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ABSTRACT

of the dissertation work submitted for the degree of Doctor of Sciences

APPLICATION OF EFFECTIVE TECHNOLOGY IN THE STORAGE-TRANSPORTATION SYSTEM OF HIGH PARAFFIN WELL PRODUCTS

Speciality: 3354.01 - Construction and exploitation of oil-gas pipelines, bases and storage

Field of science: Technical sciences

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GENERAL DESCRIPTION OF THE WORK

The topicality and development degree of the subject: Currently, the proportion of high-paraffin oil dispersion systems in the total volume of hydrocarbon raw materials in our country and in the developed oil-producing countries of the world is constantly increasing, which leads to a number of complex and important problems to solve. Therefore, one of the priority tasks facing oil engineers is to implement comprehensive measures to prevent corrosion and paraffin deposition in the storage system of this type of oil. Intensive paraffinization in relatively high paraffin oils at relatively low temperatures leads to a narrowing of the cross-sectional area of the pipelines, resulting in a decrease in well productivity and, in some cases, complete stoppage of transportation. This, in turn, does not allow for the efficient exploitation of wells, storage, transportation and pipeline transportation of oils. Thus, the exploitation process becomes much more complicated, the interrepair time is shortened, labor productivity, material costs and the cost of oil increase.

Excessive electrochemical corrosion activity of gases such as oxygen, carbon dioxide, hydrogen sulfide, mineral salts and, most importantly, sulfate-reducing bacteria in the operating environment of well product storage-transportation system leads to equipment failure before the end of its operating life. The corrosion process not only reduces operating life and increases repair costs, but also causes serious damage to the environment. Thus, corrosion damage to equipment leads to salinization of the soil with aggressive formation waters, contamination of soil and natural water bodies with oil and oil products. In addition to deterioration of the surface smoothness during internal corrosion, the formation of corrosion products not only increases the speed of the paraffin deposition process and the viscosity of oil, but also plays the role of crystallization center of paraffin hydrocarbons for the formation of oil deposits.

As in any other industry, in the oil industry, the main goal is to prevent energy losses and losses of hydrocarbon feedstock. The solution to these problems lies in the development of modern technologies and their application to the oil industry. The development of new technology requires the research of the scientific basis of the complexities and problems that arise, taking into account the physicochemical and rheological properties of high-paraffin oils. In this regard, despite numerous studies, the problems mentioned above have not yet been resolved and remain relevant.

Currently, the most cost-effective of the many methods of combating paraffin deposits in high-paraffin oil dispersion systems is the use of depressor additives. Depressor additives contributes to lower the freezing point of oil, improve its fluidity, reduce hydraulic losses, the amount of paraffin deposits on the inner surface of pipelines and equipment, as well as improve their operating conditions. On the other hand, the main advantages of depressor additives are the simplicity of application technology, good compatibility with other additives used in the production, transportation and storage systems of high-viscosity oils and high economic efficiency from their use.

One of the effective methods of protection against internal surface corrosion is considered the use of corrosion inhibitors. The method of inhibitor protection is relatively widespread and economically proven. By changing the concentration of inhibitors or using a combination of several inhibitors, it is possible to reduce or stop the corrosion rate to the allowable level without making fundamental changes in existing technology. At present, the requirements for corrosion inhibitors remain relevant due to their universal impact in the oil industry. However, applied corrosion inhibitors are generally less effective and often have a limited field of application. Obtaining, research and application of corrosion inhibitors, which combine the required properties, is one of the most important issues, as well as of great scientific and practical importance.

The aims and objectives of the research: The aim of the study is to develop an innovative method to increase the efficiency of the high-paraffin oil storage and transportation system by applying single anti-corrosion reagents to asphaltene-resin-paraffin deposits and corrosion to increase the operating life of in-field and commercial oil pipelines. The object of research is oil storage and transportation pipelines.

The following tasks are planned to achieve the goal of the research:

1. Study of bactericidal-inhibitory properties of MARZA-1 and MARZA-2 reagents.
2. Study of bactericidal-inhibitory properties of MARZA-1 + Gossypol resin compositions.
3. Study of bactericidal-inhibitory properties of MARZA-1 + MARZA-2 compositions.
4. Study of the impact of “Difron-4201” and “Difron-3970” depressor additives on the freezing temperature of model oil.
5. Study of the impact of “Difron-4201” depressor additive on paraffin deposition and thixotropic properties in model oil.
6. Study of the impact of the new composition on the freezing temperature of high paraffin oil and the rate of corrosion in hydrogen sulfide formation water on the basis of “Difron-4201” and MARZA-1.
7. Development of technology for application of Difron-4201 ”and MARZA-1 based compositions to high paraffin oils in mining conditions.

Research methods: Corrosion and rheological experimental research methods were used to solve the problems raised when conducting dissertation work.

Key provisions to be defended:

1. Experimental results on bactericidal-inhibitory properties of MARZA-1 and MARZA-2 reagents.
2. Experimental results on bactericidal-inhibitory properties of Gossypol resin and MARZA-1 based compositions
3. Experimental results on bactericidal-inhibitory properties of MARZA-1 and MARZA-2 based compositions.
4. Experimental results on the impact of “Difron-4201” and “Difron-3970” depressor additives on the freezing temperature of high paraffin oil.

5. Experimental results on the impact of “Difron-4201” depressor additive on paraffin deposition and thixotropic properties and effective viscosity in high paraffin oil.
6. Experimental results on the impact of “Difron-4201” and MARZA-1 based new composition on freezing temperature of high paraffin oil and corrosion rate in hydrogen sulfide formation water.
7. “Difron-4201” and MARZA-1 based composition application technology to high paraffin oils in mining conditions.

