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# STUDY OF THE EFFECTIVENESS OF THE DEMULSIFIER COMPOSITION ON THE DESTRUCTION OF LOCAL OIL-WATER EMULSION

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The effect of the demulsifier composition on the destruction of local oil-water emulsions was studied in this work. One of the urgent problems in the development of deposits is to increase the efficiency of the preparation of hydrocarbons in the fields. The solution of this problem makes it possible to significantly increase the degree of oil preparation, reduce the loss of hydrocarbons with drainage waters, thereby improve the environment and bring additional profit to the enterprise. A complex of theoretical and experimental studies was used, consisting in generalization and analysis of literary data, as well as by analogy, modeling, quantitative and qualitative observation, laboratory tests, conducting a multifactorial experiment, data processing using methods of mathematical statistics. Information processing tools based on computer software products were used. The results of laboratory tests of oil-water emulsion, physico-chemical analysis of water composition, new chemical reagents-demulsifiers recommended for field testing are presented. It can be concluded, based on the research conducted, that the demulsifier EASY-DE03-15 is the most effective reagent for dehydration of oil-water emulsions and desalination of MIX samples.

**Keywords:** oil, demulsifier, oil-water, emulsions, efficiency, deposit, reagent, chemistry.

# ИССЛЕДОВАНИЕ ВЛИЯНИЯ СОСТАВА ДЕЭМУЛЬГАТОРА НА РАЗРУШЕНИЕ МЕСТНЫХ ВОДОНЕФТЯНЫХ ЭМУЛЬСИЙ

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В работе изучена эффективность состава деэмульгатора на разрушение местных водонефтяных эмульсии. Одной из актуальных проблем при разработке месторождений является повышение эффективности подготовки углеводородов на месторождениях. Решение этой задачи позволяет значительно повысить степень подготовки нефти, снизить потери углеводородов с дренажными водами, тем самым улучшить экологию и принести дополнительную прибыль предприятию. Для решения поставленных задач использовался комплекс теоретико-экспериментальных исследований, заключающийся в обобщении и анализе литературных данных, а также по аналогии, моделировании, количественном и качественном наблюдении, лабораторных испытаниях, проведении многофакторного эксперимента, обработка данных с использованием методов математической статистики. Использовались средства обработки информации на базе компьютерных программных продуктов. Приведены результаты лабораторных испытаний водонефтяной эмульсии, физико-химического анализа состава воды, новых химических реагентов-деэмульгаторов, рекомендованных для полевых испытаний. На основе проведенного исследования установлено, что деэмульгатор EASY-DE03-15 является наиболее эффективным реагентом по обезвоживанию водонефтяных эмульсий и обессоливания MIX пробы.

**Ключевые слова:** нефть, деэмульгатор, водонефтяные, эмульсия, эффективность, месторождение, реагент, химия.

# ЖЕРГІЛІКТІ СУ-МҰНАЙ ЭМУЛЬСИЯЛАРЫН БҰЗУҒА АРНАЛҒАН ДЕЭМУЛЬГАТОР ҚҰРАМЫНЫҢ ТИІМДІЛІГІН ЗЕРТТЕУ

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Жұмыста жергілікті су-мұнай эмульсияларын жою үшін деэмульгатор құрамының тиімділігі қарастырылды. Кен орындарын игерудегі өзекті мәселелердің бірі кен орындарында көмірсутектерді дайындау тиімділігін арттыру болып табылады. Бұл мәселені шешу мұнайдың дайындалу дәрежесін едәуір арттыруға, дренажды сулармен көмірсутектердің жоғалуын азайтуға, сол арқылы экологияны жақсартуға және кәсіпорынға қосымша пайда әкелуге мүмкіндік береді. Қойылған міндеттерді шешу үшін әдеби деректерді жалпылау мен талдаудан, сондай-ақ ұқсастық, модельдеу, сандық және сапалық бақылау, зертханалық сынақтар, көп факторлы эксперимент жүргізу, математикалық статистика әдістерін қолдана отырып өңдеу деректерінен тұратын теориялық және эксперименттік зерттеулер кешені пайдаланылды. Компьютерлік бағдарламалық өнімдер негізінде ақпаратты өңдеу құралдары пайдаланылды. Су-мұнай эмульсиясының зертханалық сынақтарының нәтижелері, су құрамының физика-химиялық талдауы, далалық сынақтарға ұсынылған жаңа химиялық реагенттер-деэмульгаторлар келтірілген. Зертханалық зерттеулердің нәтижелерін талдай отырып, EASY-DE03-15 деэмульгаторының су-мұнай эмульсияларын сусыздандыру және Міх сынамасын тұзсыздандыру бойынша ең тиімді реагент екендігі анықталды.

