

## Development of Demulsifier Compositions for the Destruction of Emulsions and Dehydration of Heavy Oils

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### Abstract

In oils, oil products and oil fractions, which do not contain paraffins, the action of depressors is useless. In this connection, the research of depressor properties of experimental samples of demulsifying compositions became possible only in regions where highly paraffinic oils are extracted, prepared and transported. Joint researches concerning the study of effect of the developed composite reagents on the rheology of heavy oil from Zhangurshi deposit of the West Kazakhstan region was carried out at al-Farabi Kazakh National University, Institute of Combustion Problems and the Kazan Scientific-Research Technological University. Conducting a comparative evaluation of the wetting power of a number of surfactants made it possible to obtain information on the efficiency of the inversion of wetting in oil-dispersed systems during the destruction of water-oil emulsions. In this work, the express methods for determining of wetting-deterging action of a wide range of different classes and types of surfactants are used, which makes it possible to make a comparative assessment of their effectiveness in a short time. During the research, it was supposed that the washing process of adsorption hydrocarbon layer, including tar-asphaltene substances, from the surface of particles of mechanical impurities involved in stabilization of water-oil emulsion should be preceded by a wetting process.

### Abbreviation

**SNPH 4315** – composition of non-ionic surfactants in a mixture of aromatic and alcoholic solvents;

**Recod 752A** – water-soluble demulsifier – non-ionic surfactant block copolymer of ethylene oxide and propylene oxide;

**DIN 3A** – demulsifier and an oil inhibitor;

**Rekod 758** – oil-soluble type – non-ionic surfactant block copolymer of ethylene oxide and propylene oxide;

**RIF - Reapon-4B** – block copolymer of ethylene and propylene oxides based on ethylene glycol with inhibitory function;

**Diproxamine-157** – block copolymer of ethylene and propylene oxides based on ethylene diamine;

**Reapon-4B** – methanol solution of a block copolymer of ethylene oxide and propylene based on ethylene glycol;

**RENT** – reagent for heavy oil emulsions;

**Sulfanol** – mixture of sodium or potassium polyalkylarylsulfonates;

**Oleox-7** – mixture of polyoxyethylene glycol ethers of oleic acid;

**SPABR (Na/K)** – mixture of sodium or potassium salts of sulfonated polyalkylbenzene resin – a waste product of isopropylbenzene (cumene);

**SLPR** – sulfonated light pyrolysis resin – waste of pyrolysis production;

**CAD** – concentrate of alkaline drain - waste of caprolactam production;

**Component A** – block copolymer of ethylene and propylene oxides based on monoethylene glycol (RENT);

**Component B** – mixture of polyoxyethylene glycol ethers of oleic acid (Oleox-7);

**Component C** – mixture of sodium or potassium polyalkyl aryl sulfonates (Sulfanol).

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## 1. Introduction

The wetting action of surfactants, as one of the phenomena is determining the washing power, is expressed in their ability to adsorb on solid particles of mechanical impurities, changing the diphilic structure of dispersions into monophilic, or hydrophobic, or hydrophilic. As a result, if the particle surface has become monofilament, they are able to pass from the interphase boundaries into the aqueous phase or hydrocarbon medium, thus initiating the destruction of armoring shells at the surface of the globules of emulsified water. Thus, demulsifier or individual components of the surfactant reagents composition must effectively perform the removing process of adsorption layer consisting essentially of paraffins and tar-asphaltene substances (TAS) with a developed surface of dispersed particles.

Many scientists and researchers are making attempts in order to develop a mechanism for the destruction of water-emulsion oils [1–3], paying special attention to the systems stabilized by a significant number of natural emulsifiers, including mechanical impurities of different origin (rock particles, metal corrosion products, iron sulphide, etc.). However, there is still no consensus concerning the failure mechanism of restrictor shells on water droplets, dispersed in a dispersion medium-oil. Nevertheless, the variety of hypotheses reduces to the generally accepted theory of P.A. Rebinder based on the displacement of natural stabilizers from interphase boundary between oil and water surface by active compounds. The role of the wetting-deterging action puts forward additional requirements for demulsifying compounds during destruction of stable water-oil emulsions. However, the solution of this problem is not possible with the use of only one thermochemical method. Therefore, in modern literature much attention is paid to combined methods of preparation of high-viscosity and heavy oils, especially in fields that entered to late stage of development and operation, with changing production conditions and properties of oil products.

Demulsifiers are not always effective under conditions of constant alteration of properties and oil products composition, this fact is excluded the universality of their use in the fields and deposits that exploited for a long time since the beginning of their development. Therefore, the product-line expansion of demulsifying compounds is required.