Scientific novelty:

1. Experimental results on bactericidal-inhibitory properties of MARZA-1 and MARZA-2 reagents were obtained and interpreted;
2. Bactericidal-inhibitory properties of Gossypol resin and MARZA-1 based compositions were studied;
3. Bactericidal-inhibitory efficiency of MARZA-1 and MARZA-2 based compositions was studied;
4. The impact of “Difron-4201” and “Difron-3970” depressor additives on the freezing temperature of high paraffin oil was studied;
5. The impact of “Difron-4201” depressor additive on paraffin deposition, hixotropic properties and effective viscosity in high paraffin oil was studied;
6. The impact of “Difron-4201” and MARZA-1 based new composition on freezing temperature of high paraffin oil and corrosion rate in hydrogen sulfide formation water was studied;
7. “Difron-4201” and MARZA-1 based composition application technology to high paraffin oils in mining conditions was created.

Theoretical and practical significance of the work:

The experimental results obtained during the research can be used by oil industry specialists to protect the inner surface of industrial equipment from electrochemical corrosion in various aggressive environments and to improve the rheological properties of high-paraffin oils in storage-transportation systems.

The positive results obtained from the application of MARZA-1, MARZA-2 bactericidal-inhibitory reagents of organic origin and "Difron-4201" depressor additive to high-paraffin oil storage-transportation systems give grounds to say that they are economically and practically beneficial for the oil industry of our country.

The obtained scientific results show that the local product MARZA series reagents are not only a highly effective corrosion inhibitor suitable for oil industry equipment, but also have bactericidal properties that prevent the increase in SRB. They are recommended for use as an inhibitor-antibacterial agent in the oil industry due to their high corrosion protection efficiency in the carbon dioxide environment and their antibacterial properties against SRBs.

Due to the complex aggressive corrosion environment and impact of asphaltene-resin-paraffin deposition, oil storage and transportation system equipment and transport pipelines quickly break down. In order to jointly solve these problems, the technology of injection of depressor additive and inhibitor-bactericidal reagent-based composition into high paraffin oil pipelines was developed. The proposed new multifunctional composition allows to solve the problems of corrosion and paraffin deposition in the storage-transportation system of high-paraffin oils with high efficiency.

New scientific results obtained in the dissertation can be included in the relevant questionnaires, databases and international scientific information systems.

Approbation and publication: The scientific results of the dissertation were reported and discussed at the following scientific meetings.

1. Formation of a new paradigm of scientific and technological development. Scientific proceedings based on the International Scientific and Practical Conference (Belgorod, 2018)

2. Scientific-practical conference dedicated to the 100^{th} anniversary of Azerbaijan State Oil and Industry University (Baku, 2020)
3. XXXII International Scientific and Practical Teleconference “Advances in Science and Technology” (Moscow 2020)
4. XXXIV International Scientific-Practical conference “Eurasia Science” (Moscow, 2020)
5. International conference on “Actual problems of chemical engineering, APCE – 2020, dedicated to the 100th Anniversary of the ASOIU (Baku, 2020)

Publication degree of the research. 15 scientific works were published on the topic of the dissertation. 10 of them are articles, 5 report theses. Three of the articles were published by a single author, and four by periodicals included in international summary and indexing systems.

The organization where the dissertation work is carried out. Azerbaijan State Oil and Industry University, department of “Transportation and storage of oil and gas”

Structure and volume of the work: The dissertation consists of an introduction, three chapters, conclusion and 182 references , including 18 figures and 26 tables, the total volume of the work is 137 computer printed pages, 210330 characters.

Author’s personal contribution: The author plays a leading role in the analysis of literature review, problem statement, formation of new ideas, planning and implementation of experimental work, explanation and generalization of principle based results obtained by various research methods.

MAIN CONTENT OF THE DISSERTATION

In the introduction of the dissertation (9 p) the relevance of the subject is substantiated, the objectives, tasks, issues to be solved, scientific novelty, theoretical and practical significance of the work, the main provisions to be defended are reflected. The dissertation consists of three chapters.

The first chapter is a review of the literature (32 . It analyzes the research works carried out on the investigation of corrosion and paraffin deposition processes on the inner surface of oilfield equipment and identifies the issues to be solved.

It was shown that the aggressive environment that causes corrosion of the inner surface of oilfield equipment is in all cases formation water. Since the mechanism and kinetics of the corrosion process of the inner surface depends on the ratio of the formation water phase to the liquid hydrocarbon phase, the corrosion activity of such an environment is determined by the physical and chemical properties of the formation water. The rate of corrosion process varies depending on the amount of molecular oxygen, carbon dioxide, hydrogen sulfide and ionic mineral salts in the formation water.

Oilfield experience shows that hydrogen sulfide creates hydrogen fragility and surface corrosion in equipment, leading to their wear from corrosion, mechanical wear and their breakdown faster than operating life. It was noted that one of the main reasons for the presence of hydrogen sulfide in hydrocarbon feedstocks is sulfate-reducing bacteria (SRB). The vast majority of corrosion damage to oilfield equipment and pipelines is due to the effects of SRB, and this problem remains acute.

One of the main factors impacting corrosion is carbon dioxide in the operating environment. When carbon dioxide is soluble in water, the pH of the medium decreases and the medium becomes weakly acidic. Also, the rate of corrosion of steel equipment in such conditions depends on the partial pressure of carbon dioxide.

Scientists do not agree on the mechanism of paraffinization and the impact of various factors on it. The authors, who studied the impact of asphaltene-resin components on paraffin deposition, found that the shape of the solid PC changes, resulting in the formation of a highly dispersed suspension during deposition.