**Түйінді сөздер:** мұнай, деэмульгатор, су-мұнай, эмульсиялар, тиімділік, кен орны, реагент, химия.

**Introduction.** Currently, the formation of water-oil stable emulsions is observed in most oil fields of Kazakhstan, the destruction of which requires significant material and time costs. Expensive Western-made demulsifiers are mainly used to prepare commercial oil at all fields. There are many factors that stimulate the separation of water from oil, but in practice none of them allows for sufficiently deep dehydration without the use of a demulsifier. As the field is developed, the process of ”aging” of the emulsion changes, the oil-water fraction increases, the ratio of the phase interface and the number of natural stabilizers change. Under these conditions, the choice of a new effective demulsifier is quite important. The spectrum of chemical compounds used as components of demulsifying compositions is quite wide. Foreign manufacturers have in their arsenal up to several dozen compounds of each class, differing in molecular weight, relative solubility, etc.[1].

Today, fundamentally different technological schemes of oil collection and processing operate at the fields, the conditions for processing emulsions and their results differ significantly from object to object, although practically the same emulsion is processed. The variety of technological schemes and equipment used in this case has led to the fact that demulsifiers are selected separately for each object.

Most chemical companies are well trained and equip their representatives with the selection of demulsifiers and bringing the installation to optimal performance. The owners of oil fields themselves do not deal with these issues and invite representatives of other companies to select demulsifiers and develop recommendations for their use. Instead of choosing from hundreds of names of demulsifiers suitable for use only in a specific installation with all its technological features, it is necessary to develop an ideal technological scheme for oil treatment, create effective dehydrogenation equipment based on it and use a demulsifier corresponding to the type of refined oil [2].

Currently used methods of oil extraction have led to the fact that up to 90% of water is extracted with oil, forming stable oil-water emulsions stabilized with natural surfactants and resins [3]. These natural surfactants are asphaltenes, mechanical impurities, as well as heavy paraffins. Other factors stabilizing oil-water emulsions are chloride salts and the hydrogen pH of water in oil [4].

Due to the high stability of these emulsions, their destruction is possible only with the help of demulsifiers. The consumption of the demulsifier is determined by the need to obtain commercial oil with a water content of less than 0.2%, with higher water content, the cost of oil on the world market decreases, and at 1% oil is considered substandard. Since the cost of demulsifiers is quite high, the problem of reducing their consumption by increasing efficiency is very relevant. There are two ways to solve this problem [3].

1. The first, chemical-technological, consists in the development of methods for the synthesis of new reagents with demulsifying ability. The level of these developments at a number of enterprises has reached quite a satisfactory level.

2. Deeper dewatering of oil at low costs can be achieved with the help of demulsifiers consisting

of various chemical compounds, provided that a synergistic effect is manifested between these compounds. The development of such synergistic demulsifying compounds is the second way to increase their effectiveness. However, the scientific basis of this method of increasing the effectiveness of demulsifiers has not yet been developed [5].

It is important to emphasize that the demulsifiers themselves are chemical surfactants obtained by complex multi-stage chemical synthesis, which consist of several components [6].

The insufficient level of scientific validity of the development of demulsifiers is also evidenced by the lack of systematic studies of the effect on the effectiveness of demulsifiers of the solvent nature of their commercial forms, in the form in which they are supplied to fisheries enterprises that have solutions from 30% to 65% in a certain solvent. Although there is a large number of works on the influence of the nature of the solvent on the speed of physico-chemical processes, there is practically no data on the possible relationship between the effectiveness of demulsifiers and the composition of their commercial forms in the literature. Moreover, in most works with these reagents, the type of solvent is not even indicated. Insufficient attention is also paid to the consideration of the method of introducing a demulsifier into the emulsion in the conditions of field oil treatment [7].

From the above it follows the need for fundamental research of the principles that determine the mechanism of action and effectiveness of demulsifiers. Only after such a study is it possible to solve the problem of optimizing their composition and conditions of the demulsification process. At the same time, the variety of properties of oils, field development systems and demulsifiers puts optimization of their use as an important task, both in terms of technological problems and reducing the cost of reagents [8].