One of the ways to solve the problems concerning a preparation of high-viscosity and heavy oils, including oils with a high content of mechanical

impurities, in the destruction of highly resistant oil-aqueous emulsions is the use in combination with existing demulsifiers – wetting agents, detergents, flocculants, depressants and other compounds, which facilitate the removal of finely dispersed particles from impurities from armor shells on the globules of striatal water, improve the low-temperature and viscous properties of the oil disperse system.

The patent studies carried out at stage 1 made it possible to examine analogues and use two reagents of Russian production – Reapon-4B and RENT – as demulsifiers. In order to compare the effectiveness of composite compositions of a multifunctional demulsifier developed in this work, the estimation of their demulsifying, wetting, deterging and properties was made.

A nonionic water-soluble demulsifier of the brand Reapon-4B produced by JSC «Kazanorgsintez», is intended for oil field preparation. It is a block copolymer of ethylene oxide and propylene oxide based on monoethylene glycol, and is the most widely used demulsifier in oilfield preparation. The use of Reapon-4B as one of the components of composite demulsifying compounds was the result of the emergence of a large number of patents with its participation. However, a disadvantage of this demulsifier, as an individual compound, is a low demulsifying efficiency in the destruction of highly viscous oils of the coal-bearing horizon, as well as oils with a high content of mechanical impurities. Reapon-4B insignificantly improves the rheological properties of highly viscous water, saturated oil raw materials and prepared oil and practically does not reduce the solidification of oil.

The composition of RENT for dewatering, demineralization and improving the rheological properties of petroleum, containing a nonionic demulsifier: block copolymer of ethylene oxide and propylene oxide based on monoethylene glycol with an average molecular weight of 4300, distillation of the production of methyl ether of diethylene glycol, including% mass: ethylene glycol methyl ether 20.0–40.0, diethyleneglycol methyl ether 40.0–60.0, methanol 2.0–5.0, water 15.0–18.0 and solvent with the following ratio components,% mass: block copolymer of oxides of ethylene and propylene 15.0–55.0; distillation 5.0–75.0; solvent (methanol) to 100.0. The demulsifying efficiency of the RENT composition is quite high when dewatering oils with a high content of TAS and the destruction of stable water-oil emulsions stabilized by particles of mechanical impurities. However, like

any other demulsifying composition, RENT cannot claim the versatility of the application of highly viscous and heavy oils to the emulsion systems.

## 2. Experimental

The composition of the RENT was taken as the basis for the composite compositions of the multifunctional demulsifier being developed in this work. However, the disadvantage of RENT is its relatively low efficiency when removing the smallest dispersed particles of mechanical impurities and destroying stable water-oil emulsions, reducing the viscosity and solidification temperature of oil products that transported through the pipeline. In addition, it does not provide a required quality of drainage water in the absence of flotation and flocculation effects.

In this paper, a study of wetting hydrocarbon surfaces process of different nature was carried out by measuring of contact angle, which makes it possible to fix the droplet shape directly, in accordance with the procedure given in the article [4].

Table 1 shows the results of the dynamics of wetting of hydrocarbon surfaces (paraffin, resinous and asphaltene substances) with 1% of alcohol (ethanol) solutions of various classes, types, structure and purposes at a temperature of 20 °C. Hydrocarbon components are separated from the composition of highly viscous oil from field Zhan-gurshiiin Mangistau region.

The results of measuring the edge angles when wetting the surface of refractory paraffins with the number of C24-26 carbon atoms and the wide oil fraction (350–500 °C), isolated from the oil under study, show that Reapon-4B possesses the best wetting power among the best-known domestic commercial demulsifiers. This fact can be attributed to the fact that production of Reapon-4B in the oxyethylation step inevitably is accompanied by the secondary (non-targeted) reaction of ethylene oxide with water to form polyethylene glycols with different molecular weights depending on the number of forming block copolymers with different molecular weight distributions.

Paying attention to the edge angles, it can be assumed that the polyethylene glycol (PEG) with a low molecular weight of 200–400 present in the Reapon-4B composition affects the increase in the wetting power of this demulsifier, since the values of their edge angles are relatively low on any of the hydrocarbon surfaces (paraffin, oils, resins, asphaltenes), including in comparison with the de-

mulsiifier Diproxamine-157. It can also be associated with related to the different chemical nature of the initial raw material compounds during synthesis of surfactants. Preference should be given to the demulsifier RENT, which is a composition based on Reapon-4B and a mixture of methyl esters of mono- and diethylene glycols, otherwise called methyl carbitol.

