

REVIEW

of the official reviewer for dissertation work of

Bekbassov Timur «Developing polymer additives for regulating oil rheological properties», submitted for the degree of Doctor of Philosophy (PhD) in the specialty 6D072100 "Chemical technology of organic substances"

№	Criteria	Eligibility (one of the options must be checked)	Justification of the position of the official reviewer
1.	The topic of the thesis (as of the date of its approval) corresponds to the directions of development of science and/or state programs	<p>1.1 Compliance with priority areas of science development or government programs:</p> <p>1) <u>The thesis was completed within the framework of a project or target program financed from the state budget (indicate the name and number of the project or program)</u></p> <p>2) The thesis was completed within the framework of another state program (indicate the name of the program)</p> <p>3) <u>The dissertation corresponds to the priority direction of the development of science, approved by the Higher Scientific and Technical Commission under the Government of the Republic of Kazakhstan (indicate the direction)</u></p>	<p>The presented work is carried out in an actual field of research and is devoted to the development of new highly effective depressor additives based on ethylene vinyl acetate (EVA) copolymers, by means of their radiation inoculation with hydrophobic monomers of various nature.</p> <p>The work was carried out in the priority direction "Rational use of natural resources, including water resources, geology, processing, new materials and technologies, safe products and structures" within the framework of the Scientific and Technical Target Program of the Ministry of Education and Science of the Republic of Kazakhstan (BR05236419 "Creation of functionalized organic substances and materials with a wide range of possible highly effective practical applications" (deadlines 2018-2020) and the grant project AP08856723 "Development and implementation of a new approach to determining the rheological parameters of liquid-phase multicomponent systems using a new type of rheoviscosimeter" (completion dates 2020-2022)</p>
2.	Importance for science	<u>The work makes/does not make a significant contribution to science, and its importance is well disclosed/not disclosed</u>	The results obtained by the applicant during the dissertation are aimed at solving the actual applied and scientific task of developing new effective depressor additives for the transportation of Kazakh oil.
3.	The principle of independence	<p>Self-reliance level:</p> <p>1) <u>High;</u></p> <p>2) Medium;</p> <p>3) Low;</p> <p>4) No independence</p>	The dissertation work has a complex research nature. I consider the level of independence of this work to be high.

4.	The principle of inner unity	4.1 Justification of the relevance of the thesis: 1) <u>Justified;</u> 2) Partially justified; 3) Not justified.	In the conditions of the vast distances of our country and large temperature differences in the autumn-winter period, the transportation of paraffin oil requires significant energy consumption for the heating of pipelines to maintain the stability of the flow. The use of depressant additives is an effective way to reduce the cost of heating the pipeline and leads to optimization of the transportation process. Research aimed at expanding the range of available depressant additives, as well as increasing their effectiveness through chemical modification and becoming particularly relevant. The presented work is carried out in this relevant field of research and is devoted to the development of new highly effective depressant additives based on ethylene vinyl acetate (EVA) copolymers, by means of their radiation inoculation with hydrophobic monomers of various nature.
		4.2 The content of the thesis reflects the topic of the thesis: 1) <u>Reflects;</u> 2) Partially reflects; 3) Does not reflect	The content of the dissertation fully reflects the purpose, objectives, and topic of the study.
		4.3. The purpose and objectives correspond to the topic of the thesis: 1) <u>correspond;</u> 2) partially correspond; 3) do not correspond	The literary review conducted by the author, as well as the results of the dissertation, indicate that the set goals and objectives fully correspond to the topic of the dissertation.
		4.4 All sections and provisions of the thesis are logically interconnected: 1) <u>completely interconnected;</u> 2) the interconnection is partial; 3) there is no interconnection	The results obtained in the dissertation work are characterized by internal unity due to a clearly stated goal, the choice of research objects, specifically formulated research objectives aimed at realizing the goal of developing EVA copolymers based on grafted hydrophobic monomers, through electron beam grafting, as well as a method for studying the reaction mechanism using a spin trap.