Modern demulsifiers, most commonly used in the demulsification industry, are surfactants that exhibit both hydrophilic and hydrophobic groups. They have almost completely replaced the long-outdated ion-active demulsifiers [9]. When the number of moles of ethylene and propylene oxide changes, chemical compounds are obtained that are balanced in a certain way in terms of hydrophobic and hydrophilic properties and have a high demulsifying ability with respect to the emulsion of a particular oil field. The polymer surfactant, when added to an oil emulsion, is located at the interface between water and oil molecules. Hydrophilic groups focus on water, while hydrophobic groups focus on oil. The best polymer surfactants currently used worldwide are derivatives of alkoxylated materials [10].

It is known that the following basic requirements are imposed on modern demulsifiers: they must have the maximum possible demulsifying activity, be easily biodegradable, non-toxic, cheap and affordable; they must not have bactericidal activity (on which the effectiveness of biological wastewater treatment depends) and corrode metals. It is worth noting that different groups of demulsifiers have not only a number of positive properties, but also various disadvantages. So, some reagents provide separation of pure water, but the emulsion decomposes not fast enough. Other reagents contribute to the rapid destruction of the emulsion, but the wastewater contains a lot of petroleum products [11].

Many reagents are not effective enough to remove mechanical impurities. Therefore, in recent decades, compositions have been developed containing several individual compounds that exhibit a synergistic effect in the mixture, since they can provide the necessary degree of oil dehydration, where the efficiency of demulsifying the mixture of components is higher than the effect of individual components. However, until now, the main practice of developing demulsifiers on the world market is the empirical selection of their composition for water-oil emulsions of specific deposits [12].

It is known that the reagents used to bring oil to marketable condition include demulsifiers, mainly imported from abroad. This, in turn, increases the cost of oil treatment. To date, the issues of determining and applying an effective demulsifier, as well as determining its alternative or reducing its consumption, remain relevant.

The purpose of the study is to determine the effect of demulsifiers prepared using chemical reagents of the domestic EASY-DE brand for the conditions of oil preparation of Meerbush LLP as well as to prove the effectiveness of domestic-made demulsifier application in the oil and water industry.

**Methods and materials.** The methods and techniques of analysis corresponding to the goals and specific tasks of the study were used in the work. The article uses general scientific methods and approaches. To solve the tasks set, a set of theoretical and experimental studies was used, consisting of generalization and analysis of literary data, testing conducted at the deposits of Western

Kazakhstan, as well as by analogy, modeling, quantitative and qualitative observation, laboratory studies, multidimensional experiment, data processing by mathematical statistics methods. In addition, methods of constructing algorithms and flowcharts were used. Information processing tools based on computer software products were used.

The sequence of laboratory tests is as follows:

1. Simulation of the ”bottle test” with determination of laboratory conditions (demulsifier input temperature, separation temperature and time, amount of shaking and oil extraction level for centrifugation);

2. Determination of oil sampling points and composition of oil-water emulsion mixture;

3. Conducting a ”bottle test” of all provided reagents in comparison with the base reagent (used in the field) in different dosages;

4. Determination of the content of chloride salts in oil SUST 215-34;

5. Analysis of the results obtained and recommendation of demulsifiers for PIT (pilot tests) [13].

Test progress:

The tests were conducted on March 10-15, 2022.

For testing, a sample of oil was taken on February 02 from the birth of Kulzhan LLP ”Meerbusch”, Ayyrshagyl LLP ”BNGltd”.

An oil sample from the Ayyrshagyl site of BNGltd LLP was taken from the well on February 02 №141, №143, №145, №150, №151, №153, №154.

The physical and chemical properties of oil used in study are presented in Table 1.

Table 1 Physical and chemical properties of oil from the Kulzhan and Ayyrshagyl fields

| Characteristics | Crude oil from the Kulzhan oilfield | Crude oil from the Ayyrshagyl oilfield |
|---|---|---|
| Density at 200C, g/sm3 | 0.8747 | 0.8704 |
| Water content, % | 6.1 | 5.2 |
| Content of chloride salts, mg/dm3 | 1480.5 | 687.5 |
| Content of mechanical impurities, % mass. | 0.4 | 0.21 |
| Paraffin content, % mass. | 4.8 | 3.7 |

According to Table 1, these oils are relatively average in density, rich in the content of chloride salts, rich in mechanical impurities and in paraffin content in the oil as well, which complicates the demulsification process under normal conditions.

Initially, for the study, the total water content in the emulsion was determined by the express method on a centrifuge. The water content of the selected emulsion is 6%, the volume of freely separating water is 1%.