As can be seen from Table 1, the cellosolva and carbitol have low values of contact angles of wetting. However, cellosolva and carbitol are inherently related to organic esters and are not surface-active substances. In regard to hydrocarbon oil components, they can only be classified as solvents, which characterizes the low values of contact angles, especially in butyl carbitol. Such a property of esters should not be neglected, but on the contrary it is necessary to take it into account when developing new demulsifier compositions in the aspect of expanding its multifunctionality, for example, studying the action of esters to improve the rheological and low-temperature properties of petroleum feedstocks [5–7].

Adhering to the program adopted in Kazakhstan for the development of domestic production in recent years, comparison of our reagents, including the developed composite compositions of a multifunctional demulsifier (CCMD), with foreign analogs was not carried out due to technical and economic inexpediency. In addition, it is known that imported reagents are composite and, in the absence of any information on their structure, composition and structure, such a comparison, which has no practical need, would not be correct.

High-wetting ability among other surfactant classes and applications for all hydrocarbon surfaces studied is possessed by Oleox-7 detergent and wetting agents: polyalkylbenzenesulfonate – a mixture of sodium or potassium salts of the sulfonated polyalkylbenzene resin (SPABR (Na/K)); sulfonated light pyrolysis resin (SLPR) – pyrolysis production waste; concentrate of alkaline discharge (CAD) – waste of production of caprolactam.

It is stated (Table 2) that within 45–60 sec after application of the 1% alcohol solution of the surfactant under investigation, active wetting of the surface from the TAS occurs and the drop gradually spreads until the thermodynamic equilibrium is reached from the beginning to the end of the full wetting process, when the edge angle practically does not change. A wide range of investigated reagent-demulsifiers having a relatively high contact angle ( $q^\circ$ ) and being of no scientific and practical interest is not shown among the results given in Table 2.

**Table 1**  
Dynamics of wetting hydrocarbon surfaces with surfactant solutions

Surface active agents	The contact angle of wetting ( $\theta^\circ$ , deg.), during (s)																			
	Paraffin					Oil fraction					Resinous substances					Asphaltenic substances				
	10	20	30	45	60	10	20	30	45	60	10	20	30	45	60	10	20	30	45	60
Demulsifiers:																				
Diprox-amine-157	52	51	51	50	50	25	26	25	24	23	46	44	43	40	39	56	54	52	50	50
Reapon-4B	47	46	45	45	45	12	10	9	9	9	44	42	40	38	38	50	48	46	44	43
RENT	45	44	42	42	42	9	8	7	7	7	41	39	36	34	32	45	43	42	39	38
Wetting agents:																				
Sulfanol	35	35	35	34	34	15	14	13	10	8	26	26	26	25	24	34	33	33	33	32
SPABR (Na/K)	23	23	23	23	23	7	4	3	3	3	14	13	13	13	12	25	24	23	22	21
SLPS	36	35	33	32	30	14	14	14	13	12	26	22	20	18	17	31	31	29	29	28
CAD	27	26	26	26	26	9	7	5	5	5	17	15	15	14	14	27	26	25	24	24
Deterging agents:																				
Syantanol ES-3	46	46	45	45	45	28	27	26	26	26	51	48	48	48	48	55	55	55	55	55
Syantanol ALM-10	45	45	45	45	45	26	26	26	25	25	49	46	46	45	45	53	53	53	53	53
OS-20	47	47	46	46	46	29	28	28	27	27	52	49	49	49	49	56	56	56	56	56
Oxanol CS-100	51	50	50	50	50	33	32	31	30	30	56	53	53	53	53	58	58	58	57	57
Stearox-6	36	36	33	33	33	26	25	25	24	24	43	43	42	42	41	51	51	51	50	50
Stearox SP-9	31	31	29	29	29	20	20	20	20	19	35	34	34	33	33	46	46	46	46	46
Laurox-9	30	30	30	29	29	20	19	19	18	18	31	28	27	26	25	45	45	45	45	44
Oleox-5	26	26	25	25	25	18	16	16	16	16	28	27	25	24	23	42	41	40	40	40
Oleox-7	24	24	24	24	24	18	16	16	15	15	26	25	25	23	22	41	41	39	49	39
Polyglycols:																				
PEG-4	38	36	35	34	34	22	20	20	20	20	37	37	36	36	36	39	39	38	38	38
PEG-9	40	38	38	37	37	25	25	24	24	24	41	41	41	40	40	46	46	45	45	44
PEG-13	44	44	43	43	42	30	29	28	28	28	44	44	44	44	44	48	48	48	47	47
PEG-35	47	46	46	46	45	35	35	34	33	33	47	46	46	45	45	53	52	50	50	50
PEG-68	53	52	52	52	51	38	38	38	37	35	49	49	48	47	47	56	58	58	57	55
PEG-68 Esters																				
Methylcellosolve	16	15	14	13	12	-	-	-	-	-	13	8	-	-	-	21	21	21	21	20
Methylcarbitol	14	12	11	10	9	-	-	-	-	-	11	6	-	-	-	19	19	19	18	18
Ethylcellosolve	12	12	12	11	10	-	-	-	-	-	12	8	-	-	-	20	20	20	20	19
Ethylcarbitol	9	8	8	8	7	-	-	-	-	-	9	5	-	-	-	17	17	16	15	14
Butylcellosolve	10	10	10	9	8	-	-	-	-	-	9	4	-	-	-	18	18	18	17	17
Butylcarbitol	6	6	6	6	5	-	-	-	-	-	7	3	-	-	-	15	14	13	2	10