At present, there are various theories that allow to explain the formation of ARPD on the inner surfaces of oil industry equipment based on modern ideas. A relatively common theory of them explains the formation of oil sediments in terms of the crystallization temperature of solid paraffin-naphthenic hydrocarbons. This theory does not take into account determinants such as adhesion, adsorption and the impact of resin-asphaltene components on ODS. Another theory states that the RAC has a significant impact on the process of paraffinization of oilfield equipment. It is the authors of the theory who explain the process of PD formation in terms of the impact of ODS on the coagulation, aggregation and micelle formation properties of naphthenic hydrocarbons and asphaltenes.

It should be noted that in order to form a review of the literature, the analysis of the main problems arising in the storage system of high paraffin oils, both in our country and abroad, and the research work to eliminate them showed that indeed, corrosion and paraffin deposition processes need to be eliminated for the efficient transportation of this type of oil. However, in the published scientific articles, as well as in dissertations in this direction, in order to increase the efficiency of the storage system of high paraffin oils, some authors consider it expedient to eliminate corrosion, while others only consider the elimination of paraffin deposition. The dissertation is based on the fact that it is more expedient to develop an effective technology for the simultaneous elimination of both factors, namely corrosion and paraffin deposition processes, which complicate the storage and transportation of high-paraffin oils in order to obtain a higher economic effect. For this reason, local and foreign reagents against corrosion and paraffin deposition were selected and their protective effects in the laboratory were determined.

The second chapter presents the results of the study of bactericidal-inhibitory properties of MARZA-1, MARZA-2 reagents and MARZA-1 and Gossypol resin-based composition. The corrosion protection and bactericidal effects of the reagents mentioned here were determined. MARZA-1 and MARZA-2, which can be industrially produced from local raw materials, are reagents of organic origin with three layers of bonds, the molecules of which are composed of atoms of the element carbon, hydrogen, halogen and oxygen.

In order to study the corrosion protection effectiveness of **MARZA-1 reagent**, laboratory tests were performed by gravimetric method according to the known method. The experiments were carried out in 24 and 240 hours in environments with hydrogen sulfide, carbon dioxide and both gases.

The results of the study showed that as the concentration of MARZA-1 increases, the rate of corrosion decreases in all three environments and the protection effect increases. Also, the corrosion rate decreases in both reagent-free and reagent-containing environments as the test period increases. This is due to the formation of a coating of corrosion products on the surface of the samples, which shields the metal surface and performs a protective function. (Table 1)

Table 1.
Protective effects of MARZA-1 reagent in various aggressive environments

Environment	$C_{inh.}$. mg/l	K, q/m^2·hour	Delay factor, γ	K_p , mm/y	Protection effect, Z,%
1	2	3	4	5	6
H_2S	-	0,4326	-	-	-
		0,1874	-	-	-
	3,0	0,0506	8,54	0,0566	88,3
		0,0504	3,71	0,0564	73,1
	5,0	0,0328	13,18	0,0367	92,4
		0,0329	5,69	0,0368	82,4

Follow the 1 table

1	2	3	4	5	6
H_2S	7,0	0,0190	22,76	0,0212	95,6

		0,0163	11,49	0,0182	91,3
	10,0	0,0086	50,3	0,0096	98,0
		0,0080	23,42	0,0089	95,7
CO_2	-	0,2418	-	-	-
		0,06231	-	-	-
	3,0	0,0573	4,21	0,0641	76,3
		0,0247	2,52	0,0276	60,22
	5,0	0,0430	5,62	0,0481	82,2
		0,0187	3,33	0,0209	69,86
	7,0	0,0232	10,42	0,0259	90,4
		0,0080	7,78	0,0089	87,15
	10,0	0,0125	14,34	0,0140	94,8
		0,0032	11,47	0,0035	94,83
H_2S +CO_2	-	0,3416	-	-	-
		0,7612	-	-	-
	3,0	0,0792	4,31	0,0887	76,8
		0,1364	5,58	0,1527	82,07
	5,0	0,0526	6,49	0,0589	81,6
		0,0796	4,56	0,0891	89,54
	7,0	0,0290	11,77	0,0324	91,5
		0,0246	30,94	0,0275	46,76
	10,0	0,0109	31,33	0,0122	96,8
		0,0058	131,24	0,0064	99,23

Note. Duration of the experiment is 24 hours (numerator) and 240 hours (denominator)

The impact of **MARZA-1 reagent** on sulfate-reducing bacteria was investigated in the Postgate-B nutrient environment. The strains of sulfate-reducing bacteria of the “Desulfomicrobium” and “Desulfovibriodesulforicans” species taken from the formation waters of “Bibiheybatneft” OGPD field were used for the research. During the study of the bactericidal properties of MARZA-1 reagent, it was found that it effectively reduces the activity of sulfate-reducing bacteria in the “Postgate-B” nutrient environment.

The bactericidal effect (S,%) of MARZA-1 was determined based on the concentration of hydrogen sulfide produced by SRB. It was determined that the highest effect is 90% in the presence of Desulfovibriodesulfuricans bacteria at a concentration of 10 mg/l of reagent, and 85% in the presence of Desulfomicrobium.

Thus, MARZA-1 reagent drastically reduces the amount of biogenic hydrogen sulfide in “Postgate B” nutrient environment containing sulfate-reducing bacteria, but does not completely stop the sulfate reduction process. It is clear that the MARZA-1 reagent prevents the growth of sulfate-reducing bacteria in the nutrient environment, but does not completely stop the metabolic process in them.

The bactericidal and corrosion protection properties of the **new composition of 10:1 prepared on the base of Gossypol resin and MARZA-1** using diesel fuel and kerosene as solvents were studied in the laboratory in accordance with known methods. H_2S, CO_2, H_2S+CO_2 were taken as aggressive environments and 50, 70, 100 and 120 mg/l of the composition were used. Experiments were carried out in corrosion environment with the participation of both solvents, and it was found that the protective effect increases as the composition of the composition increases. The highest protective effect was observed at 100 mg/l of the composition. In the presence of solvent diesel fuel, this effect was 98% in the H_2S environment, 96% in the CO_2 environment, 98% in H_2S+CO_2 environment, and 97%, 94% and 99% in the presence of kerosene, respectively.

