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# Effect of Additive on the Process of Deposit Formation of Emulsions of Varying Degrees of Water Cut

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## Abstract

The paper reports on the process of deposit formation for water-in-oil emulsions of paraffinic and highly paraffinic oils of varying water content. The effect of additives based on polyalkylmethacrylates on the quantity and composition of deposits of water-in-oil emulsions was explored. As shown, the inhibiting ability of K-210 additive was increased upon the deposit formation of water-in-oil emulsions compared to the initial oil. Herewith, the efficiency of its foreign analogue, Flexoil additive, was reduced. As determined, the nature of a change in the composition of paraffinic hydrocarbons in emulsion deposits of anhydrous oil systems was the same in the presence of additives. Therefore there remained the same effect of additives in the presence of water in the oil system.

**Key words:** asphalt-resin-paraffin deposits, water-in-oil, emulsions, additive, paraffin hydrocarbons

## INTRODUCTION

The number of developed fields that contain oil products with increased content of paraffin hydrocarbons is currently increasing. The presence of the latter in oil systems significantly complicates recovery, transportation, and storage processes. Among other things, that is also linked to asphalt-resin-paraffin deposits (ARPD) formation [1, 2]. Due to the entrance of many fields into the late stage of development, there is high water content of the extracted products with the formation of persistent water-in-oil emulsions [3, 4].

In order to address the problems related to the accumulation of ARPD on the surfaces of oilfield equipment, plenty of methods to prevent their formation and remove have been worked out [5, 6]. The most efficient approach among them is introducing chemicals that inhibit the formation process of ARPD in oil dispersed systems (ODS) [7, 8]. However, the efficiency of polymer additives is substantially decreased when water appears in ARPD. Due to that, it is required to look into the process of deposit formation of water-in-oil emulsions in the presence of additives and determine the factors that have an effect on the efficiency of additives.

## EXPERIMENTAL

This research dealt with inhibiting abilities of polymethacrylate additives, such as Flexoil WM1470 of foreign production (Champion, Czechia) and K-210 [9] based on ordered nitrogenous polymers (dodecyl amine-modified polymethacrylates). The research objects were paraffin and high paraffin oil and stable emulsions based on them with water content between 5 and 40 mass %. The preparation of emulsions was carried out using PE-0118 mixer with a power of 150 W at a blade rotation rate of 2000 rpm for 10 min; they were later allowed to stand for 1 h at 20 °C.

The resulting emulsions are resistant for two weeks not delaminating upon heating (to 70 °C). The quantitative assessment of the process of deposit formation of oils and oil-water emulsions was carried out at the system developed using a cold rod. The temperature of the medium and the sedimentary surface was identified experimentally relying on the chill point of the initial oil. The group composition of oil and residual oil of water-in-oil emulsions was determined by liquid adsorption chromatography. The component analysis of organic compounds in oil samples was carried out by gas chromatography-mass spectrometry (GC-MS). The research used the Thermo Scientific DFS GC/MS (Germany) and a Thermo Scientific chromatographic quartz capillary column with an inner diameter of 0.25 mm, a length of 30 m, a phase thickness of 0.25 μm, and a TR-5MS stationary phase. The operation mode of the GC/MS is as follows: helium as carrier gas, evaporator and interface temperatures of 250 °C. The thermostat heating program is as follows: $t_{init}$ = 80 °C, an isotherm for 2 min, and heating at a rate of 4 °C/min to $t_{max}$ = 300 °C. The dispersity of water-in-oil emulsions was assessed by optical microscopy using Axio Lab.A1 microscope (Carl Zeiss, Germany) in transmitted light at ×450 magnification.

## RESULTS AND DISCUSSION

The degree of inhibition of the K-210 and Flexoil additives selected in 0.05 mass % concentrations is 61 and 66 mass %, and also 72 and 77 mass % for the oil from Urmansk and Verkhne-Salatskoe fields, respectively (Table 1). The introduction of water into the oil system results in an increase in the K-210 additive efficiency and a decrease in the Flexoil reagent inhibiting ability for both investigated oils.

The inhibiting ability of K-210 for water-in-oil emulsions with a water content of 5 % is maximum being equal to 76 and 69 % accordingly. Increasing water content in the emulsion to 40 % results in an insignificant (to 68 %) reduction in the degree of inhibition. The inhibiting ability of Flexoil additive is reduced by almost 7 times when the water content in the water-in-oil emulsion is increased in comparison with the initial oil. The effect efficiency of additives is directly related to their solubility. K-210 additive has amphiphilic properties; hence, its solubility is improved when water is added. Therefore the degree of inhibition in emulsions is also enhanced. Flexoil additive is soluble in organic solvents only therefore adding water to the oil system worsens the solubility of the former and as a consequence, the efficiency of its effect is reduced.