**Table 2**  
Dynamics of wetting of SAV oil from the Zhangurshi deposit by surfactant solutions

Surfactants	The marginal angle of wetting ( $q^\circ$ , deg) of the surface of the CAB at a temperature of 60 °C, during (s)				
	10	20	30	45	60
Diproxamine-157	59	58	56	54	53
Reapon-4B	45	43	40	39	38
RENT	43	36	36	35	34
Sulfanol	32	31	30	30	30
Oleox-7	35	35	35	34	33
SPABR (Na/A)	31	28	26	25	25
SLPR	32	31	30	29	27
CAD	33	32	30	29	28

As can be seen, the investigation results agree with the data (Table 2) obtained when evaluating wetting of TAS oil and have good reproducibility upon the detected patterns of change in time of contact angles for such reagents like Reapon-4B RENT sulfanol, TIA Oleox-7, SPABR (Na/K) and CAD. The preference should be given to polyalkylbenzolsulfonate – SPABR (Na/K).

In this regard, the deterging action of reagents plays an important role in achieving a significant effect of the depth of destruction of water-oil emulsions stabilized by mechanical impurities, particles of which in combination with natural emulsifiers, form a powerful armor skeleton at the interface.

Many, widely known domestic and foreign non-ionic demulsifiers – block copolymers of ethylene oxide and propylene oxide based on various starting compounds, during preparation of highly viscous oils, lead to the formation of extremely stable intermediate emulsion layers, concentrated by mechanical impurities. Textile auxiliaries and detergents, in comparison with industrial demulsifiers, have not only a high detergent effect, but also a low wetting power. The effectiveness of wetting agents action is not always directly proportional to their wetting power, therefore, in evaluating the deterging action of the surfactant, a certain role should be assigned to those reagents that are actually capable of washing out natural emulsifiers (resins and asphaltenes) from the oil-water interface and from the particles of mechanical impurities.

In this paper, the efficiency of the process of washing out hydrocarbon components consisting of tar-asphaltene substances from the surface of silica gel was determined by the method of colorimetry, which makes it possible to estimate the relative detergency of surfactants of various classes and purposes.

It has been stated (Table 3) that, in accordance with the applied procedure, the concentration of the detergent (textile-auxiliary) substance-Oleox-7 increases significantly in the suspension mixture resulting in the increase in the efficiency of removing the adsorption layer from the hydrocarbon

**Table 3**  
Detergent effect of surfactants and demulsifiers, determined by the method of colorimetry

SAS-demulsifying agents	The relative detergency of the MSot (%), at temperatures of 20/60 °C and the surfactant concentration (mg/l)				
	100 mg/l	200 mg/l	300 mg/l	500 mg/l	1000 mg/l
SNPH 4315	10/16	12/18	16/24	18/31	25/35
Rekod 752A	21/29	27/34	29/39	35/47	39/56
DIN 3A	11/14	13/16	17/21	19/26	20/29
Rekod 758	7/27	10/33	18/40	26/49	31/58
RIF	20/38	31/40	32/43	40/48	43/50
Diproxamine-157	14/34	20/35	22/37	26/38	28/40
Reapon-4B	5/10	9/12	17/24	19/26	24/33
RENT	31/46	33/51	35/52	37/54	38/62
Sulfanol	31/40	37/46	40/50	42/59	43/63
Oleox-7	43/48	49/53	53/64	60/76	68/83
SPABR (Na/K)	33/35	35/44	43/52	46/68	53/75
SLPR	27/32	31/40	38/48	41/63	49/71
CAD	36/38	39/41	41/44	42/51	44/63
Technical liquid soap	26/(27*)	39 (39*)	45(44*)	70(70*)	74(75*)