The bactericidal properties of the composition were studied in “Postgate-B” environment. Desulfomicrobium and Desulfovibriodesulfuricans of SRBs were used in this case. In the presence of both bacteria, the highest effect was observed at a concentration of 120 mg/l (95-99%). Thus, the corrosion protection and bactericidal effect of the prepared composition in these environments was higher than that of MARZA-1 reagent, which can be explained by the synergistic effect.

In order to determine the corrosion protection effect of **MARZA-2 reagent**, **in the laboratory** experiments were performed in neutral, acidic and alkaline environments for six hours. According to the mass difference, the corrosion rate and the protection efficiency of the reagent were calculated in all three environments depending on the concentration of the inhibitor.

Corrosion rate of MARZA-2 reagent in concentrations of 3-10 mg/l in neutral environment varies between 0.0782-0.0078 q/m^2·hours, protection effect 90-99%, corrosion rate in acidic environment varies between 0,3430-0,00 q/m^2·hours, protection effect 88-100%, in alkaline environment the corrosion rate varies between 0.1843 to 0.0410 g/m^2·h, and the protection effect varies between 82-96%. The comparison of the results shows that a concentration of 10 mg/l of MARZA-2 reagent is effective for all three environments. In this case, its corrosion protection efficiency is 96-100%. The reason for the significant reduction in the rate of corrosion is due to the ability of the inhibitor to hydrophobicize the metal surface. Rather, the inhibitor inactivates the electrochemical corrosion process by shielding high-energy active centers on the metal surface, isolating them from the aggressive environment. Thus, the analysis of the results obtained in all three environments shows that MARZA-2 reagent has strong inhibitory properties.

Based on the presence of sulfate-reducing bacteria in the formation water and their ability to create more corrosion aggression, the bactericidal properties of MARZA-2 reagent against sulfate-reducing bacteria were studied in “Posgate-B” environment. The selection of SRB for research is due to the fact that during the destruction of these bacteria it is possible to destroy the biocenosis formed by other physiological groups of microorganisms.

Research in the direction of destroying SRB was carried out within 15 days according to the standard method of NASE using the sequential dilution technique in “Posgate-B” environment. The sulfate-reducing bacteria used for the experiment were taken from the formation waters of "Bibiheybatneft" OGPD oil field. The experiments were carried out in sulfate-reducing bacteria with the volume of 10^3 cell/ml at a temperature of 28-30^{0}C in 3.0,5.0,7.0 and solutions with a concentration of 10 mg/l of MARZA-2 reagent.

The bactericidal effect of the reagent increases in the concentration range of 3.0-10 mg/l, and these values are 50, 68, 76 and 85%, respectively. The results of both laboratory tests suggest that the MARZA-2 reagent has a high protective effect as both an inhibitor and a bactericide (Figure 1).

Thus, it was determined that MARZA-1, MARZA-2, Gosipol resin and MARZA-1-based composition, which can be industrially produced on the basis of local raw materials, have high corrosion protection properties and high bactericidal effect against sulfate-reducing bacteria, as well as due to its high bactericidal effect against sulfate-reducing bacteria, it is economically feasible to use them in the oil industry, including in the storage and transportation of high-paraffin oils, to protect the inner surface of equipment from aggressive corrosion.

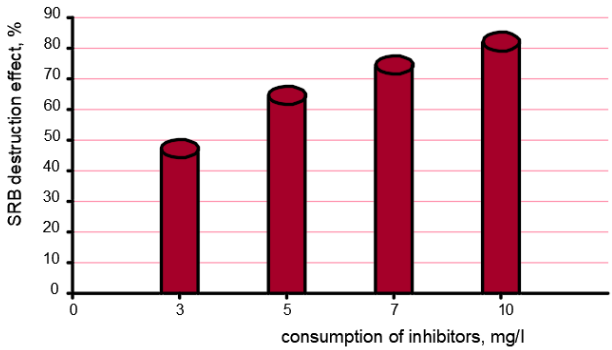

Figure 1. SRB destruction effect of MARZA-2 reagent

After studying the inhibitory-bactericidal properties of MARZA-1 and MARZA-2 reagents separately, the effect of corrosion protection in their combined bactericidal and hydrogen sulfide formation water was also studied in the laboratory. The main purpose of the study was to investigate how synergism occurs in MARZA-1 and MARZA-2 reagents, which are close in chemical composition and structure. For this purpose, five compositions (P-1, P-2, P-3, P-4, P-5) in different mole ratios of MARZA-1 and MARZA-2 reagents were prepared.

In order to determine the bactericidal properties of the compositions in the laboratory, strains of bacteria "Desulfomicrobium" and "Desulfovibriodesulforicans" were used as the object of research. The sulfate-reducing bacteria used for the experiment were taken from the formation water of "Bibiheybatneft" OGPD oil field. The impact of the compositions on the incubation period of sulfate-reducing bacteria was studied within fifteen days.

The experiments were carried out in this environment, taking into account the intensive growth of SRB mainly in "Postgate B" nutrient environment. For comparison, studies were conducted in reagent-free and reagent-added environment. The bactericidal effects of the compositions were calculated based on the amount of biogenic hydrogen sulfide formed in the environment. The highest bactericidal effect was found at a concentration of 10 mg/l of P-3 composition (99%).

The reason for the corrosion of the inner surface of the equipment of the storage and transportation system of high-paraffin oils is the presence of various gases, mineral and organic salts, mechanical mixtures and, most importantly, hydrogen sulfide dissolved in the formation waters produced with oil. Formation waters, being a natural electrolyte solution, accelerates the process of electrochemical corrosion by creating an aggressive environment on the inner surface of the pipes. From this point of view, the inhibitory properties of hydrogen sulfide formation water in the compositions prepared under laboratory conditions were studied and their corrosion protection effect was calculated.

