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Investigation of Technological Processes for Production of CompositeDemulsifier for use in Desalination and Dehydration of Oil Emulsion

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ABSTRACT: Currently, the oil industry uses various chemicals that solve several problems related to increased oil recovery, corrosion protection, destruction of water-oil emulsions, etc.The new composition was developed by way of diversification of demulsifiers for dehydrating and desalting oil, increasing the effectiveness of the composition, improving the rheological properties of oil products, as well as protecting the system for collecting, transporting and preparing oil from corrosion. We found that the synergism of the demulsifying action of the developed composite demulsifier during dehydration of oil emulsions in a certain range of component ratios is due to an extreme change in surface tension and wetting action in the micelle formation, and the dynamics of water separation in the emulsion depends on the rate of equilibrium wetting angle.

KEYWORDS: water, salts, mechanical impurities, mineral acids, alkalis, oil products, composite demulsifier, Dehydration.

I. INTRODUCTION

Mineral impurities of oil and oil products include water, salts, mechanical impurities, mineral acids, alkalis. Most mineral impurities are contained in crude oil and can be partially converted to petroleum products during processing.
However, even with deep dehydration of oil to the content of produced water of 0.1-0.3% due to its high mineralization, the residual content of chlorides is quite large: 100-300 mg/l (in terms of NaCl). Therefore, dehydration alone is not enough to prepare for the refining of most deposits. The remaining salts and water in the oil are removed by a desalting process. The latter consists of mixing of oil with freshwater, destruction of the formed emulsion and subsequent separation of washing water from oil with salts and mechanical impurities transferred to it [1].

Oil desalting is a process for removing mineral salts from a crude oil field. In most cases, these are chloride salts. The mineral salts can be contained both in the water contained in the resulting water-oil emulsion in dissolved form and directly in the oil in the form of crystals. The latter version is much less common but is also found in practice.
The need to carry out the oil desalination process is dictated, first of all, by a reduction in the corrosive effect of salts on the entire complex of metal equipment: from pipeline systems to equipment used at oil refineries. The results of numerous studies of the mineral composition of reservoir waters show that the majority of solutes are sodium, magnesium and calcium chlorides. In addition to them (depending on the deposit), iodide and bromine salts of alkali and alkaline earth metals, sodium, iron, calcium sulphides, vanadium, arsenic, germanium and others may be present. But unlike chlorides, the content of which is calculated in per cent and tens of per cent of the total amount of solute, the content of the remaining salts is calculated in hundredths, thousandths and even smaller fractions of per cent. In this regard, the mineralization of produced water is often measured by the content of chlorine ions per unit volume, followed by a conversion to the equivalent of sodium salts.

The degree of mineralization of free produced water during oil preparation and processing is determined by measuring the content of salts in a unit of oil volume. The oil itself does not contain chlorine salts. They enter it with emulsified

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water. The amount of crystalline salts is usually small and ranges from a few milligrams to 10-15 mg/l of oil. Similar situations are possible in two cases: either during oil production, salt deposits pass, and salt crystals enter it as mechanical impurities, or initially, the oil contains little finely dispersed and highly mineralized formation water, which is then dissolved in oil, and the salts remain in the form of microcrystals [2].

The absolute content of chlorides in watered oil does not give an idea of the degree of mineralization of reservoir waters. Therefore, simultaneously with the salts in the oil, its watering is determined. The latter is generally measured in %.

A. Equipment clogging - Salts are deposited mainly in hot equipment. Salts dissolved in water are released by evaporation of water. Since the latter occurs mainly on or in close proximity to the heating surface, some of the crystallized salts adhere to these surfaces, settling on it in the form of a strong crust. Sometimes these salt crusts are broken off, extracted by the flow of oil and then deposited in subsequent equipment.

B. Corrosion of equipment- Corrosion, that is, corrosion of oil refining equipment during the processing of salt oils is caused by the release of free hydrochloric acid during the hydrolysis of some chloride salts. Fuel oil, in which a significant part of the salts contained in crude oil remains, also has strong corrosive properties, which leads to premature failure of the furnace equipment of power plants and turbine engines. Reduced plant performance. The deposition of salts in the pipes, which reduces their flow sections, causes a sharp decrease in productivity. The concentration of salts in tar and fuel oil deprives the possibility of producing qualitative residual products from them.

