Research of the Physical-Chemical Properties of the Developed Composite Demulsifier Based on Local Raw Materials

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Abstract. For the first time, concrete results will be obtained and technologies for producing composite demulsifiers using local raw materials will be developed that can replace those imported from foreign republics, which are affordable, cheap and effective. The proposed demulsifier has the following main properties: high surface activity; flocculation ability; coalescing ability; wetting ability in relation to solid particles.

Keywords: concrete, raw material, composite, emulsion and demulsifier

1 Introduction

The oil industry is one of the most developing and innovative areas in the world, where new methods and technologies are constantly being developed. At present, various chemical reagents are used in the oil industry, which allow solving a number of problems associated with increased oil recovery, corrosion protection, destruction of oil-water emulsions, etc. [1]. The range of demulsifying reagents available today is not always able to solve the problems of field treatment of coal-bearing oil. Thus, the current situation requires the production of more effective reagents based on widely available domestic raw materials. In this aspect, research on the creation and improvement of new effective composite demulsifiers and production technologies based on them for the destruction of the emulsion in the composition of crude oil during its dehydration and desalination of the oil refining industry of the republic is in demand.

The main task of the demulsifier is that when adding it to an oil-water emulsion, reduce the effect emulsifiers on the surface of the droplets to such a state that coalescence of droplets becomes possible. The effect of a demulsifier on the armor shell of water can only affect established frameworks that are characteristic of an oil-water emulsion. Also, the demulsifier must have a feature - this is speed distribution. The new drop layer is initially only partially occupied surfactant. Further extends to that part layer that was originally unoccupied. The result is first concentration gradient of the surfactant at the interface.
section, which is more or less quickly compensated for a uniform distribution of the surfactant, depending on the speed of propagation [2].

Demulsifiers are surfactants capable of displacing from the surface of water globules dispersed in oil, an armor shell, consisting of polar (included in its composition) components, as well as paraffin particles and mechanical impurities. Nonionic surfactants are currently widely used in the processes of dehydration and desalting of oil due to a number of advantages over ionic surfactants. Their consumption is calculated in grams - from 5-10 to 50-60 g per 1 ton of oil. This significantly reduces the cost of transporting the demulsifier and the overall cost of dewatering and desalting processes [3].

Oil preparation is carried out using a wide range of demulsifiers (more than 100 types), characterized by a selective effect on the processed emulsions. The most effective and versatile demulsifiers for oil emulsions are proxanols 146, 186, 305, proxamine 385 and diproxamine 157.

Imported reagents for dehydration and desalting of oils are used: progalit (Germany), dissolvan 4411, separol 25 with a corrosion inhibitor (Germany), R-11 and X-2647 (Japan), L-1632 (USA), oxide-A (England) and servo-5348 (Holland), Kemelix 3448 (Great Britain), etc. Since demulsifiers "Dissolvan 3359" and "NALCO N 24-28" are imported, demulsifiers of the Russian company "KOLTEK INTERNATIONAL" LLC: "Hercules 1017" and "Hercules 1603" are widely used in the oil and gas industry of the Russian Federation.

In this regard, for the destruction of water-oil emulsions, a new composition of a composite demulsifier, "MK-DEM-4", was developed, which is a solution of compositions based on polyhydric alcohols, inorganic ingredients and organic solvent waste. Table 1. Setting Word’s margins.

2 Oil dehydration research method

The essence of the definition lies in the distillation of water from oil with a special solvent and their subsequent separation in a graduated receiver into two layers. The solvent must be free from sediment water impurities. As a solvent, you can use straight-run gasoline (Bp = 100-140°C), petroleum distillate (Bp = 100-200°C), containing no more than 3% aromatic hydrocarbons, isoctane, toluene. Before analysis, the oil is well mixed by shaking for 5 minutes, viscous and paraffinic oils are preheated to 40-50°C. After that, take a sample of oil 100 g (or 100 cm³), add 100 ml of solvent and mix the contents. The flask is connected to a receiver-trap (Dean-Stark attachment) and a refrigerator. The flask with the contents is heated to boiling and distillation is carried out until the volume of the lower aqueous phase in the receiver-trap ceases to increase, while the upper layer of the solvent should become completely transparent. Distillation time is 30-60 minutes. The drops of water remaining on the walls of the refrigerator are pushed into the trap or washed away with the solvent. Measure the amount of water in the trap and calculate the mass (X) or volume (X1) water fraction in%:

\[
X = \frac{V_o}{m} \times 100\%
\]

where Vo is the volume of water in the receiver-trap cm³; V is the sample volume, cm³; m is the mass of the sample, g.