A sample of formation water taken from well No. 1082 of "Bibiheybatneft" OGPD, SOCAR was used as an electrochemical corrosion environment. The analysis of the results shows that as the concentration of the test compositions in the formation water increases, the corrosion rate decreases and the corrosion protection effect increases. This increase was 85-98% for P-1, 92-99% for P-2, 95-99% for P-3, 75-92% for P-4 in the concentration sequences of 3.0, 5.0, 7.0 and 10 mg/l and for P-5, it varies in the range of 72-90%. As it is seen from the comparison of the figures, the corrosion protection effect of the compositions increases from P-1 to P-4, and decreases in P-4 and P-5.

From the compositions P-2 and P-3 sharply reduces the rate of corrosion in formation water at a concentration of 10 mg/l (99%). At the specified concentration, P-1 reduces the corrosion rate by 50 times, P-4 by 12.5 times, and P-5 by 10 times.

Table 2 provides a comparative analysis of the bactericidal and inhibitory properties of MARZA-1, MARZA-2 and their compositions prepared from different mole ratios. The table shows that an increase in the concentration of reagents from 3 mg/l to 10 mg/l in the environment leads to an increase in their effectiveness.

Thus, the following conclusions can be drawn from the comparative analysis of the values of corrosion protection and bactericidal effects of reagents given in Table 2.

1. The values of corrosion protection and bactericidal effects of MARZA-1 and MARZA-2 reagents are higher only than the corresponding values of P-4 and P-5 compositions.

2. Corrosion protection and bactericidal effects of P-1, P-2, P-3 compositions are higher than MARZA-1 and MARZA-2.

3. At the same time, the highest value of both corrosion protection and bactericidal effect is shown by the composition P-3.

4. In various aggressive environments, the application of P-3 composition in corrosion protection of the inner surface of oil industry equipment is more expedient.

Table 2.

Comparative analysis of bactericides and inhibitory (in acidic environment) properties of MARZA-1, MARZA-2 compositions

Brand of reagents	Concentration providing corrosion protection, mg/l	Corrosion protection effect,%	Bactericidal effect of reagents
1	2	3	4
MARZA-1	3,0	88,3	57
	5,0	92,4	67
	7,0	95,6	82
	10	98,0	87
MARZA-2	3,0	88	50
	5,0	90	67
	7,0	93	78
	10	95	85
P-1	3,0	85	59
	5,0	90	74
	7,0	97	81
	10	98	85
P-2	3,0	92	84
	5,0	96	88
	7,0	98	92
	10	99	94
P-3	3,0	95	93
	5,0	97	96
	7,0	99	97
	10	99	99
P-4	3,0	75	56
	5,0	86	70
	7,0	90	78
	10	92	81

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1	2	3	4
P-5	3,0	72	50
	5,0	84	65
	7,0	88	72
	10	90	76

The third chapter is dedicated to the study of physical and chemical properties of "Difron-4201" and "Difron-3970" additives and model oil, the impact of additives on model oil freezing temperature, paraffin deposition, thixotropic properties and effective viscosity of "Difron-4201" model oil. Also, this chapter reflects the impact of the composition prepared on the base of "Difron-4201" and MARZA-1 on the freezing temperature of high paraffin oil and the rate of corrosion in hydrogen sulfide formation water and the development of new technology for the transportation of high paraffin oils.

Table 3

Physical-chemical properties of model oil

№	Parameters	Quantity	Assignment method
1	The amount of water in the sample, %	0.2	SS 2477-65
2	Concentration, ρ_4^{20} kg/m^3	894.3	SS 3900-85
3	The amount of paraffin, %	11.6	SS 11851-85
4	The amount of resin, %	10.2	SS 11851-85
5	The amount of asphaltene, %	5.2	SS 11851-85
6	Freezing temperature, ^{0}C	16	SS 20287-91
7	Paraffin melting point, ^{0}C	57	SS 11858-83
8	The amount of sulfur, %	0.22	SS 1437-75
9	A/R	0.509	-

The physical and chemical properties of the high-paraffin model oil sample developed to study the effect of depressor additives on the rheological parameters of high paraffin oils are given in Table 3.

The model oil was prepared from a 2: 1 ratio of commercial oils from the Narimanov and Absheron deposits.

"Difron-4201" and "Difron-3970" additives produced by "EKOS-1" JSC of the Russian Federation were used to study the regularity of the impact of additives on high paraffin oil.

The selection of the additive and evaluation of effectiveness for high paraffin oil was based on its impact on oil freezing temperature. Determination of the freezing temperature of oil in the laboratory without additives and with additives was carried out in accordance with the method of RD 39-3-812-82. "Difron-3970" and "Difron-4201" were used for this purpose.

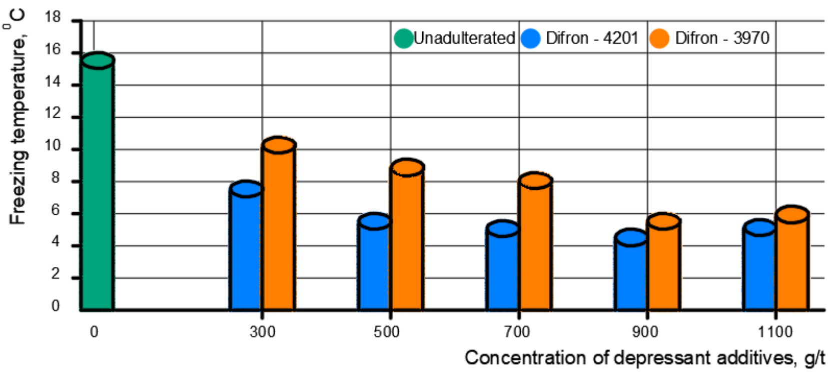

Figure 2. Impact of model oil freezing temperature on depressor additives

Analysis of the results of laboratory experiments showed that "Difron-4201" depressor additive has a more effective impact on the freezing temperature of high-paraffin oil than "Difron-3970". It should be noted that the highest effect is observed at a concentration of 900 g/t of both depressor additives. At this concentration, "Difron-3970" reduces the freezing temperature of oil from + 16^{0}C to + 7^{0}C, and "Difron-4201" additive to + 5^{0}C (Figure 2). For this reason, "Difron-4201" depressor additive was selected for high paraffin oil during the research.

