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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

DEVELOPMENT AND APPLICATION OF NEW COMPONENTS FOR OIL PRODUCTION AND TREATMENT

Speciality: 2525.01 – “Development and exploitation of oil and gas fields”

Field of science: Technical science

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GENERAL DESCRIPTION OF WORK

The actuality and study degree of the topic.

It is important to develop more promising technologies for the normal operation of oilfield equipment, such as oil extraction, primary oil treatment and transportation systems. This problem remains relevant, despite the presence of different strategies for preventing the formation of asphalt-resin-paraffin deposits (ARPD) in downhole and off-hole equipment. Chemicals are preferable to established approaches in the fight against ARPD since the known methods are not effective enough. Due to the high cost of inhibitors imported from abroad, there is a need to create new ARPD inhibitors and additives.

One of the major concerns is preventing the deposition of inorganic salts within reservoirs, downhole equipment, and production facilities in a number of oil fields which are in the final stages of development.

In systems with complex salt scales, traditional methods for preventing salt precipitation do not provide comprehensive protection. It is significant and important to conduct scientific research into the causes of salt precipitation of various scales by classifying the formed salt depositions according to their group composition and to develop new inhibitors to prevent the formation of salt deposits.

The high percentage of residual water in crude oil is one of the major issues in the oil industry. The emulsion's high-water content and mechanical impurities significantly increase the cost of oil during transportation. Due to the high stability of such emulsions, their demulsification can often be achieved with the use of demulsifiers. The development of emulsion breaking down technologies with the use of demulsifiers has always been an urgent problem. However, due tothe high cost of imported components, the cost of the composition based on themrises. In this regard, the development of new composition demulsifiers based on inexpensive and readily availablesurfactants isimportant.

Object and subject of research.

The object of research is the development and application of new ingredients in order to solve the complications arising during the oil extraction and preparation.

The purpose and main objectives of the study.

- development of new inhibitors and depressants against asphaltene-resin-paraffin deposits;
- development of salt deposits inhibitors of various origins (carbonate, sulfate, sulfide, etc.);
- development of new demulsifiers for dehydration and desalination of oil;

Methods for solving the tasks.

The problems are solved through the application of laboratory experiments, mining research and mathematical processing of measurement results.

The main positions to be defended.

1. New inhibitors and depressants against asphaltene-resin-paraffin deposits
2. Inhibitors of salt scales of various origins (carbonate, sulfate, sulfide, etc.)
3. New demulsifiers for dehydration and desalination of oil

The scientific recency of the research.

- new inhibitors and depressants have been developed against asphaltene-resin-paraffin deposits;
- inhibitors of salt deposits of various origins (carbonate, sulfate, sulfide, etc.) have been developed;
- new demulsifiers have been developed for dehydration and desalination of oil;

Theoretical and practical value of work.

New ingredients have been developed to solve the complexity that arise in the processes of oil extraction and preparation, and their use in industry has resulted in great efficiency.

"Depressor Additive" is protected by the Patent of the Republic of Azerbaijan No. 2018 0007, which is used to lower the freezing point and viscosity qualities of oils.

"Demulsifier for deep dehydration and desalination of oil" is protected by the patent of the Republic of Azerbaijan I 2019 0094.

"Depressor Additive" is protected by the patent of the Republic of Azerbaijan No. 2020 0009, which is used to lower the freezing point and viscosity qualities of oils.

Approbation and application of the work.

The materials of the thesis were reported and discussed:

- Ministry of Education of the Republic of Azerbaijan, Azerbaijan State University of Oil and Industry, Proceedings of the conference "Actual problems of development of offshore oil and gas fields" dedicated to the 100th anniversary of Israfil Guliyev, Baku-2017, p. 162-174
- Bulatov readings, Chemical technology and ecology in oil and gas industry, Collection of articles, Krasnodar 2018, Volume 5, pp.38-41
- "Modern problems of innovative technologies in oil and gas production and applied mathematics" proceedings of the international conference dedicated to the 90th anniversary of Academician Azad Khalil oglu Mirzajanzade, Baku, December 13-14, 2018 p. 377-379 Bulatov readings, Development of oil and gas fields, - Collection of articles, Krasnodar -2020, -Volume 2, -p. 43-47.

In well No. 446 in the Sangachal-Duvanni-Khara-Zira (SDKZ) field, an ND-NDP-1 inhibitor against asphaltene-resin-paraffin deposits was injected into the pump compressor pipes from the space behind the pipeline. As a result of the application, the amount of asphaltene-resin-paraffin deposits in the pump compressor pipes was reduced, and the well maintenance time was doubled. The reduction in the number of repairsresulted in an additional 87.0 tons of oil being produced.

The oil produced as a result of using the ND-12A demulsifierunder mining circumstances,was developed on the basis of surfactants and solvents for dehydration and desalination of oil emulsion, met the requirements of AZS 115-2004 and was classified as 1st group oil.

Acts on the application of measures are attached to the dissertation.

The main results of the thesis were published in 17 publications which are listed at the end of the abstract. 10 of them are articles, 4 are reports and abstracts of conferences, 3 are patents of the Republic of Azerbaijan.

The structure and scope of the work.

The dissertation work consists of introduction, 3 chapters, conclusions and recommendations, the list of references, consisting of 133 titles and applications. The volume of work is 165 computer printed text including 20 figeres, 36 tables and 2 appendices. Total volume of dissertation is 216727 symbols.

Brief content of the work.