		<p>4.5 The new solutions (principles, methods) proposed by the author are reasoned and evaluated in comparison with the known solutions:</p> <p>1) there is a critical analysis; 2) partial analysis; 3) the analysis does not represent one's own opinions, but quotes from other authors</p>	
5.	Scientific novelty principle	<p>5.1 Are the scientific results and provisions new?</p> <p>1) completely new; <u>2) partially new (25-75% are new);</u> 3) not new (less than 25% are new)</p>	<p>For the first time, 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 by radiation-initiated grafted copolymerization.</p> <p>For the first time, the kinetics and mechanism of grafted copolymerization were investigated by the spin trap method using model reactions. It is shown that the formation of active radical centers initiating grafted 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 copolymer macro chains are most active.</p>
		<p>5.2 Are the dissertation findings new?</p> <p>1) completely new; <u>2) partially new (25-75% are new);</u> 3) not new (less than 25% are new)</p>	<p>The conclusions are completely new, made on the basis of experimental results obtained for the first time, scientifically justified and do not cause doubts about the reliability due to the fact that all of them were obtained for the first time and is also confirmed by the presence of 4 patents and relevant publications, including in a highly rated specialized international journal (Journal of Petroleum Science and Engineering) with a high impact factor.</p>
		<p>5.3 Technical, technological, economic or management decisions are new and reasonable:</p> <p>1) completely new; <u>2) partially new (25-75% are new);</u> 3) not new (less than 25% are new)</p>	<p>The solutions proposed in the framework of this dissertation work can form the basis for obtaining a number of highly effective depressant additives in a waste-free way.</p>

6.	The validity of the main findings	<u>All main conclusions are</u> /are not <u>based on scientifically significant evidence</u> or well-grounded (for qualitative research and areas of training in the arts and humanities)	All the main conclusions are based on experimental results obtained using a complex of modern physico-chemical research methods, as well as confirmed by relevant publications and the presence of 4 patents.
7.	The main provisions for the defense	<p>It is necessary to answer the following questions for each provision separately:</p> <p>Provision 1.</p> <p><u>For a number of oils in the Kumkol region, the use of depressant additives to maintain and regulate rheological properties is more promising compared to the method of heat treatment.</u></p> <p>7.1 Is the provision proven? 1) proven; 2) rather proven; 3) rather not proven; 4) not proven</p> <p>7.2 Is it trivial? 1) yes; 2) no</p> <p>7.3 Is it new? 1) yes; 2) no</p> <p>7.4 Application level: 1) narrow; 2) medium; 3) wide</p> <p>7.5 Is it proven in the article? 1) yes; 2) no</p>	<p>All the provisions put forward for defense have been proven experimentally, are practically significant, and therefore non-trivial.</p> <p>All the tasks set to solve the purpose of this dissertation work have been fully solved.</p> <p>Provision 1. The developed and synthesized new depressant additives obtained by electron beam inoculation of hydrophobic monomers of various nature (butyl acrylate, butyl methacrylate, styrene) on the EVA copolymer have a significantly higher effect on the depression of the oil flow loss temperature compared to simply heat-treated oil at a temperature of 50-60 ° C.</p> <p>Provision 2. For the first time, the mechanism of inoculation of EVA copolymers was studied by the spin trap method using model reactions of the interaction of a tert-butoxyl radical with EVA macromolecules. At the same time, the author was able to quantify the contribution of the reactions of the separation of hydrogen atoms by this radical from the macro chains of ethylene-vinyl acetate copolymers with the participation of primary, secondary and tertiary EVA carbon atoms. It is shown that tertiary CH groups of macromolecules have the greatest activity in the processes of H-atom separation, which is in good agreement with the</p>

		<p>Provision 2.</p> <p><u>The main contribution to the initiation of inoculation 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 units is realized with the greatest speed.</u></p> <p>7.1 Is the provision proven? 1) proven; 2) rather proven; 3) rather not proven; 4) not proven</p> <p>7.2 Is it trivial? 1) yes; 2) no</p> <p>7.3 Is it new? 1) yes; 2) no</p> <p>7.4 Application level: 1) narrow; 2) medium; 3) wide</p> <p>7.5 Is it proven in the article? 1) yes; 2) no</p> <p>Provision 3.</p> <p><u>Grafted EVA copolymers show higher efficiency when used as depressant additives for oil treatment compared to commercially produced analogues.</u></p>	<p>previously established fundamental laws of radical processes in organic chemistry.</p> <p>Provision 3. The modified EVA samples obtained in the work were tested as depressant additives in comparison with the commercially produced EVA analog for oils in which this analog has been used for 8 years. Tests have shown high efficiency of EVA samples modified by grafting with hydrophobic monomers, at a lower specific dosage (in terms of dry residue) in comparison with the analog.</p>
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8.	The principle of reliability Reliability of sources and information provided	<p>8.1 Choice of methodology - is justified or the methodology is described in sufficient detail</p> <p>1) yes; 2) no</p> <p>8.2 The results of the thesis were obtained using modern methods of scientific research and methods of processing and interpreting data using computer technologies:</p> <p>1) yes; 2) no</p> <p>8.3 Theoretical conclusions, models, identified relationships and patterns have been proven and confirmed by experimental</p>	<p>Author in the work provides in sufficient detail the choice of radiation grafted copolymerization, as well as the methods of conducting experiments.</p> <p>All the methods of analysis used in this work are considered to be fully sufficient for conducting such a study.</p> <p>Theoretical conclusions, models, relationships, and patterns are confirmed by experimental studies of the production of grafted EVA-based copolymers with depressive activity for the oils of the Kumkol region.</p>