For example, bitumen does not withstand the norm for solubility in carbon disulphide, and in addition contains water-soluble impurities-salts, which, in particular, is unacceptable for road bitumen. Residual oils from the floor of fuel oil containing salts and corrosion-erosion products have increased ash content [3].

Fuel oil containing salts is unsuitable for the production of motor products. Also, fuel oil and tar are not suitable not only for the production of any residual products but even as fuel, since salts cause clogging of nozzles, chimneys, form precipitation on the heating surface and cause their corrosion. Depending on the salt content indicator, in the so-called commercial oil in accordance with GOST standards, three quality groups are distinguished: for the first group, the salt content indicator should not exceed 100 mg/l, for the second - 300 mg/l, for the third - 1800 mg/l. In addition, there is a separate requirement for the product to be exported - the salt content in it, as in the first quality group, should not exceed 100 mg/l [4].

II. METHODS STUDY DEHYDRATION AND DESALINATION OF OIL

The essence of the definition consists of stripping water from oil with a special solvent and their subsequent separation in a graduated receiver into two layers. The solvent shall not contain impurities of precipitate water. As a solvent, straight-run gasoline (T_{kip} = 100-140 ^{0}C), petroleum distillate (T_{kip} = 100-200 ^{0}C) containing no more than 3% aromatic HC, isooctane, toluene can be used. Before analysis oil is well mixed by 5-minute shaking, viscous and paraffin oils are preheated to 40-50 ^{0}C. Thereafter, a sample of oil of 100 g (or 100 cm^3) was taken, a solvent of 100 ml was added and the contents were stirred. The flask (1) is connected to a trap receiver (Dean-Stark nozzle) (2) and a refrigerator (3). The contents flask is heated to boiling and distillation is carried out until the volume of the lower aqueous phase stops increasing in the trap receptacle, and the upper layer of solvent must become completely transparent. Distillation time is 30-60 min. The remaining water droplets on the refrigerator walls are pushed or rinsed into a trap by the solvent. The amount of water in the trap is measured and mass (X) or volume (X_1) fraction of water in% is calculated:

$$X = Vo/m\,100;$$
$$X_1 = Vo/V\,100;$$

Where *Vo* – the volume of water in the receiver-trap cm^3; *V* - sample volume, cm^3;
m - sample weight, *g*.

Distillations (Dina-Stark),which consists in heating the sample under reflux in the presence of a water-immiscible solvent, which is distilled together with the water in the sample, where condensed water is collected in the graduated part of the trap (Dean-Stark), and the solvent is returned to the flask (Fig. 1).

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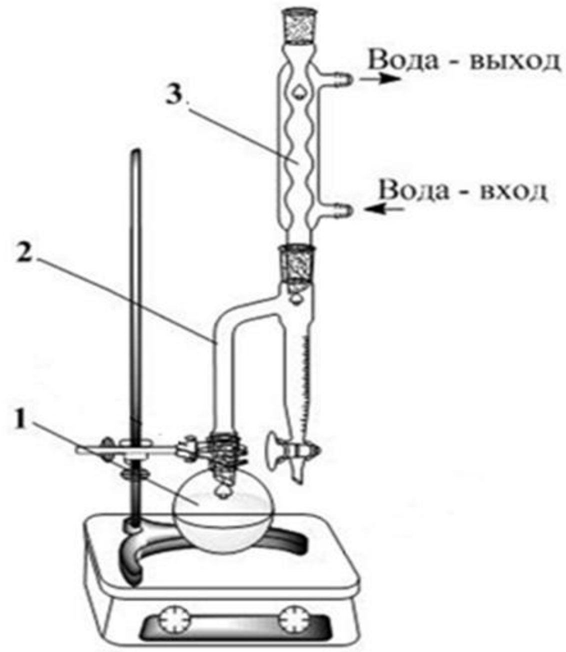


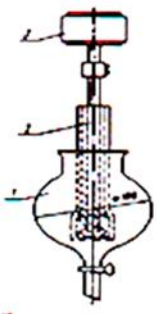
1 - flask; 2 - Dean-Stark nozzle; 3-refrigerator (reverse)
Figure 1.A device for determining the water content in oil and oil products.