The introduction describes the main provisions of the dissertation, the relevance of the research conducted on the dissertation topic is demonstrated, as well as the scientific innovations of the work, the key provisions to be defended and the methods of solving the issues are explained.

The first chapter describes the complications that arise during the extraction and treatment of oil, as well as the reasons and the mechanism of these problems and methods for resolving them.

In the first paragraph of the chapter, the review of literature sources in the field of experience in combating ARP sediments is studied. The effects of asphaltene-resin-paraffin sediments were discussed, and the causes of sediments were demonstrated. The mechanism of formation of asphaltene-resin-paraffin deposits as well as the ways of overcoming problems have been studied. Complex reagents consisting of depressants, inhibitors and demulsifiers have been investigated to improve the product fluidity and prevent the formation of ARPD in wells and pipelines. The results revealed that using complex reagents inhibits the creation of stable water-oil emulsions that affect the oil's viscosity, enhances the oil's rheological characteristics and fluidity, reduces the intensity of the formation of ARPD.

In the second paragraph of the chapter, the causes and conditions of salinization processes in oilfield conditions, the mechanism of salinization, and the causes of calcium carbonate and calcium sulfate sedimentation are described in detail. Experience with combating inorganic salt deposition has demonstrated that the most efficient solutions are based on salt deposition avoidance. Salts are prevented using a variety of approaches, depending on their composition, the nature of salinization, and the location of inorganic salts deposition. The components of compositions and reagents used to prevent inorganic salinization by chemical methods, as well as methods of acquiring them, and their mechanism of action are explained.

The chapter's third paragraph discusses an analytical assessment of oil emulsion demulsification and defines the direction of perspective chemicals in terms of demulsifier action. Modern reagents - demulsifiers are non-ionic surfactants. Substances with a mobile hydrogen atom are present as part of the hydrophobic part of the surfactant. Water, water-oil and oil-soluble demulsifiers are widely used in oil dehydration plants.

The second chapter presents the results of the creation and testing of new components for oil extraction and preparation. New inhibitors based on solvents, surfactants, and products of condensation of alkenyl phenol with formaldehyde -asphaltene-resin-paraffin oils -NDP-1, NDP-2, NDP-3, NDP-4, NDP-5, NDP- 6 and ND-NDP-1 and the results of their laboratory tests are reported in the first half of the second chapter [16].

Distillation residues of condensate and isopropyl alcohol with densities of 763 and 815 kg/m^3, as well as diesel fuel were used as solvents. A polyhydric alcohol polymer with alkylene oxides was chosen as polymer, and a phosphorus containing acid ester produced through synthesis was chosen as the surfactant. The created compositions are conventionally called NDP-1, NDP-2, NDP-3, NDP-4, NDP-5, NDP-6 and ND-NDP-1.

The NDP-1 composition is based on SFM, condensate and nanoscale (50 nm aluminum) powder. NDP-2 composition includes polymer and condensate of polyhydric alcohol with alkylene oxides, acid ether and condensate containing phosphorus with NDP-3 composition, and polymer of polyatomic alcohol with alkylene oxides and diesel fuel of NDP-4 composition. Although the components included in the NDP-5 depressor are the same as the components included in the NDP-2 composition, the mass ratios are different. NDP-6 depressor is made upof an alkylphenol-formaldehyde condensation product, condensate and nanoscale powder. The composition of ND-NDP-1 includes the product of condensation of alkylphenol with formaldehyde, a polymer of polyhydric alcohol with alkylene oxides, a cubic residue of isopropyl alcohol and a raffinate mixture of benzene reforming. It can be used both as a depressant for paraffinic and viscous oils, and as a demulsifier for stable water-oil emulsions demulsification.

The presence of a surfactant in the composition reduces the surface tension at the ARPD-solvent border, increasing the solubility efficiency and ARPD destruction. The presence of solventing components in the solvent causes the dispersed asphaltene and paraffin particles to solvate, preventing them from adhering together.

Individual inhibitory qualities are not present in the components used in the compositions. They have inhibitory and depressant properties against asphaltene-resin-paraffin oils, due to the synergistic impact in the composition.

The components are added to the flask in prescribed mass ratios and stirred at room temperature for 0.5-1.0 hours to prepare synergistic compositions. The process continues until a red brown to dark red clear liquid is obtained.

The efficiency of the developed ARPD inhibitors was tested on emulsified oils taken from wells 680 and 690 located on the area of the OGPD named after N.Narimanov. The results obtained are shown in Figure 1.

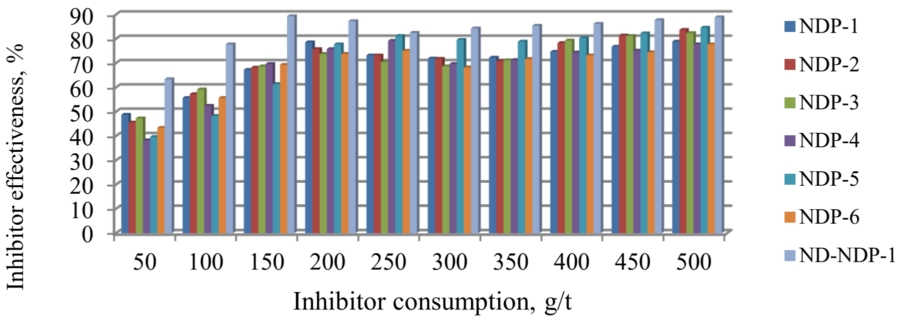

Figure 1. Dependency between consumption and efficiency of inhibitors

Laboratory investigations to determine the depressant properties of NDP-1, NDP-2, NDP-3and NDP-6 additives in oil produced from well 680 revealed that at 50 g/t they are extremely effective. At a consumption rate of 100 g/t, the NDP-2 reagent shows high efficiency as a depressant in this oil. Higher efficiency of depressants NDP-5, NDP-6, ND-NDP-1 is observed at a consumption of 10 g/t. In these cases, increasing consumption has the opposite effect. Pour point depressants appear to influence oil mainly through the adsorption process under these circumstances. Due to the adsorption mechanism, the additive consumption is minimal and generates a monomolecular layer on the surface of paraffin crystals in oil.