The emulsion samples were poured into settling tanks (V = 100ml), demulsifiers from commercial forms were dosed with a flow rate of 70 g/t at a temperature of +55 ° C and mixed with the emulsion by shaking 100 times manually. After that, the emulsion samples were maintained for 120 minutes at a temperature of +55 ° C by fixing the dynamics of water separation at certain intervals in ml.

Preparation and analysis of the initial oil emulsion. The selected sample of oil emulsion, not treated with a demulsifier, is mixed from wells taking into account the daily flow rate of each well and analyzed for the presence of free-separating water; the total water content is determined, for which the emulsion sample is centrifuged without the use of chemical reagents. The total water content of the sample indicates the maximum volume of water, the separation of which should be expected when performing tests.

Entering the demulsifier. A sample of the tested emulsion is placed in special graduated settling tanks with a volume of at least 100 ml, into each of which a predetermined amount of demulsifier is injected with pipettes-microdosers. The settling tanks are hermetically sealed and shaken on a laboratory shaker or manually to distribute the demulsifier in the volume of the oil emulsion and for good mixing. The introduction of the demulsifier is carried out at the temperature at which the oil-water emulsion is treated at the preparation plants. Calculation of the required amount of demulsifier is calculated on the volume of oil in the emulsion.

Separation. Settling tanks with emulsion treated with demulsifiers are placed in a thermostat for a

time corresponding to the time spent in pipelines and technological devices or for a certain time, for which the dynamics and difference in the effectiveness of the reagents will be clearly manifested. The temperature of the thermostating corresponds to the temperature technological mode of the installation. The test also examines an oil emulsion that has not been treated with a demulsifier (idle experiment). The amount of separated water is recorded at pre-selected intervals. In addition, the quality of the phase interface, the quality of the separated water, the appearance and thickness of the intermediate layer are recorded.

Analysis of the oil phase. 5 ml of aromatic solvent is placed in centrifuge tubes. After the separation time has elapsed, 5 ml of the oil phase is taken from the settling tanks from a certain level above the phase section and placed in centrifuge tubes with a pre-typed solvent. The contents of the test tubes are mixed and centrifuged for 5 minutes at the number of revolutions of the centrifuge rotor at least 2700 rpm. After centrifugation, the content of the released water and the emulsion layer (stable emulsion) is recorded.

Further, a laboratory emulsion destroyer is dosed into the same centrifuge tubes, the contents of the tube are mixed and re-subjected to centrifugation. The total amount of water is recorded in each tube (Figure 1).

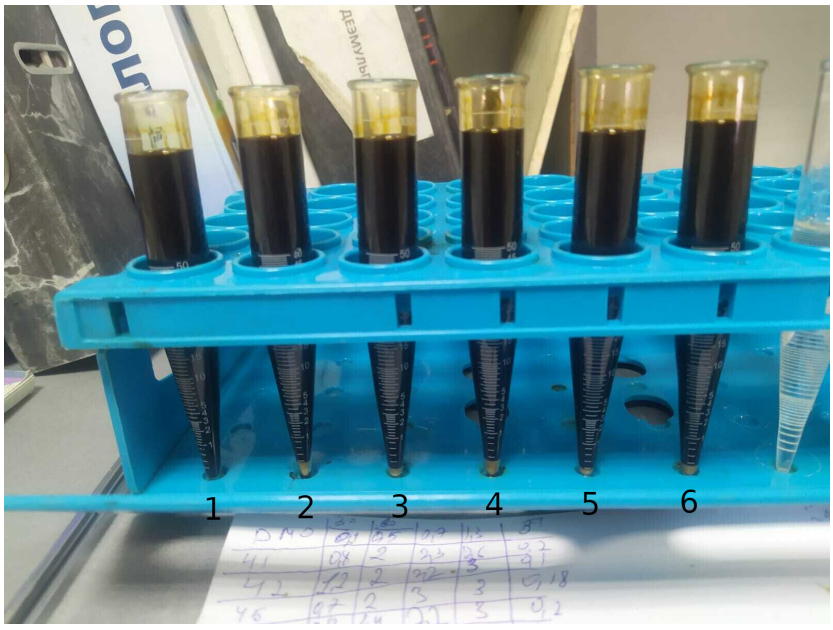


Figure 1 - Oil samples after analysis

After settling the emulsion by centrifugation, the residual water content in the emulsion is determined.

