

REVIEW OF THE OFFICIAL REVIEWER

on the dissertation work by Timur Bekbassov entitled “Developing Polymer Additives for Regulating Oil Rheological Properties” submitted for degree of Philosophy Doctor by specialty 6D072100 – Chemical Technology of Organic Substances”

N	Criteria	Criteria eligibility (it is necessary to mark one of the answer options)	Justification of the position of the official reviewer
1	The topic of the thesis (as of the date of its approval) corresponds to the development of science and/or government programs	1.1 Compliance with priority areas of science development or government programs: 3) <u>The dissertation corresponds to the priority area of the development of science, approved by the Higher Scientific and Technical Commission under the Government of the Republic of Kazakhstan (New materials based on raw substances)</u>	A problem to adjust rheological performances of highly paraffinized Kazakhstani oil for further transportation. The defended investigation leads to the development of new chemical additives reducing drastically rheological parameters of some oil in ppm amount that gives a chance for highly effective transportation of the paraffinized oil. The work was carried out in the priority direction "Rational use of natural, 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 years.), as well as the grant project AP08856723_ "Development and implementation of a new approach for determining the rheological parameters of liquid-phase multicomponent systems using a new type of rheoviscosimeter" (deadlines 2020-2022).
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 candidate performed newly synthesized grafted copolymers. Based on old copolymer Ethyl-Vinyl Acetate (EVA) new grafted construction with Butyl Methacrylate (BMA), Butyl

			Acrylate (BA), and Styrene moieties were synthesized respectively with gamma-radiation initiated radical synthesis. The synthesized chemical structure of new grafted copolymers were confirmed with EPR and FTIR independently.
3	The principle of independence	Self-reliance level: 1) High ; 2) Medium; 3) Low; 4) No independence	the following works: <ul style="list-style-type: none"> - Synthesis of grafted polymers of various type of grafts and content - Copolymer characterizations - Inhibition properties detections and the effect of the copolymers on oil inhibition with cold finger test - Pour points measurements with oil rheology and kinematic viscosity determination - DSC and microscopic analysis with data interpretation were provided by the candidate personally and were published him in several articles
4	The principle of internal unity	4.1 Justification of the relevance of the thesis: 1) Justified ; 2) Partially justified; 3) Not justified.	Kazakhstan producing highly paraffinized oil faces problems with technical possibilities for pipe transportation. Moreover, the current political troubles of the current war brought obstacles to transport oil via KTK. Adjusting rheological performances of transporting oil is seriously actual problem in the country. Furthermore, the thesis of research work is relevant to problems
		4.2 The content of the thesis reflects the topic of the thesis: 1) Reflects; 2) Partially reflects ; 3) Does not reflect	The topic of the thesis covers and reflects the content of the defended thesis. Namely, Developing Polymer Additives for Regulating Oil Rheological Properties reflects mechanism of viscosity inhibition of oil with addition of the synthesized grafted copolymer additives based on EVA. Meanwhile, name of the topic is too broad covering any polymer substrates without their classification to oil rheology adjusting.

		<p>4.3. The purpose and objectives correspond to the topic of the thesis:</p> <ol style="list-style-type: none"> 1) <u>correspond;</u> 2) partially comply; 3) do not match. 	<p>The purpose and objectives of the defended research corresponds to the broad topic of the thesis. Namely, the development of new highly effective depressant additives based on grafted EVA copolymers of various graft type and content are fully corresponded to topic and research work done by the candidate.</p>
		<p>4.4 All sections and provisions of the thesis are logically interconnected:</p> <ol style="list-style-type: none"> 1) <u>fully interconnected;</u> 2) the connection is partial; 3) there is no connection 	<p>The experimental work, their results and provisions formulated upon discussion of the results show up logical interconnection all part of the defended research. The validity of the set goal follows from the current state of affairs shown in the introduction section. Reaching results and their interpretation with formulation of scientifically proven provisions the candidate shows logical approach to finalize what he done in the conclusion part.</p>
		<p>4.5 The new solutions (principles, methods) proposed by the author are reasoned and evaluated in comparison with the known solutions:</p> <ol style="list-style-type: none"> 1) <u>there is a critical analysis;</u> 2) partial analysis; 3) the analysis does not represent one's own opinions, but quotes from other authors 	<p>The candidate suggests classical approach to the synthesis of new copolymers via γ-initiated radical polymerization, chemical structure approval and characterization. New technological approach based on less quantitative addition of the highly effective depressant with less energy and time spending for emulcification into oil flow. New practical results are proven also with issued patents of the candidate</p>
5	Scientific novelty principle	<p>5.1 Are the scientific results and provisions new?</p> <ol style="list-style-type: none"> 1) <u>completely new;</u> 2) partially new (25-75 % are new); 3) not new (less than 25 % are new) 	<p>The scientific results and provisions are completely new due mainly to characterization and behavior analysis of newly synthesized substrates – various grafted EVA copolymers. It is proven as well by peer-reviewed publication of the candidate 110298. 10.1016/j.petrol.2022.110298</p> <p>Mun G., Dergunov S.,Beksultanov Zh, Yermukhambetova B, Azhgaliyev B, Azhgaliyev N. Modified graft copolymers based on ethylene vinyl acetate as depressants for waxy crude</p>