The viscosity-flow rate dependence was studied at different temperatures (15, 17, 19 and 25 ºC). Oil from OGPD named after N.Narimanov was treated 10with NDP-1 at 30; 50; 70 and 100 g/t and its viscosity was determined at the indicated temperatures. Curves were created based on the obtained results. The results showed that as the amount of pour point depressant in the oil increased, the cost of viscosity decreased. The viscosity of the oil treated with the depressant drops more rapidly as the temperature rises.

The effectiveness of the inhibitors was also tested on an oil sample taken from well 446 of the Narimanov OGPD. This well has a daily output of 5 tons. The oil sample taken from the well has a density of 0.899 kg/m3, a paraffin content of 19.8%, and anasphaltene content of is 2.65%.

For comparison, the СНПХ-2005 reagent, which is currently used in well No. 446 of the OGPD named after N. Narimanov was taken. Consumption of СНПХ-2005 reagent in well No. 446 of OGPD named after N. Narimanov is 300-700 g/t. A comparative analysis of the effectiveness of ND-NDP-1 and СНПХ-2005 inhibitors in the oil sample taken from well No. 446 of OGPD named after N. Narimanov showed that ND-NDP-1 reagent in well oil 446 demonstrated 89,7% efficiency at 200 g/t consumption. The efficiency of СНПХ-2005 reagent at that cost was 73.6%. While ND-NDP-1 reagent is 90.1% efficient at 250 g/t consumption, СНПХ-2005 is 81.8% efficient at 250 g/t consumption.

The ND-NDP-1 reagent's high efficiency is owing to the ability of the reagent in the ND-NDP-1 reagent's composition to operate as a demulsifier and wax deposition inhibitor. The demulsifying agent in the reagent breaks down the water-oil emulsion and prevents the production of asphaltene-resin-paraffin crystals by dissolving both the salts and the mechanical impurities in the oil with water. The inhibitory ingredient in the composition prevents both adhesion and cohesion of asphaltene-resin-paraffin molecules, keeping them in suspension. Ingredients also have a depressant effect as well. From the results of laboratory tests of the developed new compositions on oils taken from different fields, it can be concluded that the new compositions are effective against ARPD by demonstrating high surface activity. The ND-NDP-1 composition is especially active, acting as a demulsifier, a depressant, and an ARPD inhibitor at the same time.

From all this it can be concluded that the selection of depressant for any oil should be done on an individual basis.

New effective pour point depressant has been developed to reduce the freezing point and viscosity of oil during oil extraction, primary treatment and transportation [7]. The main goal is to create a new effective depressant additive that can be used to lower the freezing point and viscosity properties of high paraffin oils during oil production, transportation and storage, as well as to expand the raw material base and range of depressants based on various hydrocarbon additives.

Flexoil CW 288 reagent manufactured by Champion Technologies is used as a depressant component for the preparation of the depressant additive. The addition of Flexoil CW 288 reagent, which contains a high molecular weight compound-polymer, reduces the surface tension at the asphaltene-resin-paraffin precipitate-solvent boundary, increasing the ARPD solubility efficiency, as well as prevents the formation of crystalline hydrocarbon structure, causing the temperature drop.

The composition retains a stable gas condensate (SGC, TU 51-05751745-09-97) as an organic solvent, and a light phlegm of catalytic cracking (LPCC) as an aromatic solvent. SGC and LPCC solvents are mixed to prepare depressant additives. The solvent mixture is supplied with Flexoil CW 288 reagent and mixed with a mechanical stirrer at room temperature. Stirring is continued until a homogeneous solution is formed.

As a solvent from liquid pyrolysis products from E-10, E-11 oil resins (Specification AZS 340-2009), as a heavy pyrolysis resin from A product (Specification AZS 344-2009), as well as n-heptanol (TU 6-09-2652 -65), n-octanol (TU 6-09-5533-69) and n-nonanol (TU 6-09-3331-78) were also used to develop 12 flexoil-based depressant additives [17].

Flexoil CW 288 reagent is added to the pyrolysis resin and heated to 40-50°C, stirring with a mechanical stirrerto prepare depressant additives. Stirring and heating are both continued until a homogeneous solution is formed. The heating is turned-off as soon as the mixture becomes homogeneous and the mixture is cooled to room temperature while being stirred. After alcohol addition, the stirring continues, until a homogeneous solution is formed. The depressant properties of additives were determined by determining the effective viscosity (on a rotational viscometer "Reotest 2") and freezing point (GOST 20287-74). The depressant effect is calculated by the formula (ΔT) ΔT = (Tcopp - Tdapp.), where Tcopp-crude oil pour point, Tdapp - pour point of oil with depressant additive, °C. The depressant additive dosage is 0.02-0.04% by weight of the oil.