III. DETERMINATION OF THE CONTENT OF CHLORIDE SALTS IN OIL

Thequalityofoilsuppliedtooilrefineriesisstrictlyregulatedby GOST 9965-76 [6].
Oil quality indicators are determined by analysis of oil samples in chemical-analytical laboratories or by special instruments directly on the flow in the pipeline.
The essence of the method consists of extraction of salts from oil with hot water and titration of water extract of chlorides with a solution of mercury nitrate by reaction:

$$Hg(NO_3)_2 + 2NaCl \rightarrow HgCl_2 + 2NaNO_3$$

During the analysis, the following is used: a dividing glass funnel with a capacity of 500 cm^3 with a screw or blade stirrer (Fig. 2).



1-active glass funnel; 2 mixer; 3 electric motor.
Figure 2.Extraction of salts from oil.

The content of chloride salts in commercial oil according to GOST 9965-76 shall not exceed 100 mg/l in oil of group I,

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300 mg/l - of group II and 1800 mg/l - of group III. The content of salts in water-free (raw) oils reaches tens of thousands of milligrams per litre.Saltcontentisdeterminedasper GOST 21534-76 [6] bytitrationof salt solution with reagent interacting with chlorine ions. Two methods are used: the first is based on the extraction of chlorides from oil with water and the titration of water extract with a solution of silver nitrate with an indicator. The second method consists of incomplete dissolution of the oil suspension in an organic solvent and the potentiometric titration of the obtained solution.

IV. RESEARCH RESULTS

Themodificationcompositedemulsifier - "МК-ДЭМ-4" is a solution of compositions based on polyhydric alcohols, inorganic ingredients and wastes of organic solvents.
Testswerecarriedoutduringdehydrationanddesalinationofthe“Sovligar”oilfieldoilemulsion, thephysicalandmechanicalpropertiesofwhicharegiveninTable 1.

Table 1. Indicators of oil from the “Sovligar” field.

№	Description of indicators	Test methods	“Sovligar”oilresults
1	Density kg/m3	GOST 3900	893,9
2	Sulphur content,%	GOST 1437	1,12
3	Water content,%	GOST 2477	4
4	Content of chloride salts mg/dm3	GOST 21534	1574
5	Freezing temperature ^{0}C	GOST 20287	-15
6	Fur. impurity, %	GOST 6370	0,24

The oil emulsion brought from the “Sovligar” field was poured into a container with a volume of 1000 ml.The contents of the container were mixed by shaking for 10 minutes.The prepared emulsion was poured into 90 ml separating flasks (4 flasks in total).Prepared 3%, 100% solutions of demulsifier "MK-DEM-4" and 3%, 100% solutions used in the practice of demulsifier - diproxamine-157M.Sequentially, starting from the first tube, the calculated amount of demulsifier brand "MK-DEM-4" 10% (10 ml of 100%) was introduced and the emulsion was stirred for 1 minute.The calculated amount of a demulsifier brand MK-DEM-4 0.3% (10 ml of 3%) was injected into the second tube, and the calculated amount of the demulsifier diproxamine 157-M 10% (10 ml of 100%) was injected into the third tube.In the fourth tube, 0.3% diproxamine 157-M (10 ml of 3%) used in practice (10 ml of 3%) was also introduced for comparison with the data obtained using the developed demulsifier.The prepared solutions were placed in a water bath at 90-100 ^{0}C.Then every 30 minutes for 2 hours, the water separating from the oil emulsion was measured.Table 2 shows the results of studies of the effect of the developed composite demulsifier "MK-DEM-4" depending on the holding time of the treated oil at a temperature of 100^{0}C.

Table 2. The amount of separated water (ml) from the oil emulsion during its destruction under the influence of the developed "МК-ДЭМ-4" demulsifier and diproxamine for a certain time at 100 ^{0}C.