No. 1 Analysis. MICH Test of Meerbusch30% LLP + BNG 70% LLP.

6 settling tanks with oil of m/r Kulzhan and Ayyrshagyl were installed with the addition of a demulsifier in them in the equivalent of 70 grams / ton. Various models of the EASY-DE demulsifier were added to the tubes and one tube was with a basic demulsifier labeled as ”EASYDE 03-15”.For the reliability of the results, the analyses were carried out several times.

No. 2 Analysis. MIX Meerbusch+BNG 50% : 50%

6 settling tanks with oil were installed m/r Kulzhan and Ayyrshagyl with the addition of a demulsifier in them in the equivalent of 70 grams / ton. Various models of the EASY-DE demulsifier were added to the tubes and one tube was with a basic demulsifier labeled as ”EASYDE 03-15”. Another test tube was left without the addition of reagents to compare the work and determine the effectiveness of our reagents. For the reliability of the results, the analyses were carried out several times.

No. 3 Analysis. MIX Meerbusch+BNG 30% : 70%

6 settling tanks with oil were installed m/r Kulzhan and Ayyrshagyl with the addition of a demulsifier in them in the equivalent of 70 grams / ton. Various

models of the EASY-DE demulsifier were added to the tubes and one tube was with a basic demulsifier labeled as ”EASYDE 03-15”. Another test tube was left without the addition of reagents to compare the work and determine the effectiveness of our reagents. For the reliability of the results, the analyses were carried out several times.

**Results and discussion.** The results of the tests on 6 samples are shown in Tables 2-4.

Table 2 - Results of MICH Test of Meerbusch30% LLP + BNG 70% LLP

| Reagent | Amount of separated water, ml | | | | | | Residual water, % | Interfacial layer, % |
|---|---|---|---|---|---|---|---|---|
| | *15 min* | *30 min* | *45 min* | *60 min* | *90 min* | *120 min* | | |
| ДНЭ-М | 0,1 | 0,1 | 0,3 | 0,5 | 0,7 | 1,3 | 0 | 0 |
| ED 03-15 | 0,1 | 0,1 | 0,1 | 0,1 | 0,1 | 0,2 | 0,2 | 0,15 |
| ED 03-41 | 0,4 | 0,8 | 1,6 | 2 | 2,3 | 2,6 | 0,2 | 0,16 |
| ED 03-42 | 0,7 | 1,2 | 1,6 | 2 | 2,2 | 3 | 0,1 | 0,1 |
| ED 02-45 | 0,3 | 0,7 | 1,4 | 2 | 3 | 3 | 0,18 | 0,1 |
| ED 01-46 | 0,4 | 1,4 | 1,8 | 2,2 | 2,8 | 3 | 0,2 | 0,2 |

** ED – EASY-DE*

*Reagent dosage:70 g/ton*

*Process temperature at the facility:55-500C*

*Water content in oil:6%*

Table-3. Results of MIX Meerbusch+BNG 70% : 30% analysis

| Reagent | Amount of separated water, ml | | | | | | Residual water, % | Interfacial layer, % |
|---|---|---|---|---|---|---|---|---|
| | 15 min | 30 min | 45 min | 60 min | 90 min | 120 min | | |
| Without reagent | 0,1 | 0,1 | 0,3 | 0,4 | 0,4 | 0,5 | 0,9 | 0 |
| ДНЭ-М | 0,1 | 0,1 | 2 | 4 | 4,4 | 5 | 0,1 | 0 |
| ED 03-15 | 0,4 | 2,5 | 2,6 | 2,8 | 3 | 3,5 | 0,1 | 0 |
| ED 03-40 | 0 | 0,15 | 0,5 | 1 | 1 | 1 | 0,2 | 0 |
| ED 02-14 | 0,3 | 2,5 | 3,8 | 5 | 6 | 6,5 | 0,4 | 0 |
| ED 01-09 | 0,4 | 1 | 3 | 5 | 5,3 | 6 | 0,2 | 0 |