The depressant properties of the developed additives were determined for the oil collected from the No. 690 production well of the Azneft PU named after N.Narimanov. The oil was heated to 60°C and mixed with paraffin hydrocarbons that precipitated in the pipes extracted from the wells. This oil contains ~ 22% paraffin hydrocarbons and has a freezing point of + 31°C. The effective viscosity of the crude oil was determined at temperatures close to freezing point (+ 35°C and + 40°C). Oil viscosity at + 35°C is 21.7 mPa·s, whereas at+ 40°C it is- 17.4 mPa·s.

The developed depressant additives reduce the freezing temperature of the oil sample taken from the production well No 690 of the OGPD named after N. Narimanov (ΔT = 29-38), at + 35°C from 21.7 mPa·s to 9.4 mPa·s and at + 40ºC it decreased from 17.4 mPa·s to 6.7 mPa·s. The inhibitory effect of ARPD is 60.9%.

The effect of depressors on the rheological properties of the oil sample taken from the No.71 production well of the OGPD named after N. Narimanov was also investigated. The tests were performed on Anton Paar Rheolab QC at 25 ºC, 30 ºC, 35 °C and 40 ºC compared to crude oil. Curves of dynamic viscosity and shear stressdependency on the shear rate were created based on the research. According to the results, the oil in this well displays non-Newtonian pseudoplasticity. When the reagent was added to the oil at a consumption of 400 g/t, the viscosity of the oil reduced sharply and remained constant regardless of the velocity gradient. The dependence of the shear stress on the shear rate was a straight line passing through the origin, indicating the change from non-Newtonian pseudoplastic to Newtonian once the reagent was added.

According to experimental tests, the newly developed depressant additives reduce the freezing temperature and viscosity properties of high paraffin and asphalten-resin oils, allowing to improve the rheological properties by converting non-Newtonian pseudoplastic oil to Newtonian oil.

The second paragraph of the second chapter discusses the components used to inhibit various salt deposits in oilfield equipment and pipelines and the results of their laboratory studies.

Compounds based on nitrogen compounds, hydrochloric acid and anionic inactive polymers have been developed against carbonate and sulfate deposits [8]. The key components in the preparation of salt deposition inhibitors and salt solvents were water-soluble polymer-type compounds and inhibited hydrochloric acid. amino alcohols and ammophos, carboxymethylcellulose (CMC-600) and polyacryamide (PAM) were used as nitrogen-containing compounds as anionic polymers.

The produced reagents have a long-term effect as a salt scale inhibitor due to their adsorption-desorption features and are highly effective. Surface treatment with an inhibitory composition containing hydrochloric acid reduces surface tension at the "rock-oil-inhibitor solution" interface. In this case, the roughness of the rock increases, due to the chemical interaction of hydrochloric acid with carbonate minerals. Hydrochloric acid alters the wettability of the rock by removing the oil layer from its surface. This ensures that the salt deposition inhibitor is absorbed consistently and completely. The aqueous solution of the amine compound has a negative effect on the formation of salt layers by reducing the tension at the interface between the phases. The anionic polymer prevents the formation of sulfate and carbonate salts by sequestering calcium ions. The results of the inhibitory effect on calcium carbonate water are shown in Figure 2.

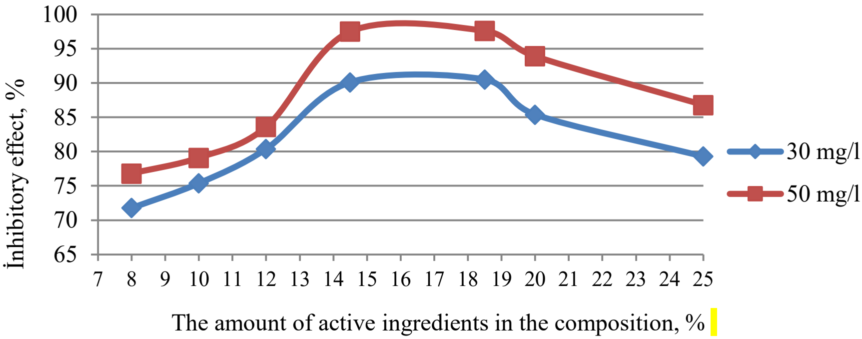

Figure 2. Determination of the protective effect of the inhibitor in calcium carbonate water

The effect of inhibiting salt precipitation by low (4, 6 and 8% by weight) and high (17 and 20% by weight) compounds of nitrogen-containing compounds has been studied. Nitrogen content of less than 10% and more than 15% of the compound leads to a weakening of the relevant properties of salt deposition inhibitors. The incapacity of nitrogen-containing compounds to adapt to water with high mineral concentration explains why their inhibitory activities deteriorate when their content exceeds 15%. At a dose of 50 mg / l, carbonate precipitate inhibitors with an ideal active ingredient level of 14,5-18,5% show a 98 percent protective efficacy.

The next work involved developing a composite reagent for removing salts from the transport of hydrogen-sulfide produced water from a number of production wells in the 1st area of the Garachukhur field as well as studying and applying it as a neutralizer and salinity inhibitor. Depending on the existing technological conditions in the mine, a composition has been created that has an inhibitory effect against sulfide sediments formed as a result of mixing and ion-exchange reactions during the extraction of produced water (along with oil) [4, 18]. The composition includes raw materials such as sodium hypochlorite (GOST11086-76), ammophos, CMC-Na-1000. The composition, which demonstrates the inhibitory properties of hydrogen-sulfide-containing oil-bearing aquifers and anti-salinization, is conventionally called NDI-1.

