ABSTRACT

of thesis for the degree of Doctor of Philosophy (PhD) in the specialty 6D072100 – "Chemical technology of organic substances"

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Development of polymer reagents for oil rheological properties regulation

The relevance of the problem. The annual increase in the consumption of hydrocarbon raw materials on a global scale naturally leads to an increase in the volume of its transportation. The issues of delivering raw materials to processing facilities are more acute than ever for transporters. An increase in the share of heavy oils in the transported mixtures leads to problems of pumping through main pipelines in the cold season.

This issue is particularly acute in Kazakhstan, where most of the transported oil has a significant proportion of paraffins in its composition, which leads to a high pour point and deterioration of rheological properties with a decrease in temperature.

There are several approaches to solving this problem. In Kazakhstan, the most common are 2: thermal control and chemical method. Thermal control means constant heating of pipeline sections when pumping oil to maintain a stable temperature of transportation. This method is very energy-intensive and requires capital expenditures in the form of heating stations along the oil route and, accordingly, maintenance of these installations. The chemical method of flow control includes the treatment of pumped oil with additives of special functional substances of various nature, so-called depressant additives, capable of improving the rheological properties of oil in low-temperature operation. Currently, industrially produced depressant additives based on ethylene vinyl acetate (EVA) copolymers are most widely used in Kazakhstan. However, these additives do not always show the required efficiency, which decreases with a decrease in their concentration in oil and may also depend on the origin and characteristics of the processed oil. This circumstance determines the relevance of research aimed at expanding the range of available depressor additives, as well as increasing their effectiveness by chemical modification.

The purpose of the thesis research is to develop new highly effective depressant additives based on ethylene-vinyl acetate copolymers, by their radiation-initiated grafting copolymerization with hydrophobic monomers of various nature.

Research objectives:

- systematic study of temperature influence on the rheological properties of oil from the Kumkol group of oilfields, as well as assessment of the effectiveness of the current commercial depressant additive "Randep-5102”.

- development and optimization of the radiation process grafting with hydrophobic monomers of various nature (butyl acrylate, butyl methacrylate, styrene) with ethylene-vinyl acetate copolymers;

- spin trap study of the mechanism and kinetics of radical grafting copolymerization involving ethylene-vinyl acetate copolymers and hydrophobic monomers of ethylene-vinyl acetate copolymers;

- study the effectiveness of the obtained grafted copolymers of ethylene-vinyl acetate copolymers as depressant additives and compare them with the commercial reagents used in a number of parameters;

Research methods: The paper presents the results of testing samples generally recognized in the industry. The properties of the developed depressant additives were investigated by a complex of physicochemical methods: radiation-initiated copolymerization method, gravimetry, differential scanning calorimetry (DSC), polarized light microscopy, rotational viscometry, rheology, cold finger method, electron paramagnetic spectroscopy (EPR), IR-Fourier spectroscopy, determination of pour point temperature.

Objects of research: copolymers of ethylene-vinyl acetate, monomers of butyl acrylate, butyl methacrylate, styrene, a number of oils of the Kumkol region.

Subject of research: radiation grafting copolymerization with ethylene-vinyl acetate copolymers and monomers of various nature (butyl acrylate, butyl methacrylate, styrene), oil rheology, the effect of using new grafted ethylene vinyl acetate copolymers as depressant additives.

The main provisions submitted for protection:

- for a number of oil of the Kumkol region, the use of depressant additives to maintain and regulate rheological properties is more promising compared to the heat treatment method;

- the main contribution to the initiation of grafting copolymerization of hydrophobic monomers with ethylene-vinyl acetate copolymers is made by active centers formed when the hydrogen atom is separated from the copolymer macrochain, while the process of separation of the H atom from the CH groups of vinyl acetate EVA links is realized with the greatest speed;

- grafted EVA copolymers show higher efficiency when used as depressant additives for oil treatment compared to commercially produced analogues;

The main results of the study:

1. The influence of temperature on the rheological properties of oil from the Kumkol group of oilfields has been systematically investigated. The patterns of preheating are determined. It is established that with an increase in heating above the point of formation of paraffin crystals, the rheological properties of oils improve. However, carrying out this process in open containers can lead to losses of light fractions of oil, which in the future will require a higher heating temperature to improve rheological properties. It is shown that for this type of oil, use of the chemical treatment with depressant additives, accompanied by modification of primary paraffin crystals in the volume of oil, is more effective.

