 95-98°C, for 2.0-2.5 hours and further modification in the presence of fatty acids of gossypol resin for 0.5-1.0 hours, at a temperature of 60-70°C;

– based on electron microscopy data is shown that when the polymer is modified, the hydrophilization of the system occurs, thereby the microstructure of macromolecules changes from an insoluble crystalline state to an amorphous one, which can regulate the solubility of the polymer;

– shown the production of composite polymer stabilizers of the SANVSA-2 and SANVSA-3 series is achieved by hydrolysis of polyacrylonitrile with different molecular weights of 4-6% sodium hydroxide and 4% sulfuric acid at a temperature

of 95-98°C for 2.0-2.5 hours with modification in a pH=4-6 medium for 30-40 minutes with fatty acids of gossypol resin or formalin and sodium thiosulfate with the formation of hydrophilization of the solution system;

– the results of the physico-chemical properties of aqueous solutions of synthesized composite polymers and the justification of the position that they belong to amphoteric polyelectrolytes;

– establishment of the optimal concentration of stabilization of 15% suspensions of Darbaza bentonite clay (0.5%) and resistance to a saline environment at temperatures of 180-200°C and concentrations of 20% NaCI, 2% $CaCI_2$;

– obtained the patent for invention RK №35935 "Method for producing composite reagent for drilling fluids" and international patent for invention №IAR 06728 "Drilling reagent";

– a technology has been developed for the production of composite polymer stabilizers of heat-resistant drilling fluids in a saline environment;

– mathematical modeling of the main parameters of the process of obtaining composite polymers and an assessment of the economic efficiency of their use in the drilling of oil and gas wells.

Justification of the novelty and importance of the results obtained:

– shown the copolymerization reaction of acrylonitrile and vinylsulfonic acids using initiators of sodium bisulfite and potassium persulfate in the preparation of the composite polymer stabilizer SANVSA-1 proceeds at pH=3-6, temperature 20-35°C, monomer ratio 80:20, time 2.0-2.5 hours. Optimal modification conditions in the presence of fatty acids were determined, time – 0.5-1.0 hours, temperature– 60-70°C;

– found the hydrolysis of polyacrylonitrile with a different molecular weight of 4-6% sodium hydroxide and 4% sulfuric acid proceeds at a temperature of 95-98 ° C for 2.0-2.5 hours with modification in pH =4-6 for 30-40 minutes by fatty acids of phosphor resin or formalin and sodium thiosulfate. Stabilizers of the SANVSA-2 and SANVSA-3 series were obtained and effective conditions for their production were determined;

– based on the data of physico-chemical research, i.e. elemental analysis, electron microscopy and IR spectroscopy, it is shown that the synthesized composite polymers belong to amphoteric multifunctional polymers (amide, imide, carboxyl, sulfogroups, etc.);

- rheological, filtration and technological properties, the mechanism of interaction of reagents and the effectiveness of stabilization (concentration 0.25 and 0.5%) as part of the drilling mud;

– the resistance of the polymer drilling reagent to aggressive media has been proven, which is 180-200°C. At temperatures above 200°C, the polymer drilling reagent loses its original properties.

The theoretical and practical significance of the work. The theoretical significance lies in carrying out the processes of copolymerization of acrylonitrile with vinylsulfonic acid by step hydrolysis and modification of the resulting new multifunctional (amide, imide, carboxylate, sulfogroup, etc.) thermo-salt-resistant composite polymer stabilizer SANVSA-1 drilling fluids. Preparation of SANVSA-

2 and SANVSA-3 series stabilizers using the method of hydrolysis of polyacrylonitrile of various molecular weights and using sodium hydroxide with iseric acid, followed by modification in the presence of fatty acid or formalin of gossypol resin and sodium thiosulfate. The practical significance of the work lies in the development of a technology for obtaining thermally stable and stable composite polymer stabilizers in solutions with a high salt content. According to the results of the dissertation, patents for invention №35935 "Method for producing composite reagent for drilling fluids" and international patent for invention №IAR 06728 "Drilling reagent" were obtained. Field tests have been conducted at "Munaygazproekt" LLP for the use of composite polymer stabilizers for drilling fluids. The results of the study have been introduced into the educational process in the discipline "Chemistry and physics of polymers".

Compliance of the dissertation with the directions of scientific development or state programs. The dissertation work was performed at the Department of "Technology of inorganic and petrochemical industries" at the M.Auezov South Kazakhstan research University, the research laboratory "Petrochemistry and composite polymer materials" and within the framework of grant financing "Zhas Galim-2022" AR14972915 "Development of technology for obtaining thermosalt-resistant composite polymer stabilizers of drilling fluids for drilling deep wells".

The doctoral student's personal contribution to the preparation of each publication.

13 scientific works were published on the theme of the dissertation, including in international scientific publications included in the Scopus database – 1; 4 articles in publications recommended by the Committee for Quality Assurance in the Field of Science and Higher Education; international and republican conferences – 6 articles, also received 2 patents for the invention.

1. Aticle "Synthesis and preparation of polyacrylonitrile and vinyl sulfonic acid in the presence of gossypol resin for drilling fluids" in the Rasayan Journal of Chemistry – review and analysis of data, obtaining and processing of results.

2. Article "Obtaining and studying the filtration and technological properties of drilling fluids based on acrylonitrile, vinyl sulfate and fumaric acid" in the journal "Herald L.N. Gumilyov" – review and analysis of the literature data, obtaining and processing the results.

3. Article "Obtaining composite polymer materials to improve the rheological properties of drilling fluids" in the journal "Oil and Gas" – prepared a literary review, summarized and processed the data obtained.

4. Article "Study of rheological properties of bentonite clays stabilized with butylmethacrylate and acrylonitrile copolymers in the presence of gossypol resin" in the journal "Herald of KBTU" – review of literature sources was prepared and analyzed, the results were obtained and processed.

5. Article "Thermal stability of synthesized water-soluble polymers for drilling fluids" in the journal "Oil and Gas" – discusses and obtains experimental data.

The author's contribution to the preparation of each publication is given in the dissertation.

The structure and scope of the dissertation. The dissertation work consists of an introduction, four chapters, a conclusion, a list of references and appendices. The work is presented on 105 pages, including 10 pages of appendices, contains 16 tables, 38 figures. The list of sources used includes 185 titles.