The NDI-1 reagent is a bactericidal composition, soluble in water. Hydrogen-sulfide neutralizer and salt scale inhibitor effects of NDI-1 reagent have been studied in both formation water and model formation waters in accordance with RD 39-0147276018094. The amount of H_2S in a sample of H_2S produced water is determined iodometrically. At the consumption rate of 300 g/t, the composition exhibits a maximum neutralizing effect and a 98.5% inhibitory effect against salinity at the same cost. The given in Table 1.

Table 1

Neutralizing and anti-salinity effects of NDI-1 reagent in oil reservoir waters taken from production wells in the 1st area of Garachukhur field

Well№, horizon	Well watering, %	Effects at variousconsumption (g/t) of compositions, in %						
		10	25	50	100	200	250	300
250 IV	99,6	10,8* / 35,0	23,1 / 52,5	31,5 / 63,0	53,5 / 72,5	75,0 / 81,5	86,5 / 93,5	100,0 / 98,5
857 IX	97,7	19,4 / 42,0	39,3 / 63,0	53,5 / 75,6	80,2 / 83,5	90,0 / 92,5	100,0 / 98,0	100,0 / 98,0
402 VII	99,6	42,5 / 28,3	68,0 / 35,1	87,5 / 43,5	100 / 56,5	100 / 68,0	100 / 75,8	100 / 90,0
275 VIII	99,2	13,0 / 35,1	21,5 / 43,5	32,1 / 56,5	58,5 / 70,0	76,0 / 81,5	100 / 90,0	100 / 98,0
279 QÜG	98,4	18,5 / 38,5	27,5 / 47,0	41,0 / 58,0	60,0 / 73,5	78,0 / 85,0	100,0 / 93,0	100,0 / 98,0
302 IV	95,9	45,0 / 41,5	73,0 / 55,0	100,0 / 67,5	100 / 75,0	100 / 85,0	100 / 90	100 / 96,0
318 V	99,4	40,0 / 42,5	65,0 / 57,0	100,0 / 70,0	100,0 / 76,5	100,0 / 83,0	100,0 / 95,0	100,0 / 99,0
879 V	98,8	75 / 45,3	100 / 58,5	100 / 71,5	100 / 78,0	100 / 85	100 / 96,0	100 / 98,0

** in the form a neutralizing effect, in the denominator an inhibitory effect against salinity*

The reagent's effects on oil reservoir water retrieved from individual wells vary as well. As can be seen from Table 1, the consumption of NDI-1 reagent as a neutralizer in a chloride-calcium-type formation water (well 250) with a relatively high content of hydrogen sulfide (306 mg/l) is 300 g/t as a neutralizer, and the inhibitory effect against salinity at the same cost - 98.5%.The complete neutralization of the reagent sodium-hydrocarbonate type aquifers and the inhibitory effect against salinity were determined at relatively low costs - 100-200 g/t. Reagent consumption was investigated at concentrations ranging from 10-300 mg/l, depending on the type of produced water.

Thus, studies once again confirm that NDI-1 reagent is multifunctional, it is recommended to use it as a neutralizer in hydrogen-sulfide formation waters for oil extraction, preparation and transportation systems.

The third paragraph of the second chapter deals with the development and study of compositions to ensure the dehydration and desalination of high-viscosity oils, as well as to improve their rheological properties. A number of research have been undertakenas a result of the analysis of difficult-to-break down water-oil emulsions to investigate the factors that ensure the high quality of commercial oil, depending on the necessary justifications [1]. Composition demulsifiers were developed based on non-ionogenic surfactant laprol-3603-2-12 and laprol 4202-2B SFM, isopropyl alcohol and methyl alcohol and non-demulsifying additives [3]. Laprol 4202-2B-30 (TU 2226-039-0576680), laprol-3603-2-12 were used in the preparation of the composition for deep dehydration and desalination of water-oil emulsions as a block joint polymer based on ethylene- and propylene oxides ethylene glycol. Methanol (GOST 2222-95) and isopropyl alcohol (GOST 9805-84) were used as solvents.

The developed compositions of demulsifiers are marked ND-1A - ND-26A. ND-1A and ND-2A from a 50% solution of a mixture of laprol 4202 and laprol 3603-2-12 in methanol and isopropyl alcohol, respectively, ND-3A and ND-4A laprol 3603-2-12 50%

solution in methanol and isopropyl alcohol, respectively, ND-5A and ND-7A laprol-4202-2B in 50% solution in methanol and isopropyl alcohol, respectively, ND- 6A and ND-8A are made up of 45% laprol 4202-2B, 5% basic substance and 50% methanol and isopropyl alcohol, respectively, and ND-9A is 45% laprol 3603-2-12, 5% basic substance and 50% isopropyl alcohol.

For the preparation of oleic acid complexes oleic acid (TU 10-04-02-62-98), morpholine (TU 6-09-649-85), piperidine (TU 6-09-3673-74), pyridine (GOST 13647-78), triethanolamine (TEA) TU 2423-061-05807977-2002 were used [8, 10, 14].