			oil and their effect on the rheological properties of oil/ Journal of Petroleum Science and Engineering, Volume 213, 2022
		5.2 Are the dissertation conclusions new? 1) completely new ; 2) partially new (25-75 % are new); 3) not new (less than 25 % are new)	The conclusions finalized in the thesis are completely new in the synthesis of grafted EVA copolymers and behavior modulation of the with Kumkol oil mixture. The synthesized copolymers and this part of oil mixture show together effective results in untypically smaller concentration of the depressant to give new data and information about depressed oil behavior.
		5.3 Technical, technological, economic or management solutions are new and reasonable: 1) completely <u>new</u> ; 2) partially new (25-75 % are new) ; 3) not new (less than 25 % are new)	In opinion it would be honest to assess only effects of technological solutions which is new, reasonable and industry-orientated. Those could be proven as well with 3 patents issued by the candidate on new substances and its viscosity depressive effects on Kumkol oil mixture. It is difficult to assess correctly economical and managerial effectiveness of the investigation.
6	Validity of key findings	<u>All the main conclusions are/are not based on scientifically significant evidence or reasonably well substantiated</u>	All the main <u>conclusions are based on scientifically significant evidence (2 independent methods at least)</u> or reasonably well substantiated and classified via publications, conference presentation and patent issues. Депрессорная присадка для парафинистых нефтей Патент на полезную модель, № 6124, 2021/0127.2 10.02.2021 Депрессорная присадка для парафинистых нефтей Патент на полезную модель, № 6125, 2021/0128.2 11.02.2021 Депрессорная присадка для парафинистых нефтей Патент на полезную модель, № 6126, 2021/0129.2 11.02.2021 Депрессорная присадка комплексного действия для транспорта нефтесмесей Патент на изобретение РК, № 33622, 2020/0402.1 11.06.2020

7	The main provisions for the defence	<p>It is necessary to answer the following questions for each provision separately: <u>Provision 1</u> - or 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.</p> <p>7.1 Is the provision proven? 1) <u>proven</u>; 2) rather proven; 3) rather unproven; 4) unproven.</p> <p>7.2 Is it trivial? 1) yes; 2) <u>no</u>.</p> <p>7.3 Is it new? 1) <u>yes</u>; 2) no.</p> <p>7.4 Application level: 1) narrow; 2) <u>average</u>; 3) wide.</p> <p>7.5 Is it proven in the article? 1) <u>yes</u>; 2) no.</p>	<p>For the first time, by the method of conventionally initiated radical grafted copolymerization, copolymers with grafted hydrophobic macrochains to EVA copolymers were obtained, very promising as depressant additives capable to noticeably improve the rheological properties of the treated oil.</p>
		<p><u>Provision 2</u> - 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.</p> <p>7.1 Is the provision proven?</p>	<p>The spin trap method was used for the first time to study the features of inoculation copolymerization with EVA, which allows obtaining direct quantitative information about the mechanism and kinetics of radical processes. In this case, the reactions of a tert-butoxyl radical with EVA macromolecules were used as model reactions. The method of determination was used to show that active radical centers initiating grafting copolymerization are formed mainly as a result of the separation of the hydrogen atom of the ethylene-vinyl acetate copolymer macro chains, and in this process the tertiary CH groups of vinyl acetate monomer units of the</p>