Currently, the problems of combating oil deposits generated on the inner surface of pipelines and other equipment have become acute in many oil-producing countries, including our country, due to the commissioning of high-paraffin oil fields. That is why the effective control of asphaltene-resin-paraffin deposits is one of the most important issues. Thus, in addition to deteriorating the technical and economic performance of the processes of production, storage, transportation of oil through pipeline, oil deposits increase demand for energy and increase the possibility of accidents. In other words, the accumulation of paraffin deposits in the equipment currently used in the storage and transportation system of high-paraffin oils leads to technological complications, reduced production and equipment failure.

Currently, there are many methods to combat paraffin deposits. However, experiments show that the use of depressor additives is the best way to prevent ARPD during the transportation and storage of high-paraffin oils in complex geotechnical conditions. The use of depressor additives in the prevention of paraffin deposits does not differ from other methods only in terms of technological effectiveness. The effect of the addition of reagent at temperatures above the initial temperature of paraffin crystallization does not depend on the thermohydrodimamic conditions of the oil moving through the pipeline.

Based on the above-mentioned issues, the process of ARPD formation in high paraffin model oil with the participation of “Difron-4201” depressor additive was studied in the laboratory. For this purpose, the “Coldfingertest” method was used to evaluate the effectiveness of depressor additives and determine the optimal consumption rate. This method is based on the deposition of paraffin sediments from a moving oil on a cold metal surface.

The experiments were performed at temperatures of 0^0C, 5^0C, 10^0C, 15^0C, 20^0C, 25^0C, 30^0C of “Coldfingertest” for 2 hours. The mass of oil sediments accumulated on the surface of “Coldfingertest” at each temperature for 0, 20, 40, 60, 80, 100, 120 minutes was determined by analytical weighing.

Experiments for model oil samples with added concentrations of 300, 500, 700, 900, 1100 g/t of "Difron-4201" were repeated under the same conditions and based on the results obtained at different concentrations of "Difron-4201" and at different temperatures of "Coldfingertest" its efficiency was calculated based on the following mathematical dependence

$$K=\frac{m_1-m_2}{m_1}\cdot 100\%$$

where: K is the efficiency of depressor additive;

m_1 is the mass of ARPD in additive free environment;

m_2 is the mass of ARPD in the environment with depressor additive.

Figure 3 shows the efficiency of depressor additive at 5^0C temperature of "Coldfingertest" against ARPD.

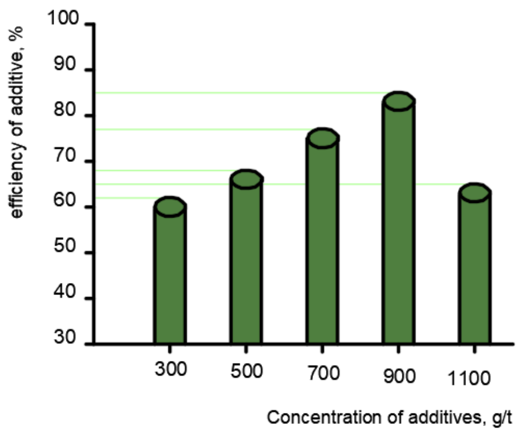

Figure 3. Efficiency of "Difron 4201" against paraffin deposition

As it is seen from the obtained results, "Difron-4201" can be used in high-paraffin oils as an effective means against ARPD and its optimal consumption rate is 900 g/t.

High paraffin oils are rheologically complex liquids belonging to non-homogeneous and unbalanced dispersed systems with thixotropic properties, which tend to form structures at low temperatures. The reason for the thixotropic properties of oils is the presence of high-molecular compounds such as paraffin, asphaltene and resin, which tend to form structures.

The study of the rheological properties of thixotropic oils shows that non-Newtonian properties of oil are formed at low temperatures due to the components of asphaltene, resin and paraffin in the dispersed state in the oil system. In this case, the resin components in the oil give it elasticity, and the paraffin components give it non-linear-viscous properties. The rheological properties of thixotropic oils change during their flow and during their subsequent cessation. During the flow, the paraffin structure of the oil collapses, and when it stops, it is restored. In other words, thixotropy is a feature of the highly paraffin dispersed oil system that can be restored over time.

The thixotropic properties of high-paraffin model oil at low temperatures (10^0C, 15^0C, 20^0C) were studied in the laboratory through a rotation viscometer "Reotes-2".

The experiments were performed both in reagent-free samples and in the samples with different concentrations of "Difron-4201". It was found that as the concentration of the additive increases, the area of hysteresis loop decreases, and the greatest reduction occurs at a concentration of 900 g/t of the additive.

The correct determination of the various rheological properties of individual dispersed oil systems is of great importance in preventing significant energy losses in the calculation of their mode of operation, as well as in increasing the efficiency of transporting such dispersed systems through pipelines.

In this regard, it is especially important to correctly determine the limit shear tension and effective viscosity of viscous-plastic oils, both in theoretical reports and in practice.