** ED – EASY-DE*

*Reagent dosage:75 g/ton*

*Process temperature at the facility:55-500C*

*Water content in oil:6%*

Table-4 - Results of MIX Meerbusch+BNG 50% : 50% analysis

| Reagent | Amount of separated water, ml | | | | | | Residual water, % | Interfacial layer, % |
|---|---|---|---|---|---|---|---|---|
| | *15 min* | *30 min* | *45 min* | *60 min* | *90 min* | *120 min* | | |
| Without reagent | 0,1 | 0,2 | 0,2 | 0,2 | 0,2 | 0,2 | 0,9 | 0 |
| ДНЭ-М | 0,1 | 0,2 | 2000,2 5 | 0,3 | 0,3 | 0,3 | 0,1 | 0 |
| ED 03-09 | 0,1 | 0,15 | 0,3 | 0,3 | 0,3 | 0,3 | 0,1 | 0 |
| ED 03-42 | 0 | 0,25 | 0,5 | 1 | 1,2 | 1,2 | 0,2 | 0 |
| ED 03-15 | 0,1 | 0,2 | 0,3 | 0,4 | 0,4 | 0,4 | 0,4 | 0 |
| ED 01-10 | 0,4 | 0,9 | 3 | 3,5 | 3,5 | 4,5 | 0,2 | 0 |

According to the results of analyzes of oils in different ratios, demulsifiers DE 03-15, DE 03-42, as well as DNE-M showed good results in separating water from crude oil.

Reagent DE 03-15 works effectively with a crude oil in a ratio of 70:30 (Meerbusch: BNG), as well as 50:50 (Meerbusch: BNG), when oil with a significant content of mechanical impurities and chloride salts is mixed with oil, which contains relatively more paraffins .

At a ratio of 30:70 (Meerbusch: BNG), where oil with a high paraffin content predominates, the effectiveness of the demulsifier decreases. In this case, the DE 03-42 reagent is more effective.

Demulsifier 03-15 is more preferable for the preparation of these oils in a 50:50 ratio, since the economic cost of this reagent is significantly lower compared to analogues, and the phase boundary between the oil and water layers is thinner.

A comparative analysis of the research results showed that at a settling temperature of +55° With the most effective demulsifier for the preparation of water-oil emulsions, the Meerbusch LLP+ BNG LLP is EASY-DE03-15.

The dynamics of water release from water-oil emulsions in the free phase exceeds the indicators of tested demulsifiers. Residual content of water and undisturbed emulsion in the settled oil: the demulsifier of the EASY-DE03-15 brand is superior to other reagents showing a smaller amount of water and undisturbed phase. The quality of the oil-water phase section: the intermediate layer in the settling tanks is not noticed.

The released water has no turbidity, transparent without noticeable traces of oil.

The content of chloride salts in oil has decreased by 3 times due to the fact that the inorganic chloride salts, which are dissolved in the aqueous phase, separated along with water.

As a result of the conducted research, it can be concluded that the resulting composition in the oil processing in field conditions reduces the influence of aggressive media on the metal surface, as well as reduces the formation of salt deposits and prolongs the formation time of deposits. Because of this, various salt deposits contained in oil allow it to settle in tanks with raw materials. When preparing oil for processing, reducing the content of reservoir water and salts prevents the formation of deposits on the surface of the equipment.

It has been established that the EASY-DE 03-15 demulsifier is the most effective reagent for dehydration of oil-water emulsions and desalination of MIX samples of Meerbusch LLP + BNG LLP. The demulsifier EASY-DE 03-15 works perfectly with medium-density oil that contains various natural impurities, such as chloride salts, mechanical impurities, and paraffins. The relatively average density of oils also indicates that they might also contain asphaltenes in a certain amount, which also stabilize the oil-water emulsion.

**Conclusion.** Thus, the results of research reveal that Demulsifier EASY-DE03-15 is recommended for conducting pilot industrial testing to obtain the final result of applicability at the facilities of dewatering and desalination of oil samples of Meerbusch LLP + BNG LLP except for the treatment of oil with fresh water.

Analyzing the stability of oil emulsions depending on the washing water, according to the demulsifier flow rates that ensure its separation, it was found that the effectiveness of the demulsification process is influenced by the interaction of two factors: the aqueous phase and the degree of its dispersion. Since the process of demulsification of oil using a demulsifying reagent is associated with the destruction and adsorption displacement of natural stabilizers at the oil-water boundary by demulsifying molecules, an increase in water content has a strong effect on the consumption of oil by the reagent.

Thus, the results of the conducted experimental studies show that with an increase in the water saturation of oil, the consumption of the demulsifier decreases. At the same time, by purposefully increasing the water saturation of the finished rheologically complex oil to its maximum value, it is possible to reduce the consumption of the demulsifier several times without reducing the efficiency of the oil dewatering process. In this connection, it can be stated that the effectiveness of using demulsifiers of domestic production was proved. Use of domestic demulsifier has certain advantages over imported ones [14].

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