Determination of the content of chloride salts in oil. The quality of oil supplied to refineries is strictly regulated by State Standard 9965-76 [4].

Oil quality indicators are determined by analyzing oil samples in chemical analytical laboratories or using special instruments directly on the flow in the pipeline.

The essence of the method consists in extracting salts from oil with hot water and titrating the aqueous extract of chlorides with a solution of mercury nitrate according to the reaction:
The content of chloride salts in commercial oil according to State Standard 9965-76 should not exceed 100 mg/l in oil of group I, 300 mg/l in group II and 1800 mg/l in group III. The content of salts in non-hydrated (crude) oils reaches tens of thousands of milligrams per liter [4].

The proposed demulsifier has the following main properties: high surface activity; flocculation ability; coalescing ability; wetting ability in relation to solid particles.

The more effective the demulsifier, the faster the process of destruction of the armor shells on water droplets is carried out and the less it is required to carry out the process.

The most effective and used in the largest quantities of the currently used demulsifiers are nonionic surfactants.

Nonionic surfactants, the second most popular group of surfactants after anionic surfactants, have polar heads. They are the mildest surfactant of all and are used in combination with anionic surfactants as a secondary cleaner, thickener and foam stabilizer.

Water and oil molecules repel each other, so it is impossible to completely wash off oil with water. Molecules of surfactants are hydrophilic at one end, that is, they are attracted to water molecules, and at the other end, they are hydrophobic and lipophilic (repel from water, but are attracted to fats or oil) [5]. This unique property allows them to reduce the surface tension between water and oil. As a result, large drops of oil are broken up by water with a surfactant into smaller and smaller droplets. Detergents that also contain surfactants act on the same principle. Water cannot wash away greasy dirt as hydrophobic fat molecules repel water. However, armed with surfactants, water begins to tear off small pieces from dirty spots and carry them away (Fig. 1).

**Fig. 1.** Destruction of water-in-oil emulsions with the addition of a demulsifier

After the introduction of a demulsifier into the oil-water emulsion, a chemical reaction does not play a major role among the ongoing physical and chemical processes. The main role is played by: the phenomenon of adsorption, wetting, change in interfacial surface tension, etc. The concentration of the chemical demulsifier affects the surface tension.

Obviously, the determination of the surface activity of reagents is an important key to understanding the mechanism of action of demulsifiers in water-oil emulsions. But this measurement cannot give an adequate prediction of the effectiveness of a demulsifier for a particular oil.

Most likely, surface activity should be one of the arguments of the complex equation of the demulsification process, which should also include such parameters as: concentration of the reagent in the emulsion; its ability to wet natural oil emulsifiers; its colloidal and chemical properties. Important characteristics of oil should also be taken into account - density, viscosity, diameter of water globules, age of emulsion, content of resins, asphaltenes, paraffins, etc.
Results and discussion

For the investigated composite demulsifier, the surface tension at the water-air interface was determined by the stalagmometric method. The essence of the method lies in the fact that the weight of the droplet is determined, which is detached from the capillary and is held by the forces of surface tension [6].

The stalagmometric method for determining the surface tension of a liquid with a device called a stalagmometer is based on establishing the mass of a liquid droplet slowly forming and torn off from the end of the capillary. In practice, it is more convenient to determine not the droplet mass, but its volume or the number of droplets in a reservoir with a known volume. The number of drops is counted as the liquid flows out through the capillary. A comparative method is used to determine the surface tension of a liquid. It consists in counting the number of drops n0 of the reference liquid, the surface tension σ0 of which is known, and the number of drops nx of the test liquid with the surface tension σx. The surface tension of the test liquid is calculated using the equation:

\[ \sigma_x = \sigma_0 \frac{n_0 \rho_x}{n_x \rho_0} \]

where \( \rho_0 \) and \( \rho_X \) are the density of the reference liquid and the test liquid, respectively; 72.75 - surface tension of water at 20 °C, dyne / cm.