Based on the above-mentioned, the impact of "Difron-4201" additive on a number of rheological parameters of high paraffin oil was studied in the laboratory. The research process in “Reotes-2” viscometer was carried out at a wide temperature range (6^0C, 8^0C, 10^0C, 12^0C, 15^0C, 20^0C, 30^0C, 40^0C, 50^0C) and in the range of speed gradient from 0.1 to 35 s^{-1}.

In order to study the impact of “Difron-4201” additive on the rheological parameters of model oil, samples with the addition of additives of different concentrations (300, 500, 700, 900, 1100 g/t) were studied in the same way as in additive-free oil. The values of rheological parameters calculated according to the Balkli-Gershelya model were calculated.

Thus, the positive impact of “Difron-4201” depressor additive on the limit shear tension and effective viscosity of model oil was confirmed by the results of experiments conducted on “Reotes-2” viscometer. It was found that when the concentration of the additive increases to 900 g/t, the value of the limit shear tension decreases to 15 at 15°C; 8^0C-16.5; 10^0C-18.3; 12^0C-46.3 and 15^0C -65.2 . Also, in the specified concentration ranges the effective viscosity value of model oil decreases to 6^0C-5.6; 8^0C-2.6; 10^0C -2.8; 12^0C-3.8 and 15^0C-5.1.

Depressor additives applied against asphaltene-resin-paraffin deposits in oils with complex rheo-physicochemical properties in developed oil countries are chemically polymeric substances of organic origin. Due to the difficulties in obtaining such substances, their sale price is quite high. Therefore, the use of depressor additives in the pipeline transportation of high-paraffin oils is often less cost-effective than other existing methods. However, the application of depressor additives has the advantages of significantly improving the rheo-physical and chemical parameters of high paraffin oils, the stability of the additive to oil, simplicity of the process, low costs during implementation. For this reason, based on these advantages, it is important to maintain the reliability of depressor additives by significantly reducing the cost of additives and the operating costs of heating high-paraffin oil during the application of the additive. On the other hand, as noted above, currently available depressor additives are synthesized on the basis of high-cost chemicals, and it is not expected that additives based on cheaper raw materials will be developed in the near future. For this reason, in order to maintain the advantage of applying depressor additives to high paraffin oils, it is advisable to develop new application technologies designed to reduce costs and first test them in the laboratory. On the other hand, one of the important problems to be solved during the transportation of high-paraffin oil through the pipeline is the protection of the inner surface of the pipelines from electrochemical corrosion. It should be noted that one of the factors complicating the fluidity of oil by increasing its viscosity during transportation is the corrosion of the inner surface. Thus, the violation of the smoothness of the surface during internal corrosion, the formation of corrosion products not only increases the speed of the paraffin deposition process and the viscosity of oil, but also serves the formation of oil deposits, playing the role of paraffin hydrocarbon crystallization centers.

As noted, during corrosion, the smoothness of the inner surface of the pipeline is lost and the surface becomes rough. In this case, the adhesion of oil deposits to the surface and the increase in their volume intensifies. Therefore, it is more expedient to simultaneously solve the problems of paraffin deposition and corrosion on the basis of the principles of a complex approach to increase the efficiency of the storage and transportation system of high paraffin oils. More precisely, it is necessary to prepare a reagent or composition that has a high effect against both corrosion and paraffin deposition. It is from this point of view that for the first time compositions were prepared from different mole ratios of “Difron-4201” and MARZA-1 reagents for different purposes and their impact on high paraffin model oil freezing temperature and corrosion rate in hydrogen sulfide formation water taken from well 1082 of “Bibiheybatneft” OGPD was studied in the laboratory.

Analysis of the results of the study on the compositions of “Difron-4201” and MARZA-1 reagents prepared in different concentrations showed that the composition of 700 g/t “Difron-4201”

+ 10g/t MARZA-1 = 70: 1 has a high impact both on corrosion protection and reducing oil freezing temperature. Therefore, only the results of laboratory research of this composition are given in the dissertation in Figure 5, respectively.

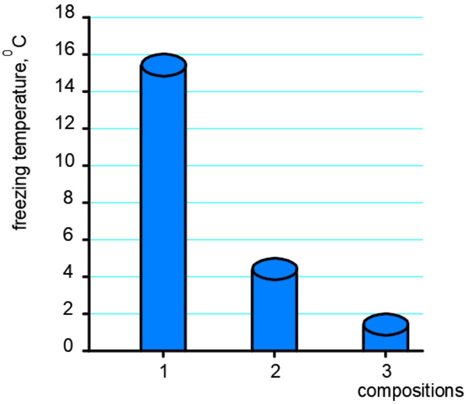

Figure 4. The impact of the composition ("Difron-4201" + MARZA-1 = 70: 1) on the freezing temperature of the model oil. 1-model oil, 2-model oil + 900g/t "Difron-4201", 3-model oil + 700g/t "Difron-4201" + 10g/t MARZA.

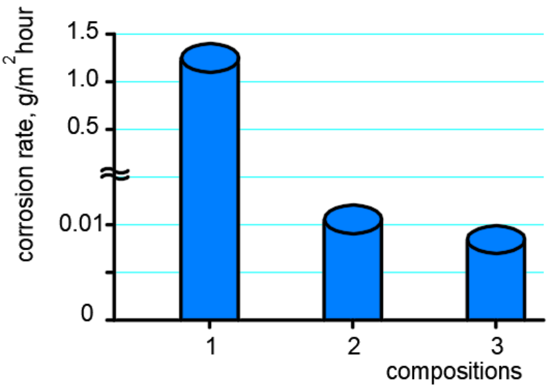

Figure 5. The impact of the composition ("Difron-4201" + MARZA-1 = 70: 1) on the corrosion rate. 1-formation water, 2-formation water + 10mg/l MARZA-1, 3-formation water + 10g/t MARZA-1 + 700g/t "Difron-4201"

As it is seen from the figures, the joint mixture of both reagents has an effective impact on the freezing temperature of high paraffin oil and the corrosion rate in hydrogen sulfide formation water. Thus, while "Difron-4201" additive reduces the freezing temperature of the model oil from +16^{0}C-dən +5^{0}C at a concentration of 900 g/t, the new composition of "Difron-4201" + MARZA-1 = 70: 1 reduces the freezing temperature to + 2^{0}C. Also, the studied composition significantly reduces the corrosion rate in hydrogen sulfide formation water compared to MARZA-1. Thus, as a result of laboratory studies, it was found that the new composition of "Difron-4201" + MARZA-1 = 70: 1 not only has a high protection efficiency, but also reduces the consumption of depressor additives from 900 g/t to 700 g/t. .