		<p>research (for areas of training in pedagogical sciences, the results have been proven on the basis of a pedagogical experiment):</p> <p>1) yes; 2) no</p>	
		8.4 Important statements are confirmed / partially confirmed / not confirmed by references to current and reliable scientific literature	Important statements are confirmed by references to relevant and reliable scientific literature.
		8.5 Used literature sources are sufficient /not sufficient for a literature review	The author in his work provides 92 references to relevant and reliable scientific works of domestic and foreign researchers.
9	Practical value principle	9.1 The thesis has theoretical value: 1) yes; 2) no	The dissertation work undoubtedly has important theoretical significance. The proposed methods for obtaining grafted EVA-based copolymers can be considered new. In addition, for the first time, the mechanism of EVA copolymer grafting was studied by the spin trap method using model reactions of the interaction of a tert-butoxyl radical with EVA macromolecules
		9.2 The thesis is of practical importance and there is a high probability of applying the results obtained in practice: 1) yes; 2) no	The practical significance of the work is to expand the arsenal of methods for producing polymers capable of interacting with paraffin crystals and acting as depressant additives to reduce the temperature of oil pour point.
		9.3 Are the practice suggestions new? 1) completely new; 2) partially new (25-75% are new); 3) not new (less than 25% are new)	All proposals are absolutely new, which is confirmed by published scientific articles and patents.
10.	The quality of writing and design	Academic writing quality: 1) high; 2) average; 3) below average; 4) low.	The dissertation work is written in scientific language and professional style. The formulations of the main provisions and conclusions are of a complete research nature. I believe that the dissertation work of Timur Muratovich Bekbassov fully complies with the requirements of the Committee for Quality Assurance in Education of the Ministry of Education of the Republic of Kazakhstan, which are applied to dissertations for the degree of Doctor of Philosophy (PhD) in the specialty "6D072100 - Chemical

			technology of organic substances", and its author undoubtedly deserves the award of the desired degree, for solving the relevant applied and scientific tasks for the development of new effective depressant additives for the transportation of Kazakhstani oil
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Comments:

1. The applicant developed depressant additives and tested on samples of commercial oil from the fields of the Kumkol region. It would be good to see data from field tests of these additives.
2. The proposed scheme of industrial production does not indicate the possibility of using electron beam inoculation for the synthesis of depressant additives.
3. In this work, the mechanism and kinetics of grafted copolymerization involving EVA and hydrophobic monomers are investigated by the spin trap method on model reactions of separation of the H atom by a tert-butoxyl radical from EVA macrochains. According to the reviewer, a more visual picture of the mechanism of radiation-initiated inoculation copolymerization could be obtained by directly using the radiolysis of EVA solution in the presence of a spin trap with varying radiation dose.

However, the comments made in general do not affect the very positive impression of the presented dissertation work, which is performed at a high scientific level.

In reviews, official reviewers indicate one of the following solutions:

- 1) **to award the degree of Doctor of Philosophy (PhD) or Doctor of Specialization.**
- 2) send the thesis for revision (except for cases of thesis defense in the form of a series of articles);
- 3) refuse to award the degree of Doctor of Philosophy (PhD) or Doctor of Specialization.

Copies of the reviews of the official reviewers are handed over to the doctoral student no later than 5 (five) working days before the defense of the thesis.

Official Reviewer:

PhD, Oilchemistry, researcher

“Institute of polymer materials and technology”

(place of work, academic title)


(signature)



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