The process of synthesis is described in general because complex salts of oleic acid with different amines are synthesized in the same way in different proportions, and it is considered expedient to give their conventional names. Oleic acid is introduced to an amino material in a closed flask with a mechanical stirrer, and is stirred on a regular basis. The reaction mixture is stirred continuously at 60^0C for 2-2.5 hours. When the reaction is completed and the acquired substance is cooled to room temperature, it solidifies into a solid mass. The synthesized quaternary amine based on triethanolamine is conditionally called TEAOL, morpholine based quaternary amine OTMK, piperidine based quaternary amine OTPPK and pyridine based quaternary amine OTPK.The synthesized amine compounds are amphiphilic. This amphiphilic structure, which is characteristic of surfactants, is due to the presence of a polar amine group and a non-polar hydrocarbon radical in the quaternary amine salts. The dissociation of amine salts results in the formation of an anion consisting of a cation and an organic acid residue containing an amine group. Quaternary amines incorporate surface activity properties such as adsorption to the phase boundary, surface layer formation, micelle formation, and etc. It should be noted that the compositions based on the obtained complex salts contain quaternary amines in the form of a 75% solution in methanol and isopropyl alcohol. Therefore, in all cases, the obtained solids are dissolved in methanol and isopropyl alcohol and taken as a 75% solution in the calculations, respectively, ips-TEAOL, met-TEAOL, ips-OTMK, met-OTMK, ips-OTPK, met-OTPK, ips-OTPPK, called met-

OTPPK. Alcoholic solutions of the synthesized quaternary amines and conventionally called ND-10, new compositions based on a 47% solution of laprol 4202-2B-30 in isopropyl alcohol were developed.

The composition of demulsifiers based on complex salts is given in Table 2.

Table 2

Composition of demulsifiers based on complex salts

Composition	The amount of quaternary amines in alcohol,%		The amount of ND-10A in the composition, %
ND-11A	ips-TEAOL	5	95
ND-12A	Met- TEAOL	5	95
ND-13A	ips-TEAOL	3	97
ND-14A	Met-TEAOL	3	97
ND-15A	ips- OTMK	3	97
ND-16A	Met- OTMK	3	97
ND-17A	ips- OTMK	5	95
ND-18A	Met- OTMK	5	95
ND-19A	ips- OTPK	3	97
ND-20A	Met- OTPK	3	97
ND-21A	ips- OTPK	5	95
ND-22A	Met- OTPK	5	95
ND-23A	ips OTPPK	3	97
ND-24A	Met- OTPPK	3	97
ND-25A	ips- OTPPK	5	95
ND-26A	Met- OTPPK	5	95

Developed ND series of demulsifiers, which may break down water-oil emulsions in the initial primary treatment of oil, are effective reagents that are soluble in both oil and water.

The compositions quickly break down oil emulsions, create a clear boundary between the separation of water and oil phases, ensure a minimal quantity of residual water in the oil phase, prevent the formation of an intermediate layer. Physico-chemical properties of the developed demulsifying compositions were studied. The demulsifying properties of the prepared compositions were studied in samples of high-viscosity oil emulsions. Known procedures for dehydration of water-oil emulsions were used to test the demulsifying activity of the produced compositions. The demulsifiers available for testing are added to the water-oil emulsion in specific amounts and stored in the thermostat for a period under specific conditions. The amount of residual water in the oil after demulsification was determined by the Dina-Stark method [GOST-2477-2014]. Laboratory tests of the developed compositions were carried out with continuous water-oil emulsions taken from the Absheronneft, Neft Dashlari, N. Narimanov and H.Z.Taghiyev OGPD fields. The results of laboratory tests of OGPD oil named after H.Z. Taghiyev are shown in Figure 3.

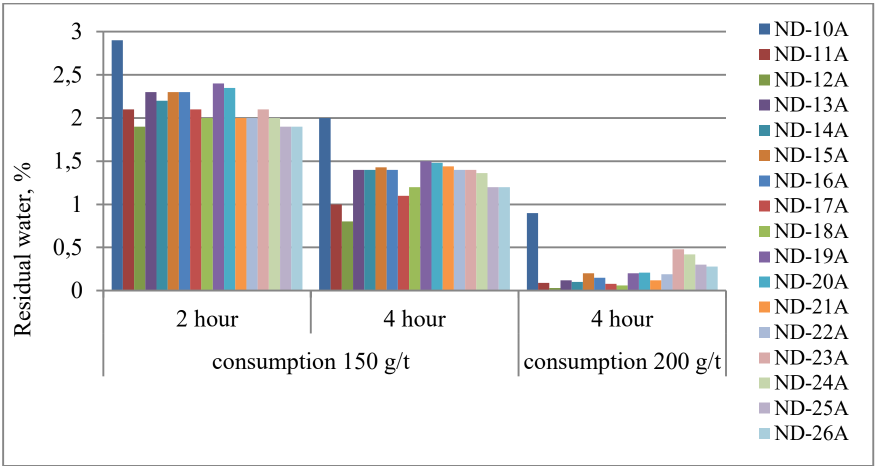

Figure 3. Results of the effect of demulsifiers on the dehydration of oil produced in the Buzovna-Mashtagha field of the OGPD named after HZ Taghiyev

Studies have been conducted on the initial treatment of water-oil emulsions and the selection of appropriate effective demulsifiers for the dehydration of hard-to-breakwater-oil emulsions (HBWOE) formed during [12]. The selection of effective demulsifiers for the initial treatment of the oil was made by bottle-testing in comparison with Dissolvan -4411. ND-type ND-10A, ND-12A, ND-18A) samples were selected as demulsifiers. A hard-to break water-oil emulsion was sampled from a vertical stationary reservoir (VSR) at a depth of 3 m (bottom) and treated with demulsifiers. The amount of primary water in HBWOE was 25.95%, and mechanical mixtures were 11.2%. A bottle-test method was used to select a high-effect demulsifier.