2. A number of depressant additives have been developed by radiation grafting of various nature hydrophobic industrially available monomers (butyl acrylate, butyl methacrylate, styrene) on ethylene vinyl-acetate copolymers. During the synthesis of grafted copolymers, a number of experiments were carried out to select the optimal radiation dose. At the same time, 5 variations of the absorbed radiation dose were tested (from 110 to 160 kGy in increments of 10 kGy). It was found that the most optimal radiation dose is equal to 130 kGy.

3. By the EPR method using 2-methyl-2-nitrosopropane as a spin trap, the kinetics and mechanism of grafting copolymerization of monomers to ethylene vinyl acetate copolymers were investigated. It is shown that at the primary stages of the process, active radical centers initiating grafting copolymerization are mainly formed as a result of the

separation of an atom from the macro chains of ethylene-vinyl acetate copolymers from primary, secondary and tertiary carbon atoms (– CH, - CH2 and – CH3). It is established that the process of separation of the H-atom from the tertiary carbon atom is carried out at a higher speed.

4. It has been established that the new depressant additives provide an improvement in the rheological properties of oil at lower dosage rates compared to the commercial analogue – "Randep-5102". A number of dosages comparable in the amount of specific active substance with a commercial analogue were studied. With all comparable dosages of the 3 best reagents obtained in this work, the candidates showed results superior to the commercial analogue. With an increase in dosage rate of new depressant additives, a more pronounced effect of the rheological properties improvement of the treated oil was observed.

5. Using the cold finger method, it was found that the obtained depressant additives have a more pronounced inhibitory effect against paraffins compared to commercial analogues. All tested samples showed a higher level of paraffin inhibition in the finger test, which simulates the movement of oil through a cold pipeline. The inhibition level was consistently above 70% for all tested samples, with the best result being 88%. These indicators can be considered very good by the standards of the industry.

6. It is shown that when oil is treated with newly grafted EVA copolymers, a more stable effect of the rheological parameters improvement of oil over time is achieved compared with the use of commercial additives. In particular, the gEVASt24C sample showed a higher stability of the properties of the processed oil superior to the commercial analogue. This indicates the prospects of using a depressor additive based on gEVASt24C for oil treatment in order to safely operate the pipeline in the cold season.

Substantiation of the novelty and importance of the results obtained.

- For the first time, by the method of radiation-initiated grafted copolymerization, new depressant additives based on ethylene-vinyl acetate copolymers containing grafted macro chains representing a sequence of hydrophobic monomer units of various nature were obtained;

- For the first time, the kinetics and mechanism of grafting copolymerization with the participation of monomers on ethylene vinyl acetate copolymers and hydrophobic monomers have been investigated by the spin trap method using model reactions. It is shown that the formation of active radical centers initiating inoculation copolymerization is carried out as a result of the separation of an atom from the macro chains of ethylene-vinyl acetate copolymers, and in this process the tertiary CH groups of vinyl acetate monomer units of the macro chains of copolymers are most active.

- For the newly grafted EVA copolymers obtained, a high efficiency of their use as depressant additives has been established, namely, when processing oil with it, a stable effect of improving the rheological properties of oil (reducing viscosity) is achieved over time, as well as a well-expressed ability to inhibit the process of paraffinization of oil. It is shown that the new additives obtained have higher efficiency at comparable specific dosages compared to commercial analogues.

Theoretical significance of the results.

The results of the spin trap study of kinetics and the mechanism of grafted copolymerization with the participation of ethylene-vinyl acetate copolymers are a significant contribution to the development of theoretical concepts in radical polymerization processes, data in the study of new depressor additives on the physico-chemical properties of oil can be considered as a scientific contribution to the rheology of

oils, as well as to the development of ideas about the mechanism of influence of polymer reagents on the structure and properties of oils.