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		<p><u>Provision 3</u> - grafted EVA copolymers show higher efficiency when used as depressant additives for oil treatment compared to commercially produced analogues.</p> <p>7.1 Is the provision proven? 1) <u>proven</u>; 2) rather proven; 3) rather unproven; 4) unproven. 7.2 Is it trivial? 1) yes; 2) <u>no</u>. 7.3 Is it new? 1) <u>yes</u>; 2) no. 7.4 Application level: 1) narrow; 2) <u>average</u>; 3) wide. 7.5 Is it proven in the article? 1) <u>yes</u>; 2) no.</p>	<p>All the grafted copolymers obtained were studied as depressant additives and showed higher efficiency in comparison with Randep-5102, a commercial product that has been used for oil transportation for more than 6 years. It should be noted that the resulting compounds can be used immediately after synthesis without purification as part of the reaction mixture. This feature makes the whole process of EVA modification waste-free, and therefore environmentally friendly and rational.</p>
8	The principle of reliability	<p>8.1 Choice of methodology - is justified or the methodology is described in sufficient detail 1) <u>yes</u>;</p>	<p>Plausible and fully described synthesis, at least 2 independent methods for substances characterization make</p>

	Reliability of sources and information provided	2) no.	chosen methodology justified and sufficient
		8.2 The results of the dissertation work were obtained using modern methods of scientific research and methods of processing and interpreting data using computer technologies: 1) <u>yes</u> ; 2) no.	Most methods used in the thesis are digitalized such as FTIR, EPR, SEM etc
		8.3 Theoretical conclusions, models, identified relationships and patterns have been proven and confirmed by experimental research: 1) <u>yes</u> ; 2) no.	All theoretical conclusions, identified relations and patterns, any interpretation have been made or speculated on the basis of proven and confirmed experimental data
		8.4 <u>Important statements are confirmed</u> / partially confirmed / not confirmed <u>by references to the current and reliable scientific literature</u>	All statements in the thesis are consistent with results and analysis of current research in the field of synthetic polymers and graft radical polymerization. All statements of the obtained results are made up on comparative analysis with literature published in reputable scientific journals.
		8.5 <u>Used literature sources are sufficient</u> / not sufficient <u>for a literature review</u>	All reliable references to the scientific literature are sufficiently enough for completed reviewing. Most of 94 articles are from the last 5 years published in peer-reviewed journals
9	Practical value principle	9.1 The thesis has theoretical value: 1) <u>yes</u> ; 2) no.	The most important theoretical value based on study of spin trap kinetics as well as the mechanism of radical grafted polymerization
		9.2 The thesis is of practical importance and there is a high probability of applying the results obtained in practice: 1) <u>yes</u> ; 2) no.	The scientific results obtained in the work are aimed at solving the urgent scientific task of creating and researching new grafted EVA copolymers with butylacrylate, butylmacrylate and styrene based on industrially available compounds as effective depressant additives.
		9.3 Are the practice suggestions new? 1) <u>completely new</u> ;	The newly grafted copolymers obtained in the work can be recommended to use as highly

		2) partly new (25-75% are new); 3) not new (less than 25% are new).	effective depressant additives for oil treatment in order to safely operate the pipeline in the cold season.
10	The quality of writing and design	Academic writing quality: 1) high; 2) average ; 3) below average; 4) low.	The thesis could be assessed as average quality due mainly to some minor inaccuracies and grammar mistakes, however it keeps the work scientifically valuable

Shortcomings in the content and design of the dissertation.

1. In section 2.7, in the conditions for rheological measurements, the author provides test conditions with a rotation speed of 30 sec⁻¹ and a temperature range of 60°C and below. The temperature range of its choice is clear, while the rotation speed is not justified.

2. The author obtained utility model patents for synthesized compounds. However, it is worth mentioning that this type of intellectual property is not sufficiently protected, and the reviewer believes that such developments should be protected at least by a patent for an invention.

3. In the work, the process of interaction of a tert-butoxyl radical with EVA macromolecules, which was obtained by thermolysis of the corresponding material initiator, was used as model reactions to study the mechanism of grafted copolymerization with EVA by the spin trap method. At the same time, in the presented work, grafted copolymerization was carried out by radiation irradiation of a reaction mixture containing EVA and the grafted monomer. In this connection, the question arises, how adequately does the mechanism of the studied conventionally initiated process of grafted copolymerization with the participation of EVA reflect the data obtained in the process of a materially initiated model radical reaction?

However, it can be stated that the above comments on the dissertation work of T.M. Bekbasov, in general, does not affect its main provisions, conclusions and scientific results, which solve an important scientific and practical problem.

Decision: I support the award of the PhD degree by specialty «6D072100 - Chemical technology of organic substances» defended by Timur Bekbasov.

The official reviewer:

Rinat M. Iskakov, PhD, Professor, Satbayev University.

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