\* Note: The deterging effect was evaluated for 5 min in a thermostatic cell

components from the surface of the solid particles of the dispersed phase. The demulsifiers SNPH 4315, diproxamine (DIN) 3A, Diproxamine-157 and Reapon-4B, even with increasing concentration, do not show a sufficiently pronounced washing ability, which can probably be explained, from the point of view of the low value of the critical concentration of micelle formation and solubilization of the surfactant, which is poorly manifested in aqueous solutions, and in organic solvents, for example, alcohols among demulsifiers. REM, Records 752A and 758, RIF have relatively low detergent action with respect to hydrocarbon components (TAS) among demulsifiers, and among the wetting agents – Sulfanol, SPABR (Na/K), CAD and technical liquid soaps.

The fact of the importance of the wetting and washing abilities of surfactants is confirmed by numerous laboratory and experimental tests of various investigators in the dehydration and desalting of oils containing mechanical impurities, using composite demulsifiers containing at least one of the surfactants investigated as a component of the wetting-washing action

At the same time, for many reagents there is no directly proportional dependence and the general trend of the detergent effect on the temperature and concentration of the solution. In this case, there is a clear pattern between the ability of surfactants to wet TAS and wash them off the surface of particles of mechanical impurities. For example, Oleox-7, showing a high wetting power, is superior to the effect of detergent action of other reagents, both at 20 °C and 60 °C.

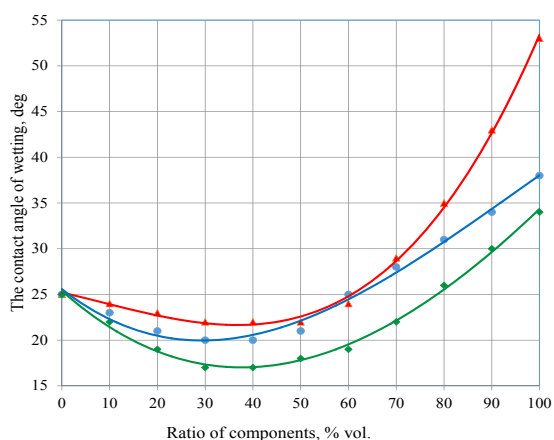


Fig. 1. Synergic dependences of the wetting power of binary mixtures demulsifier:sulfonated polyalkylbenzene resin: D-157:SPABR(Na/K) R-4V:SPABR(Na/K) RENT:SPABR (Na/K).

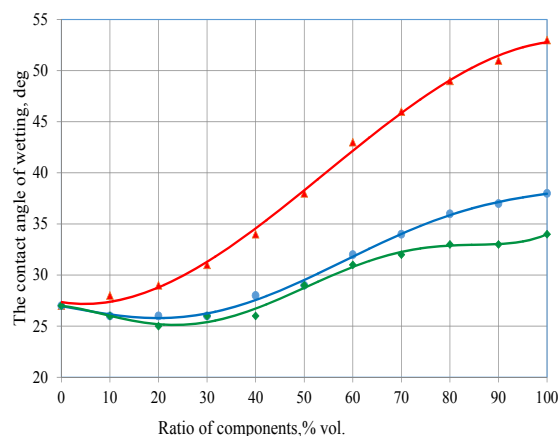


Fig. 2. Synergic dependences of the wetting power of binary mixtures demulsifier:sulfonated light pyrolysis resin: D-157:SLPR R-4V:SLPR RENT:SLPR.

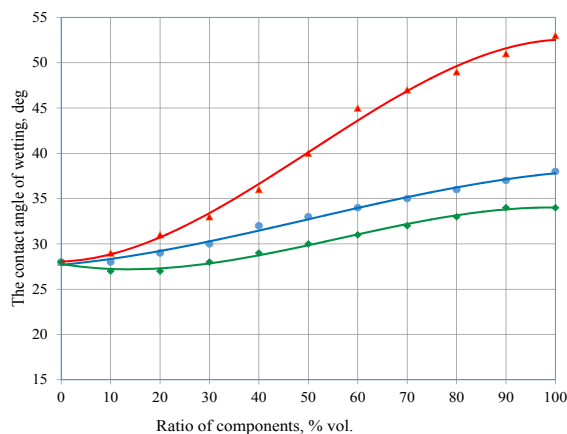


Fig. 3. Synergic dependencies of the wetting power of binary mixtures demulsifier: concentrate of alkaline discharge of caprolactam production: D-157:CAD R-4V:CAD RENT:CAD.