Practical significance of the results.

According to leading experts, the least energy-intensive and efficient transportation of energy resources and raw materials is one of the fundamental principles of rational production. The use of chemical methods of oil treatment during its low-temperature transportation is the most optimal in the conditions of Kazakhstan. Obtaining highly effective depressant additives at lower dosages to provide more efficient transportation is always in demand. Obtaining them in a rational, waste-free way increases the value of these products, both from the point of view of sustainable production development and economic benefits.

The newly grafted copolymers obtained in the work can be recommended to use as highly effective depressant additives for oil treatment in order to safely operate the pipeline in the cold season.

The results obtained in this work can be considered as a scientific and applied basis for obtaining a number of highly effective depressor additives in a waste-free way.

Approbation of the work. The main results of the thesis were reported and discussed at Problems of theoretical and experimental chemistry conference (Ekaterinburg 2021), international conference "Modern problems of organic substances and materials"(Almaty 2019), International Scientific Conference of Students and Young Scientists «FARABI ALEMI»(2021).

The personal contribution of the author consists in the direct execution of the experimental part of the work, participation in the analysis, generalization and interpretation of the experimental data obtained.

Publications. As a result of research on the topic of the thesis, 10 scientific papers were co-authored, including 2 articles in republican specialized publications recommended by the Committee for Control in the Field of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, 1 article in an international scientific journal included in the Scopus database (Journal of Petroleum Science and Engineering), 4 patent 3 of which are utility models and 1 patent for invention, as well as materials and abstracts of 3 presentations at international scientific conferences, symposiums and seminars.

The structure and scope of the thesis. The dissertation work consists of an introduction, 3 main sections, a list of references, 92 titles. The work is presented on 91 pages, contains 43 figures and 27 tables.

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

The doctoral student was directly involved in the preparation of depressant additives, obtaining experimental data, processing and interpretation of experimental results, and also participated in the implementation of physico-chemical studies for the design of the article Modified graft copolymers based on ethylene vinyl acetate as depressants for waxy crude oil and their effect on the rheological properties of oil, (Journal of Petroleum Science and Engineering, Volume 213, 2022, 110298, ISSN 0920-4105,https://doi.org/10.1016/j.petrol.2022.110298).

The doctoral student was directly involved in the preparation of depressant additives, obtaining experimental data, processing and interpretation of experimental results, and also participated in the implementation of physico-chemical studies for the design of the article New domestic developments in the field of depressant additives.

"Randep-5105" is the next generation of effective reagents for oil pipelines in Kazakhstan, (NEWS OF THE SCIENTIFIC AND TECHNICAL SOCIETY "KAHAK", 2020, №2(69)).

The doctoral student was directly involved in the preparation of depressant additives, obtaining experimental data, processing and interpretation of experimental results, and also participated in the implementation of physico-chemical studies for the design of the article new domestic developments in the field of depressor additives. development of radiation technology for modification of petroleum additives based on ethylene-vinyl acetate, (PROCEEDINGS OF THE SCIENTIFIC AND TECHNICAL SOCIETY "KAHAK", 2020, №2(69)).

The doctoral student was directly involved for the registration of a patent for utility model No. 6126 (Published in Bul. No. 49 of 10.12.21) depressant additive for paraffinic oils.

The doctoral student was directly involved for the registration of a patent for utility model No. 6125 (Published in Bul. No. 49 of 10.12.21) depressant additive for paraffinic oils.

The doctoral student was directly involved for the registration of a patent for utility model No. 6124 (Published in Bul. No. 49 of 10.12.21) depressant additive for paraffinic oils.

The doctoral student was directly involved for the registration of patent No. 35204 (Published in Bul. No. 28 of 16.07.21) Complex action depressant additive for the transport of oil mixtures.

In addition, the doctoral student was directly involved in obtaining and discussing experimental data published in 3 abstracts of international conferences.