Tests for demulsification of HBWOE were carried out with ND-12A, ND-10A, ND-18A reagents. Demulsifiers were emulsified at a consumption of 200 g / t. The demulsification time was 6 hours and the temperature was 71ºC. After demulsification, the amount of water in the oil decreased to 0.41%, 1.58% and 0.97%, respectively. Thus, the ND-12A demulsifier is more effective than other modifications due to its ability to affect the emulsion. For this reason, ND-12A reagent was used as a demulsifier during subsequent bottle tests. Reagent ND-12A was used in 4 concentrations to determine the optimal specific consumption of the demulsifier: 150 g / t; 200 q / t; 250 q / t; 300 q / t. The results of bottle tests were 0.69%, 0.41%, 0.00% and 0.00%, respectively. According to these results, the consumption of demulsifier at 250 g / t is the optimal specific consumption rate for ND-12A. For this reason, the dosing of ND-12A demulsifier was carried out at a rate of 250 g / t during the next bottle-tests. The kinetics of the fragmentation of HBWOE taken from VSR was studied. The results of the study showed that the decomposition of HBWOE is practically completed within 7 hours of precipitation at a temperature of 71ºC. Similar bottle-tests were performed at 61ºC and 65ºC and with a settling time of 5 hours. In these cases, the amount of residual water was 0.0% and 0.43%, respectively. When the settling period is 7 hours, the amount of residual water is reduced to a minimum in both cases. The oil phase is practically pure up to the exact border of the phase separation, according to layer analysis (interval analysis) of the dewatering depth of the HBWOE sample. It should be noted that bright green thin crystalline streaks were observed on the inner surface of the chemical glass in the lower part of the liquid (i.e., in the zone of water mixed with mechanical impurities). These thin bands belong to the iron compounds and are located in the form of particles in the adsorption coatings around the water globules in the HBWOE before the demulsification process. Due to the high surface activity of the ND-12A demulsifier, the iron particles were squeezed out of the coatings as a result of adsorption competition and re-adsorbed on the surface of the chemical glass in layers. The presence of particles within the adsorption coating enables the water-oil emulsion's high stability. Therefore, the displacement of the particles from the adsorption coating around the water globules facilitates the thermochemical decomposition of the highly stable emulsion. This is conclusive proof that the ND-12A demulsifier is superior to the Dissolvan-4411.

ND-12A was selected as a high-effect demulsifier. Unlike the Dissolvan-4411, the ND-12A demulsifier allows for the almost complete demulsification of HBWOE with an accurate phase separation boundary, with minimal residual water in the oil and the normal amount mechanical impurities.

For the initial treatment of oil and water for general water-oil emulsions of S.Nurjanov, Zapadnaya Prorva, J.Dosmukhambe-tovskoye and Aktobe (Republic of Kazakhstan) fields, research work was carried out on the selection of the appropriate effective emulsifier [5]. The research was carried out in comparison with the base demulsifier F-929 (made in Japan) used in oil refining technology. In addition, the compatibility (or compatibility) of the developed ND type demulsifier with the base demulsifier has been studied.

A method and composition for the separation of stable oil emulsions of oil-sludge type have been developed [6, 11]. According to the method, water and a non-ionic demulsifier are introduced to a continuous oil emulsion as a mixture with other reagents, heated and mixed. As a non-ionic demulsifier, it contains a block polymer of ethylene- and propylene oxide based on glycerin with a molecular weight of 3000-5000, and as a second secondary reagent it is mixed with liquid glass (Na2SiO3) alkali (NaOH) in a ratio of 9: 1 (by mass). Laprols 3003, 3603-2-12, 5003-2B-10 are obtained from the polymerization of propylene oxide with glycerin and then with the ethylene oxide. Their molecular weight is 3000-300, 3600-300, 5000-300, respectively. Preparation of demulsifiers laprol 3003 or laprol 3603-2-12 or laprol 5003-2B-12 in a ratio of 40:60 (in% by weight) with light gas oil (conventional names I, II and III), as well as Flexoil CW-288 reagent with laprol 3003 or laprol 3603-2-12 or laprol 5003-2B-12 in a ratio of 20:20:60 (in% by weight) with a mixture of light gas oil (equivalent names IV, V and VI) room is carried out by stirring until complete dissolution is obtained at room temperature. Flexoil CW-288 reagent has depressant properties but does not have the ability to demulsify. When this reagent is mixed with laprol equivalent, however, its has a strong demulsification ability. In this scenario, it appears that laprol and Flexoil CW-288 have a synergetic effect. The second reagent is prepared by mixing the liquid glass with alkali in a ratio of 9: 1 (by weight).

When non-ionic demulsifiers are added into an oil sludge emulsion, they concentrate around the phase separation border. The second reagent (wetting agent) is adsorbed on the surface of mechanical mixtures, hydrophilizes it and displaces the adsorbed oil emulsifiers from the surface of mechanical mixtures contained in the emulsion-dispersed coating of the water droplet.

A demulsifier with high demulsification capacity has been developed for deep dehydration and desalination of oil at low specific consumption in high temperature processes in oil refineries [13, 16]. The demulsifier consists of a non-ionizing surfactant, sodium naphthenate obtained from the alkali treatment of light petroleum products, in addition, the anionic surfactant that keeps one percent aqueous solution of carboxymethylcellulose in the following proportions (mass%) of components: non-ionizing surfactant 1, 0-4.0%, sodium naphthenate obtained from alkali treatment of light oil products 30-40, carboxymethylcellulose one percent aqueous solution of sodium salt.