№	Demulsifier	Time, min.			
		30	60	90	120
Oil from the Sovligar field					
1	«МК-ДЭМ-4» 3%	8,5	8,6	8,8	9
2	«МК-ДЭМ-4» 100%	11,6	12	12,2	12,5
3	Diproxamine 3%	8,5	8,6	8,8	8,9
4	Diproxamine 100%	11,6	11,7	11,8	12

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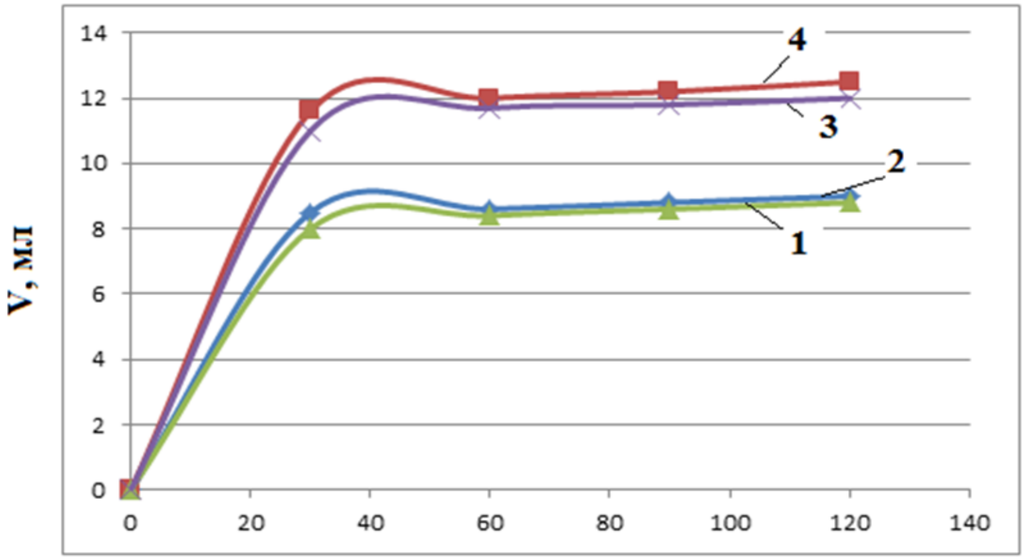

1-Diproxamine (3%); 2- "MK-DEM-4" (3%); 3- Diproxamine (100%);
4- "MK-DEM-4" (100%)

Figure 3. The amount of released water (ml) from the emulsion during its destruction under the influence of the developed "МК-ДЭМ-4" demulsifier and diproxamine for a certain time at 100^{0}C.

After the separation of water, an analysis was carried out for the water content in the oil emulsion according to GOST 2477. From the separation flask, the separated water was poured, 90 ml of samples were taken from the top of the residual oil emulsion and mixed with heavy naphtha 100 ml, after which it was heated on an electric stove at a temperature of 100 ^{0}C. The results are shown in Table 3 below.

Table 3. The amount of water in the composition of the oil emulsion after exposure to the developed "MK-DEM-4" and diproxamine.

№		Method	OilSovligar	"MK-DEM-4" 3%	"MK-DEM-4" 100%	Diproxamine 3%	Diproxamine 100%
1	Watercontent,%	GOST 2477	4	4	1,2	5,2	2

Next, we conducted laboratory tests of the modified composite demulsifier brand "МК-ДЭМ-4" for comparison with the currently used demulsifier "Diproxamine-157M" in practice in order to study the process of desalination of oil emulsions.The studies were carried out according to the following procedure (GOST-21534):The results are shown in the figure below.

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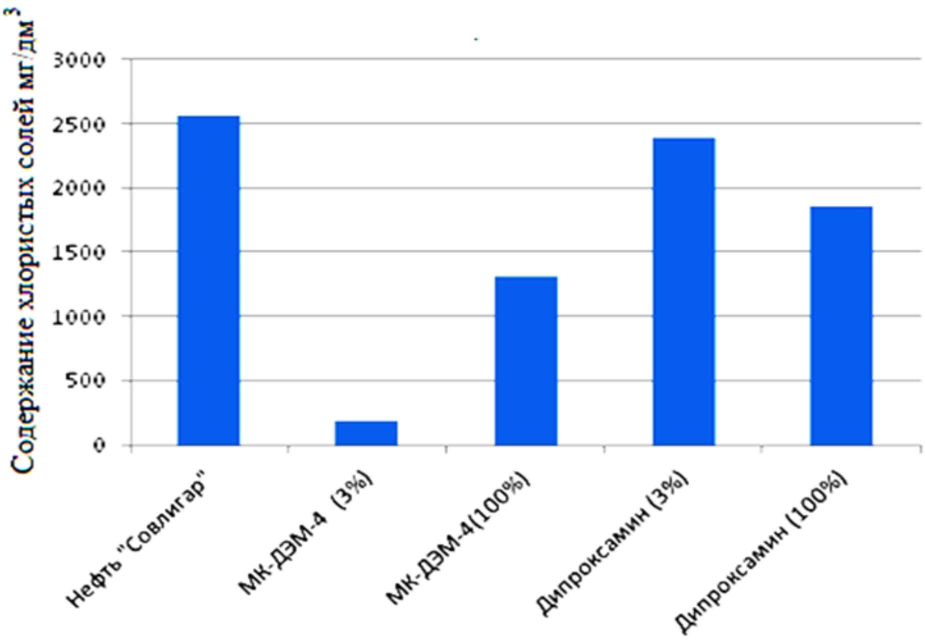