Of the synthesized surfactants, the greatest interest was attracted by "MK-DEM-4", as the most effective. By the effect of lowering their surface tension of a 3% aqueous solution to 37.4 N/m at a temperature of 20°C, its specific electrical conductivity, it is characterized as a nonionic surfactant and anionic surfactant.

Table 1 shows comparative analyzes of the surface tension of an aqueous solution of the developed composite demulsifier "MK-DEM-4" and diproxamine 157 M.

<table>
<thead>
<tr>
<th>Concentration, %</th>
<th>Surface tension, N/m</th>
<th>Composite demulsifier &quot;MK-DEM-4&quot; (Uzbekistan)</th>
<th>Diproxamine-157 (LLC &quot;Kation&quot;, Russia)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,0</td>
<td>49,2</td>
<td>40,4</td>
<td></td>
</tr>
<tr>
<td>2,0</td>
<td>40,4</td>
<td>40,15</td>
<td></td>
</tr>
<tr>
<td>3,0</td>
<td>37,4</td>
<td>40,0</td>
<td></td>
</tr>
</tbody>
</table>

The results of the analyzes showed that the composite demulsifier "MK-DEM-4" at 3% concentration showed better results in comparison with the demulsifier diproxamine 157M. At the same time, surface activity is inherent in them, they significantly accelerate the process of demulsification of oil-water emulsions. A decrease in the surface tension of the demulsification system is direct evidence of the acceleration of the process of coalescence of dispersed water in oils.

The analysis of the IR spectrum of the synthesized composite demulsifier "MK-DEM-4" was also studied (Fig. 2).
Fig. 2. Analysis of the IR spectrum of the synthesized composite demulsifier "MK-DEM-4"

The data show that as a result of the reaction, a covalent bond was formed, which coincides in intensity and frequency range.

When studying the functional groups of the obtained composite demulsifier using the IR spectrum, chemical shifts were revealed at 1716.36 cm\(^{-1}\) in ester groups (carbonyl), at 1654.51 cm\(^{-1}\) in amine groups and hydroxyl groups (OH band at 3303.56 cm\(^{-1}\)).

The absorption peak in the wavelength range of the order of 3100-3600 cm\(^{-1}\) is due to the presence of bound O-H groups in the reagents, the presence of which indicates the ability of the demulsifier to form hydrogen bonds. The more such bonds, the more actively this reagent will interact with water. Since the composite demulsifier works at the water-oil interface, the presence of such bonds will increase its efficiency due to its higher adsorption capacity. Absorption peaks in the wavelength range of 1550-1750 cm\(^{-1}\) indicate the presence of a large number of carbonyl groups in the composite demulsifier, which contain free radicals, which will also increase the energy of interaction with hydrocarbon particles of the composite demulsifier with the components of the oil-water emulsion, and, consequently, and its activity.

Demulsifiers for breaking water-in-oil emulsions must meet the basic requirements:

1. ensure a high degree of oil dehydration at a minimum flow rate, a minimum heating temperature of the emulsion and a minimum settling time;
2. dissolve well in one of the phases of the emulsion;
3. prevent stabilization of the opposite type of emulsion;
4. have a high surface activity for displacing natural emulsifiers from the surface of water droplets;
5. to form an adsorption hydrophilic layer on the surface of water droplets, which does not prevent droplets from merging;
6. to reduce as much as possible the surface tension at the interface with the minimum consumption of demulsifier;
7. do not coagulate in formation waters;
8. do not cause corrosion of pipes and equipment;
9. be inexpensive, versatile, transportable, do not change their properties due to temperature changes, do not degrade the quality of oil.

We carried out laboratory tests of the composite demulsifier "MK-DEM-4" for comparison with the demulsifier "Diproxamine-157M" currently used in practice in order to study the desalting process of oil emulsions [7,8]. The research was carried out according to the following method (State standard -21534). The results obtained are shown in Table 2 below.
The results of the analyzes showed that the demulsifier "MK-DEM-4" at 3% concentration when tested in laboratory conditions showed a better result in comparison with the demulsifier currently used at the plant LLC "Bukhara NPZ" diproxamine. We carried out experimental tests of a chemical demulsifier in the amount of 100 liters of "MK-DEM-4" brand for desalting and dehydrating oil emulsions at the operating production unit ELOU-2 with employees of the Bukhara refinery [9].