The low content of non-ionizing surfactant (1-4% by weight) leads to its weak demulsifying activity. The presence of one percent aqueous carboxymethylcellulose solution in sodium, on the other hand, boosts the demulsification activity and, consequently, the desalination effectiveness. An aqueous carboxymethylcellulose solution functions as a slippery lubricant between the component particles. This substance also possesses stabilizing and binding capabilities.

The third chapter deals with the application of the developed methods in mining conditions. In order to implement the application in this chapter, wells were classified based on indicators of daily production of wells, inter-repair period, production parameters during the inter-repair period and wells were selected on the basis of hyperbolic distribution [15]. It was considered expedient to evaluate the selection of objects for application according to the above-mentioned criteria. A total of 52 paraffin from the SDXZ field of OGPD named after N.Narimanov were inspected for this purpose. Based on the distribution of wells according to the distribution of the above criteria, 6 wells belonging to groups I and II were selected for the application according to the production parameters, and for the period between repairs, 6 wells were selected.

From the selected wells, mining tests of a new ND-NDP-1 reagent developed on the basis of laboratory tests against asphaltene-resin-paraffin deposits in the pump compressor pipes of well No. 446 in the SDXZ field of the OGPD named after N.Narimanov were carried out. As a result of the application, the amount of asphaltene-resin-paraffin sediments in the pump compressor pipes was reduced and the well maintenance time was doubled. Due to the reduction in the number of repairs, 87.0 tons of additional oil was produced. The well was transferred to group II according to the production indicator between the repair period and the inter-repair period. An act on the application has been received.

Mining test was conducted on the ND-12A demulsifier, which was developed using surfactants and solvents for dehydration and desalination of oil emulsion. The results of the test show that the quality indicators of the oil prepared with ND-12A demulsifier after settling for 8 hours met the requirements of AZS 115-2004. The results were positive, and the prepared oil was characterized as group I oil in accordance with the requirements of AZS 115-2004 and handed over to the Oil Pipelines Department.

The ND-12A demulsifier developed on the subject was successfully tested at the demulsification unit of the Azneft PU Absheronneft OGPD located in the Complex Oil Treatment and Transportation Area and based on the results it was recommended to be applied in other OGPDs.

CONCLUSIONS

1. New inhibitors and depressants have been developed for asphalten-resin-paraffin sediments.

- Inhibitors prevent the formation of AQP sediments by demonstrating an efficiency of 83.3% at a rate of 150 g/t.

- Depressors designed to reduce the freezing point and viscosity of high-paraffin oils during oil extraction, transportation and storage also have an inhibitory effect of 60.9%, indicating depressing effect ΔT = 29-38 ^oC.

2. Inhibitors of salt deposits of various origins have been developed:

- Inhibitors of carbonate and sulfate deposits with an optimal content of active substances of 14.5-18.5% have a 98% protective effect at a consumption of 50 mg/l.

- The composition used to prevent the formation of mainly sulfide-containing sediments have a maximum neutralizing effect at a rate of 300 g / t, and against salinization have a inhibitory effect of 98.5% at the same cost.

3. Compositions with demulsifying and deep desalination properties of water-oil emulsions of different deposits have been developed.

- Demulsifiers developed for stable oil emulsions fully meet the requirements of AZS 115-2004 Group I oil by dehydrating oils from various oil fields in a short period of time with 30-250 g/t rows up to 0.03% and with basic demulsifiers in terms of both reagent consumption and demulsification time demonstrate higher quality compared.

- Methods and compositions for the decomposition of durable oil emulsions of oil-sludge type have been developed. The amount of residual water, salts and mechanical impurities remaining in the oil as a result of treatment of cuttings with demulsifiers meets the requirements of GOST 51858-2002.

- The new demulsifier developed for deep dehydration and desalination of oil in refineries has reduced the amount of salts to a minimum by consuming 15 mg less than the base demulsifier -30 mg/l.

4. As a result of application of ND-NDP-1 inhibitor in the well selected on the basis of daily production of wells, inter-repair period, production parameters during the inter-repair period, the amount of asphaltene-resin-paraffin sediments in pump compressor pipes decreased and well inter-repair period increased by two times. Due to the reduction in the number of repairs, 87.0 tons of additional oil was produced.

5. The quality indicators of the oil prepared as a result of application of ND-12A demulsifier under mining conditions, which was developed using surfactants and solvents for dehydration and desalination of oil emulsion, met the requirements of AZS 115-2004 and were delivered as group 1st oil given.

Main content of dissertation reflected in the following works:

1. Agha-zadeh, A.D., Samedov, A.M., Alsafarova, M.E., Akbarova, A.F. Investigation of factors ensuring high quality of commercial oil as a result of analysis of difficult-to-decompose water-oil emulsion depending on the necessary arguments // “Ministry of Education of the Republic of Azerbaijan, Azerbaijan State University of Oil and Industry, Israfil Guliyev's 100th anniversary Materials of the conference on "Actual problems of development",- Baku-2017, - pp. 162-174

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

[8, 14, 15, 18] - performed independently.

[1, 2, 3, 4, 6, 9, 10, 11, 12] - statement of the problem, research work and analysis of the results.

[5, 7, 13, 16, 17] - the shares of the authors are the same.

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