Figure 3. The amount of salt in the oil emulsion after exposure to the developed "МК-ДЭМ-4" anddiproxamine.

The results of the obtained analyses showedthatthedemulsifier "МК-ДЭМ-4" at 3% concentration during testing in laboratory conditions showed a better result comparedtothedemulsifiercurrentlyusedat the Bukhararefinery LLC diproxamine.The bulk of commercial water and salts dissolved in it, mechanical impurities are separated in fisheries. Finaldewateringanddemineralizationarecarriedoutatrefineriesatelectricdemineralizingplants (ELOU) [8-9]. The main apparatus of ELOU is an electro dehydrator, where, in addition to the electrical treatment of the oil emulsion, water is also deposited (precipitation), that is, it is also a settler.

We conducted pilot tests of 50 litres of the chemical reagent of demulsifier "МК-ДЭМ-4" brand for desalination and dehydration of oil emulsions at the existing production plant ЭЛОУ-2 with employees of Bukhara refinery.
A 3% demulsifier solution with water was prepared for loading into a 10 m3 tank. To prepare 1 m3 of 3% solution, 970 litres of industrial water and 30 litres of demulsifier (100% concentration) were collected into the E-4 tank. During the addition of the demulsifier, steam condensate bubbling was performed and after the demulsifier addition was stopped, the steam condensate supply was closed and the solution was heated to approximately 50^0C. At the same time, the level in the E-4 capacity was 10% of the total level. With the help by the pump ELOU-1 of N-1a crude oil of PBC 58, 59 tanks were pumped over with an expense of 50 m3/hour and went for ELOU-2 installations according to production schedules of TR 16472899-012:2019. At the same time, from the tank E-4 with a solution of 3% of the demulsifier of "МК-ДЭМ-4" grade was dosed into the incoming crude oil at the suction of the unit pump. In this mode, the process line ЭЛОУ-2 was flushed at a flow rate of 59 m3/h for 6 hours, while the purified oil was sent to PBC 45.
During the course of the test, the quality control of crude oil at the inlet from the plant, refined oil at the outlet from the plant and directly from the refined oil tank was carried out. Analyses of the sampled samples were carried out in TSL according to the 20^0C density, chloride salt content, water content, mechanical impurities content (Table 4).

Table 4. Physical and chemical properties of the developed composite demulsifier.

Время	Place of selection	Density 20^0C, kg / m^3	Content of chlorine salts, mg / dm^3	Water content, %	Content of mechanical impurities, %
-	**The standard**	**Not rated**	**Not rated**	**No more than-0,1**	**No more than-0.03**

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	output				
18:00	inlet	809	27,9	0,07	
	outlet	790	3,8	0,04	0,03
20:00	inlet	808	16,3	0,07	
	outlet	815	4,4	0,04	0,03
00:00	inlet	811	21,5	0,07	
	outlet	778	4,5	0,04	-
04:00	inlet	805	24,4	0,07	
	outlet	777	4,7	0,04	-
	46 PBC	782	5,0	0,04	-
08:00	inlet	795	767,5	1,5	
	outlet	792	6,2	0,04	0,032
	46 PBC	782	4,9	0,04	-