For loading into a container with a volume of 10 m3, a 3% solution of demulsifier with water was prepared. To prepare 3 m3 of 3% solution, technical water in the amount of 2910 liters and 90 liters of demulsifier (100% concentration) were collected in the E-4 tank. During the addition of the demulsifier, bubbling with steam condensate was carried out, and after stopping the addition of the demulsifier, the supply of steam condensate was closed and the solution was heated to approximately 500C. At the same time, the level in container E-4 was 90 cm of the level.

With the help of the ELOU-1 N-1a pump, crude oil from the tanks RVS 58 was pumped at a rate of 120 m3/h and sent to the ELOU-2 units in accordance with the technological regulations TR 16472899-012: 2019. At the same time, from tank E-4 with a solution of 3% demulsifier brand "MK-DEM-4", it was dosed into the incoming crude oil at the pump inlet of the installation.

In this mode, the ELOU-2 technological line was flushed with a flow rate of 120 m3/h for 2 hours, while the refined oil was sent to the RVS 45.

In the course of the experiment, the quality control of crude oil at the inlet from the unit, refined oil at the outlet of the unit and directly from the reservoir with refined oil was carried out. Analyzes of the samples taken in the central laboratory of the "Bukhara Oil Refinery" were carried out in terms of density at 200C, the content of chloride salts, the content of water, and the content of mechanical impurities.

Table 3 shows the quality of oil after pilot testing.

### Table 2. The amount of salt in the composition of the oil emulsion after exposure to the developed "MK-DEM-4" and diproxamine

<table>
<thead>
<tr>
<th>№</th>
<th>Demulsifier</th>
<th>The content of chloride salts mg/dm³ (GOST-21534)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
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<tr>
<td>4</td>
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</table>

Table 3. Oil quality after pilot tests

<table>
<thead>
<tr>
<th>№ n/н</th>
<th>The name of indicators</th>
<th>Unit of measurement</th>
<th>Initial oil indicators</th>
<th>The actual results c &quot;MK-DEM 4&quot;</th>
<th>The actual results with diproxamine</th>
</tr>
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<tbody>
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</table>
The developed composite demulsifier "MK-DEM-4" is much cheaper than the existing one and its cost is 17404 soums per liter. For example, existing demulsifiers like Russian dioproxamine cost 160 rubles/kg (22,534.4 soums), Kazan demulsifier Dissolvan 3359 costs 470 rubles/kg (66,194.8 soums).

The developed composite demulsifier "MK-DEM-4" for 100 liters costs 1,740,400 soums, for 1 ton the cost is 17,404,000 soums.

Table 4 shows the comparative costs of the composite demulsifier "MK-DEM-4" and dioproxamine 157 M.

Table 4. Comparative costs of composite demulsifier "MK-DEM-4", dioproxamine 157 M and dissolvan 3359

<table>
<thead>
<tr>
<th>Comparative cost per ton.</th>
<th>Composite demulsifier &quot;MK-DEM-4&quot; (Uzbekistan)</th>
<th>Diproxamine-157 (LLC &quot;Kation&quot;, Russia)</th>
<th>Dissolvan 3359 (Kazan demulsifier)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>123572.84 rubles</td>
<td>1653.85 $ USA</td>
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<tr>
<td></td>
<td></td>
<td>22534.4 soums</td>
<td>2141.30 $ USA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>66194.8 soums</td>
<td>6290.30 $ USA</td>
</tr>
</tbody>
</table>

Thus, the developed composite demulsifier "MK-DEM-4", prepared on the basis of local raw materials, inorganic ingredients and waste organic solvents, can be successfully used in the process of dehydration and desalting of oil.

4 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 liter 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 State Standard 9965, O’zDSt 3032: 2015) with salt content up to 200.0 mg/dm3. Economic efficiency in the production and use of 100 tons of composite demulsifier - "MK-DEM-4", only due to the difference in prices (excluding transportation costs) with the Russian Diproxamine 157, is more than 513 million soums.

References


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