Based on the results of laboratory experiments, the technology of application of a new composition of high-paraffin oils during transportation by pipeline in the field was developed and a new technological scheme was developed for its implementation in the field.

It is proposed to use the following technological equipment when applying the new composition of "Difron-4201" + MARZA-1 = 70: 1 to high paraffin oils:

-capacity for preparation of additive solution;
-capacity to store additive solution;
- capacity to store MARZA-1 reagent,
-capacity to store the solvent;
-dosing capacity;
-dosing pump;

Capacities must have a measuring scale and be provided with a heater.

The technological parameters of the devices should be as follows.

-pressure in capacities - atmospheric pressure;

- temperature of additive solution in capacities-35-40^{0}C;

-the temperature of oil-50-60^{0}C when the additive is added

A simple technological scheme for the implementation of the process of pumping a new multifunctional composition to the moving oil is shown in Figure 6. “Difron-4201” depressor additive is added to high-paraffin oil in the form of a 30% solution in diesel fuel.

The proposed technology provides a simultaneous solution of the two main problems, i.e., paraffin deposition and corrosion, which cause complications in the storage and transportation systems of high-paraffin oils, as well as obtaining high economic efficiency.

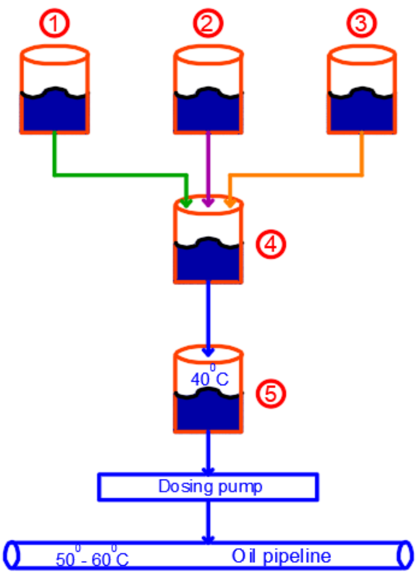

Figure 6. Technological scheme of application of the composition (“Difron-4201” + MARZA-1 = 70: 1) to high paraffin oil.

1- capacity for "Difron-4201" additive; 2- capacity for MARZA-1 reagent; 3- capacity for solvent; 4-capacity for mixer; 5-dosing capacity.

CONCLUSION

1. As a result of the study of bactericidal-inhibitory properties of MARZA-1 and MARZA-2 reagents, it was determined that both reagents have high protection and bactericidal efficiency due to minimization of electrochemical corrosion rate at 10 mg/l concentrations.
2. Two new multifunctional compositions of different composition with different protective composition were developed and studied from reagents that can be produced on the basis of local raw materials, which have a higher protection efficiency than the components in the existing aggressive environments of the oil industry.
3. The effect of "Difron-4201" depressor additive on the freezing temperature of high paraffin oil in the amount of 900 g/t was studied and the temperature was reduced from + 16^{0}C to + 5^{0}C.
4. As a result of experimental studies, it was determined that the optimal concentration of "Difron-4201" has a significant effect on the thixotropic properties, paraffin deposition process, limit shear tension and effective viscosity of high paraffin oil in the range of 900 g/t.
5. The impact of the new composition developed on the basis of "Difron-4201" and MARZA-1 on the freezing temperature of high paraffin oil and the rate of corrosion in hydrogen sulfide formation water was studied and compared to the components, more effective results were obtained.
6. For the first time in the transportation of high-paraffin oils, the technology of application of a new composition against internal corrosion and paraffinization in mining conditions was developed.

7. Based on the results of numerous laboratory studies, MARZA-1, MARZA-2, “Difron-4201” reagents and compositions based on them can be widely used against the complications that may occur in the storage and transportation system of high-paraffin oils in mining conditions.

The main content of the dissertation has been published in the following scientific works:

1. Gurbanov, H.R. Corrosion inhibitor in environments containing sulfuric hydrogen and carbon dioxide/ H.R. Gurbanov, S.M. Mammadli, A.V. Gasimzada //Formation of a new paradigm of scientific and technical development. Proceedings of the materials of the International Scientific and Practical Conference, Belgorod, - May 30, 2018 Part I, - pp. 130-134.
2. Gurbanov, H.R. Combating with corrosion in oil and gas production equipment in conditions of bacterial contamination/ H.R. Gurbanov, S.M. Mammadli //Journal “World Science”, -2018. No. 6(15), - pp. 158-163.
3. Qurbanov, H.R. Research of bactericidal-inhibitor effect in corrosion protection of oil mining equipment / H.R. Gurbanov, M.B. Adigozalova, S.M. Mammadli // Azerbaijan Oil Industry, -2019. №1, -pp. 38-41.
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storage of oil products and hydrocarbons, -2020. No. 10, -pp. 37-41.

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In the works carried out with co-authors, the personal work of the author:

[4], [6], [9], [10], [12] - performed independently.

[3], [[14], [15]- statement of the problem, research work and analysis of the results.

[1], [2], 5], [7], [8], [11], [13] - the shares of the authors are the same.

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