The received results of skilled tests showed that 3% solution with the application of a de-emulator of "MK-DEM-4" on ELOU-2 installation of the Bukhara oil refinery with an average expense 1 litre of the solution on 1 ton of crude oil work effectively when using oil of the Group "0" with contents by the content of salts up to 27.9 mg/dm3 and the content of water up to 0.07%. Next, pilot tests of the chemical reagent of the demulsifier in the amount of 100 litres of the "МК-ДЭМ-4" brand were carried out for desalination and dehydration of oil emulsions at the current production plant ЭЛОУ-2 with employees of the Bukhara refinery. A 3% demulsifier solution with water was prepared for loading into a 10 m3 tank. To prepare 3 m3 of 3% solution, 2910 litres of industrial water and 90 litres of demulsifier (100% concentration) were collected into the E-4 tank. During the addition of the demulsifier, steam condensate bubbling was performed and after the demulsifier addition was stopped, the steam condensate supply was closed and the solution was heated to approximately 50 ^{0}C. At the same time, the level in the E-4 tank was 90 cm of the level. With the help by the pump ELOU-1 of N-1a crude oil of PBC 58 tanks was pumped over with an expense of 120 m3/hour and went for ELOU-2 installations according to production schedules of TR 16472899-012:2019. At the same time from the tank E-4 with a solution of 3% of the demulsifier of the grade МК-ДЭМ-4 was dosed to the incoming crude oil at the suction of the unit pump. In this mode, the process line ЭЛОУ-2 was flushed at a flow rate of 120 m3/h for 2 hours, while the purified oil was sent to PBC 45. During the course of the test, the quality control of crude oil at the inlet from the plant, refined oil at the outlet from the plant and directly from the refined oil tank was carried out. Analyses of the sampled samples were carried out in TSL according to the 20 ^{0}C density, chloride salt content, water content, mechanical impurities content (Table 5).

Table 5. Physical and chemical properties of the developed composite demulsifier.

Время	Place of selection	Density 20^{0}C, kg / m^{3}	Content of chlorine salts, mg / dm^{3}	Water content, %	Content of mechanical impurities, %
-	**Output rate**	**Not standardized**	**Not more than -5.0**	**No more than-0,1**	**No more than-0.03**
16^{00} 07.07.2020	inlet	775,9	205,7	0,2	-
	outlet	774,8	4,9	0,04	0,03
	46 PBC	776,0	4,7	0,04	-
18^{00} 07.07.2020	inlet	800,0	44,9	0,1	-
	outlet	799,9	7,0	0,04	-
20^{00} 07.07.2020	inlet	798,5	92,3	0,1	-
	outlet	796,2	7,1	0,04	-
22^{00} 07.07.2020	inlet	795,7	196,4	0,1	-
	outlet	797,3	5,4	0,04	-
00^{00} 08.07.2020	inlet	797,6	108,9	0,1	-
	outlet	795,3	4,9	0,04	0,03
01^{00}	46 PBC	793,0	5,0	0,04	-

08.07.2020					
02⁰⁰ 08.07.2020	inlet	797,1	86,4	0,1	-
	outlet	794,9	4,7	0,04	-
04⁰⁰ 08.07.2020	inlet	794,8	75,7	0,1	-
	outlet	796,6	4,7	0,04	-
06⁰⁰ 08.07.2020	inlet	798,3	71,0	0,1	-
	outlet	793,9	4,9	0,04	-
08⁰⁰ 08.07.2020	inlet	795,0	23,6	0,1	-
	outlet	794,0	4,7	0,04	-
	46 PBC	798,0	4,7	0,04	-
10⁰⁰ 08.07.2020	46 PBC	796,0	3,5	0,04	-

V. CONCLUSIONS

The obtained results of experimental tests showed that a 3% solution using the MK-DEM-4 demulsifier at the ELOU-2 unit of the Bukhara refinery with an average consumption of 1 litre of solution per 1 ton of crude oil works effectively when using Group 0 oil (up to 50 mg / dm3), Group “1” (up to 100 mg / dm3), Group “2” (up to 300 mg / dm3), (according to GOST 9965, O'zDSt 3032: 2015) with salt content up to 200.0 mg / dm3.

It has been established thatthedevelopeddemulsifier - "MK-DEM-4" can be successfully used in the process of dehydration and desalting of oil.

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