### 3. Results and discussion

In this section, the task was to determine the dependence of the change in the wetting action of the surfactant on the basis of the detection of synergic effects, therefore, the most effective compositions of binary mixtures of reagents were examined and investigated at various ratios.

The surface tension of solutions of surfactant mixtures, like many other properties, is not an additive value [8–10]. In the course of the work, it was stated that the dependence of the wetting power (Fig. 1–3) and detergent action (Fig. 4) of binary mixtures was not additive. To evaluate the wetting power and detergent action, two-component composite compositions were used with the participation of demulsifiers: Reapon-4B, Diproxamine-157, RENT and wetting agents: SPABR (Na/K), SLPR and CAD, depending on the ratio of components.

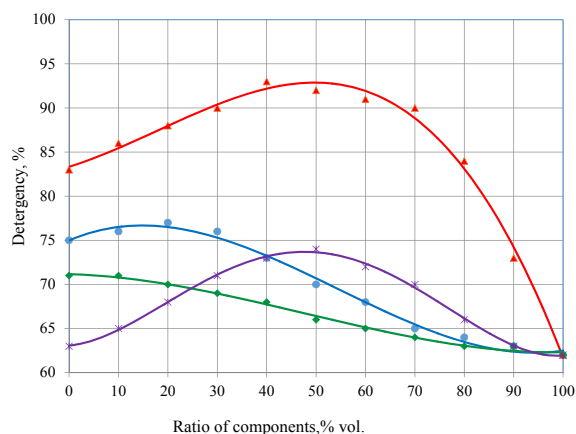


Fig. 4. Deterging ability of binary mixtures based on demulsifier RENT, detergent Oleox-7 and wetting agents SPABR (Na/K), SLPS, CAD: RENT:Oleox-7 RENT:SPABR (Na/K) RENT:SLPS RENT:CAD.

As can be seen from the obtained dependences, the contact angle is the smallest value for the two-component mixture of RENT: sulfonated polyalkylbenzene resin with a component ratio of 40:60. The synergic effect in the joint action is obvious, since all the dependencies have a clear deviation from the additive line.

The choice of SPBR (Na/K), SLPR and CAD as wetting agents was based on the economic feasibility of further use of these substances in the composition of the demulsifier, because they are waste products of organic and petrochemical synthesis. The cost of waste compared to other industrial raw materials is negligible, so the cost of production of useful sulfonated products based on them will also be significantly lower than that of industrial surfactants, for example, sulfonol.

Based on the results obtained in assessing the wetting power of binary mixtures, the demulsifier RENT, wetting agents SPABR (Na/K), SLPR, CAD and textile auxiliary Oleox 7 are used to determine the washing action. As can be seen, the synergic effect is characteristic of all the compositions studied. However, the most pronounced synergic dependence is the curve related to the binary mixture of RENT: Oleox-7. At the same time, the relative detergency capacity of the RENT: Oleox-7 composition in the ratio 40:60, respectively, has a maximum value equal to 93%, while the deterging action even at the extremum points (max) of all other formulations does not exceed 80%.

The study of all synergic mixtures as compositions to improve the low-temperature properties of the oil of the Zhangurshi deposit does not yield any positive results. Obviously, this is due to the lack of components in the synergistic mixtures of surfac-

tants that can depressor properties. In addition, the content of paraffin wax in the oil of the Zhangurshi deposit proved to be so insignificant (no more than 5% by weight), that it is practically impossible to reveal to determine the effectiveness of the surfactant. Consequently, in subsequent experiments, it is necessary to conduct studies on highly paraffinic oils, and additives such as depressants should be added to the composition of synergic surfactant mixtures. In this regard, the high-paraffin oil of the Aktobe deposit of the Republic of Kazakhstan selected at the Saygak Terminal oilfield facility was chosen as the research object. Commodity oil, prepared on a commercial thermochemical plant, i.e. after dehydration and demineralization, had the following physicochemical characteristics:

1. Absolute density – 0.842 g/cm<sup>3</sup>;
2. Water cut of oil – traces;
3. Salt content – 20 mg/l;
4. The content of mechanical impurities - 0.021% by weight;
5. Kinematic viscosity – 345.3 ÷ 348.1 mm<sup>2</sup>/s (with three parallel measurements);
6. The point of solidification – plus 14 °C.

The tests were carried out at the Institute of Combustion Problems and of the al-Farabi Kazakh National University.

During the development of a multifunctional demulsifier, the aim of the experimental studies was to determine the change in the point of solidification and the kinematic viscosity of oil before and after treatment with synergic mixtures (RENT with Oleox-7, SPABR (Na/K), SLPR, CAD in 1:1 ratios) a low-molecular sevilene in an amount of 1.0% by weight was applied to the commercial form of the test mixtures of the reagents.

Sevilene is a low-molecular copolymer of ethylene with vinyl acetate, for example NMSEV-113. It is readily soluble in average distillate fractions of petroleum feedstocks, methanol, and residual residues of methyl, ethyl and butylcellosolves. When the temperature of the petroleum feedstock is lowered, the linear chain of sevilene, having a greater molecular weight than the refractory petroleum paraffins, acquires a thermodynamically stable structure in the form of a coil within which the emerging nuclei of paraffin crystals are blocked and lose the ability to remain the center of crystallization of other refractory hydrocarbon structures. At the same time, the oil dispersed system becomes aggregatively stable, which leads to a reduction in the point of solidification and an improvement in the rheological properties of the petroleum feedstock.

For the practical use of a depressant additive, it was necessary to dissolve sevilene in the composition of synergic surfactant mixtures. However, the dissolution of sevilene until a homogeneous system was not realized. Therefore, a solvent was preliminarily chosen, which at the same time has a good dissolving power, both with respect to surfactant and sevilene.

Any organic solvents (benzene, toluene, xylenes, ethylbenzene, chloroform, carbon disulphide, carbon tetrachloride, etc.), as well as petroleum fractions (gasoline, petroleum ether, naphtha, kerosene, diesel fraction, etc.) show a high solvent ability to other organic compounds and substances, including surfactants and sevilene. However, the listed solvents were not taken into account because of the high cost, which undoubtedly would have a significant increase in the cost of production of the final product, the multifunctional demulsifier.

Methanol and other low molecular weight alcohols readily dissolve surfactants and are widely used to impart low-temperature properties and mobility to surfactants in the production of many demulsifiers. They have a relatively low cost, but practically do not dissolve sevilene. Higher molecular alcohols (isoamyl alcohol, hexanol, heptanol, octanol, etc.) satisfactorily dissolve sevilene, but are deficient products of organic and petrochemical synthesis with high added value.

The most acceptable in terms of price and solvent capacity for both surfactant and sevilene are waste products cellosolve – carbitols (methyl, ethyl, propyl, butyl ethers di-, tri-, tetra- and pentaglycols). However, in recent years, carbitols, despite belonging to the waste category, have found wide application as solvents in the oil industry and many other industries of domestic production. Therefore, they were transferred from the waste to the target products. As a result, carbitols have acquired a certain value, but commensurate with alcohols (methanol and ethanol), and are included in the price lists of facto-

ries that produce cellosolva. Nevertheless, the availability and reasonable price for carbitols allowed to make a choice on these types of effective solvents.

In the process of mixingsynergic compositions based on demulsifier, detergent and wetting agents, respectively: RENT; Oleox-7; (1% solution of sevilene in carbitol) with the help of a homogenizer, four commercial forms of a multifunctional demulsifier containing 40% by weight of the active basis, were prepared by cipher:

A – 40% by weight. RENT: Oleox-7: sulfonol (1: 1: 1) + 1% by weight, sevilene in 60% by weight, carbitol;

B – 40% by weight. RENT: Oleox-7: SPABR (Na/K) (1: 1: 1) + 1% by weight, sevilene in 60% by weight, carbitol;

C is 40% by weight. RENT: Oleox-7: SLPR (1: 1: 1) + 1% by weight, sevilene in 60% by weight, carbitol;

D is 40% by weight. RENT: Oleox-7: CAD (1: 1: 1) + 1% wt., sevilene in 60% by weight carbitol.

The choice of demulsifier, detergent and wetting agents for the above formulations was based on the results of the evaluation of the wetting contact angle and the relative deterging action characteristic for each of the functional properties of a given surfactant.

The produced samples of the composite demulsifier were taken for the preparation of 1% alcoholic solutions (in ethanol), which are further used in the demulsification of an artificially prepared water-oil emulsion. The resulting model emulsion was characterized by the following indicators:

1. The size of the globules of water is 5–10  $\mu\text{m}$ ;
2. Water content oil – 30% of mass;
3. The content of salts – 55000 mg/l;
4. The content of mechanical impurities is 0.023% by weight.

Demulsification was carried out at a temperature of 60 °C in oil sedimentation tanks with a specific consumption of reagent samples of 100 g/t.

**Table 4**  
Oil demulsification results using samples of synergic mixtures of a composite demulsifier

Composition No	Consumption, y/t	t, °C	The amount of water released (% vol) at the time of sludge (min)							The residual water content in oil, % wt.	The residual content of salts in oil, % wt.
			5	10	20	30	60	90	120		
1. A	100	60	4.5	4.5	4.5	11.5	23.5	29.0	30.0	0.45	81.0
2. B	100	60	4.0	5.0	5.0	14.0	26.5	29.0	30.0	0.36	74.8
3. C	100	60	3.5	4.0	4.5	9.0	20.5	26.0	29.5	0.49	96.5
4. D	100	60	2.0	2.5	3.5	7.0	16.0	22.5	28.1	1.89	37.5



**Table 5**  
Results of determination of the point of solidification of oil using samples of synergetic mixtures of a composite demulsifier

Composition No	Consumption, y/t	The point of solidification of oil, °C before treatment with reagents	The point of solidification of oil, °C after treatment with reagents
1. A	100	+14	minus 19
2. B	100	+14	minus 18
3. C	100	+14	minus 16
4. D	100	+14	minus 15

**Table 6**  
Results of determination of kinematic viscosity of oil using samples of synergic mixtures of a composite demulsifier

Composition No	Measurement temperature, °C	Consumption, y/t	Kinematic viscosity of oil, mm <sup>2</sup> /s before treatment with reagents	Kinematic viscosity of oil, mm <sup>2</sup> /s after treatment with reagents
A	20	100	346.7	94.5
B	20	100	347.1	212.9
C	20	100	346.0	148.4
D	20	100	345.3	268.0

The process of demulsifying the model emulsion system was necessary to obtain dehydrated oil suitable for evaluating the effectiveness of the depressor additive (sevilene) in the composition of synergetic mixtures with different ingredients, that is, samples of composite demulsifiers A, B, C and D. To assess the effectiveness of demulsifying oil, an analytical control on the results of sludge dynamics and quantitative indicators of the quality of dehydrated oil (residual water and salt content). Then, dehydrated oil was used to determine the low-temperature and viscous properties and to change them depending on the effectiveness of the test demulsifier samples.

The results of experimental studies of synergic mixtures of reagents are given in Tables 4–6.

The results given in the tables allow to judge the high efficiency of the synergic composition of the composite demulsifier under the cipher «A», which ensures the achievement of indicators that meet the requirements for the prepared oil, and suitable for further transportation through the pipeline, the kinematic viscosity of the oil is below 100 mm<sup>2</sup>/s, and the point of solidification is reduced by 23 °C. By the content of water and salts, oil meets the requirements of GOST R 51858-2002 for 1-group quality.

#### 4. Conclusions

1. Laboratory investigations of surface activity, wetting, washing, depressing and demulsifying

abilities of experimental samples of composite compositions were carried out. The results showed that samples of demulsifiers, including in their composition:

a) component A – block copolymer of ethylene oxide and propylene oxide based on monoethylene glycol (RENT), component B – mixture of polyoxyethylene glycol ethers of oleic acid (Oleox-7), component C – mixture of sodium or potassium polyalkylarylsulfonates (Sulfanol);

b) component A – block copolymer of ethylene oxide and propylene based on monoethyleneglycol (RENT), component B – mixture of polyoxyethylene glycol ethers of oleic acid (Oleox-7), polyalkylbenzenesulfonate – mixture of sodium or potassium salts of sulfonated polyalkylbenzene resin SPABR (Na/K);

c) component A – block copolymer of ethylene oxide and propylene based on monoethyleneglycol (RENT), component B – mixture of polyoxyethylene glycol ethers of oleic acid (Oleox-7), sulfonated light pyrolysis resin (SLPR) – waste of pyrolysis production exhibit high surface activity, better wetting power and detergency, depressant property and the necessary demulsifying efficacy in the destruction of water-oil emulsions.

2. The compositions of demulsifiers under the ciphers «B, C and D» are inferior to the «A» composition in all respects. However, considering that the ratio of demulsifier, detergent and wetting agents 1: 1: 1 in the mixture cannot be considered optimal

and universal for all surfactants studied and cannot be the basis for expecting the maximum synergistic effect in their joint action, which may well manifest itself in some other ratios. In this regard, in carrying out further research, this fact should be taken into account and it will be necessary to determine the most optimal ratios of all the ingredients in the compositional composition of the multifunctional demulsifier. In addition, the composition of the composite demulsifier with the participation of sulfonol in subsequent studies will not be considered in view of the high cost of the latter. Instead of sulfonol, sodium or potassium salts of sulfated aromatic base waste (SPABR (Na/K), SLPR, CAD) can be successfully used, which are junk materials that can be purchased at petrochemical plants at a symbolic price. Of course, this requires additional research.

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