The use of the most efficient additive, K-210, has an effect not only on the quantity but also on the composition of oil and water-in-oil emulsions (Table 2). The concentration of paraffin hydrocarbons (PHC) is significantly reduced in the composition of deposits isolated from the initial oil and the oil enriched with additives compared to hydrocarbon content in the initial oil. The presence of water in the oil system leads to a significant decrease in the PHC fraction in the composition of deposits. Herewith, the trend to decrease

Table 1

Deposit formation of oil and oil-water emulsions in the presence of additives

| Samples | Quantity of ARPD, g/100 g | K-210, 0.05 mass % | | Flexoil, 0.05 mass % | |
|---|---|---|---|---|---|
| | | Quantity of ARPD, g/100 g | Degree of inhibition, % | Quantity of ARPD, g/100 g | Degree of inhibition, % |
| *Urmansk field* | | | | | |
| Residual oil | 41.5 | 16.4 | 60.5 | 14.1 | 66.0 |
| Emulsion, 5 % | 39.4 | 9.3 | 76.4 | 31.5 | 20.1 |
| Same, 10 % | 40.1 | 11.9 | 70.3 | 31.6 | 21.2 |
| Emulsion, 20 % | 41.3 | 13.0 | 68.5 | 35.9 | 13.8 |
| Same, 30 % | 41.6 | 13.0 | 68.8 | 36.1 | 13.2 |
| Emulsion, 40 % | 41.5 | 13.4 | 67.7 | 37.8 | 8.9 |
| *Verkhne-salatskoe field* | | | | | |
| Residual oil | 53.5 | 14.9 | 72.3 | 12.3 | 77.0 |
| Emulsion, 5 % | 49.5 | 15.4 | 68.9 | 29.6 | 40.2 |
| Same, 10 % | 48.3 | 15.3 | 68.3 | 35.6 | 26.2 |
| Emulsion, 20 % | 47.2 | 15.2 | 67.8 | 40.8 | 13.5 |
| Same, 30 % | 45.6 | 14.7 | 67.7 | 41.4 | 9.2 |
| Emulsion, 40 % | 39.8 | 12.8 | 67.8 | 36.1 | 9.2 |

TABLE 2

Group composition of oil sediments and water-in-oil emulsions isolated in the presence of additives

| Samples | Without additive | | | K-210 | | |
|---|---|---|---|---|---|---|
| | WHCF (*n*-alkanes) | Resins | Asphaltenes | WHCF (*n*-alkanes) | Resins | Asphaltenes |
| | | | *Urmansk field* | | | |
| initial oil | 85.3 (6.6) | 13.1 | 1.6 | | – | |
| residual oil | 78.8 (6.8) | 18.5 | 2.7 | 80.1 (1.2) | 16.3 | 3.4 |
| emulsion, 5 % | 74.9 (7.6) | 16.4 | 8.7 | 75.5 (1.3) | 17.7 | 6.8 |
| same, 10 % | 78.6 (8.3) | 15.6 | 5.8 | 74.9 (1.5) | 20.7 | 4.4 |
| emulsion, 20 % | 76.2 (8.9) | 18.6 | 5.2 | 72.5 (1.9) | 21.0 | 6.5 |
| same, 30 % | 78.2 (10.5) | 17.6 | 4.2 | 76.4 (1.8) | 17.0 | 6.6 |
| emulsion, 40 % | 78.0 (14.5) | 18.6 | 3.4 | 76.2 (2.3) | 17.7 | 6.1 |
| | | | *Verkhne-Salatskoe field* | | | |
| initial oil | 94.6 (11.2) | 5.4 | – | | – | |
| residual oil | 87.3 (11.5) | 12.3 | – | 93.4 (9.7) | 6.6 | – |
| emulsion, 5 % | 87.1 (11.7) | 12.9 | – | 89.6 (9.8) | 10.4 | – |
| same, 10 % | 89.9 (12.0) | 10.1 | – | 90.5 (10.5) | 8.5 | – |
| emulsion, 20 % | 90.5 (12.5) | 6.8 | – | 92.4 (10.7) | 5.6 | – |
| same, 30 % | 94.9 (12.6) | 5.1 | – | 96.0 (11.2) | 4.0 | – |
| emulsion, 40 % | 95.1 (13.1) | 4.9 | – | 96.1 (12.0) | 3.9 | – |

*Note.* WHCF stands for wide hydrocarbon fraction.

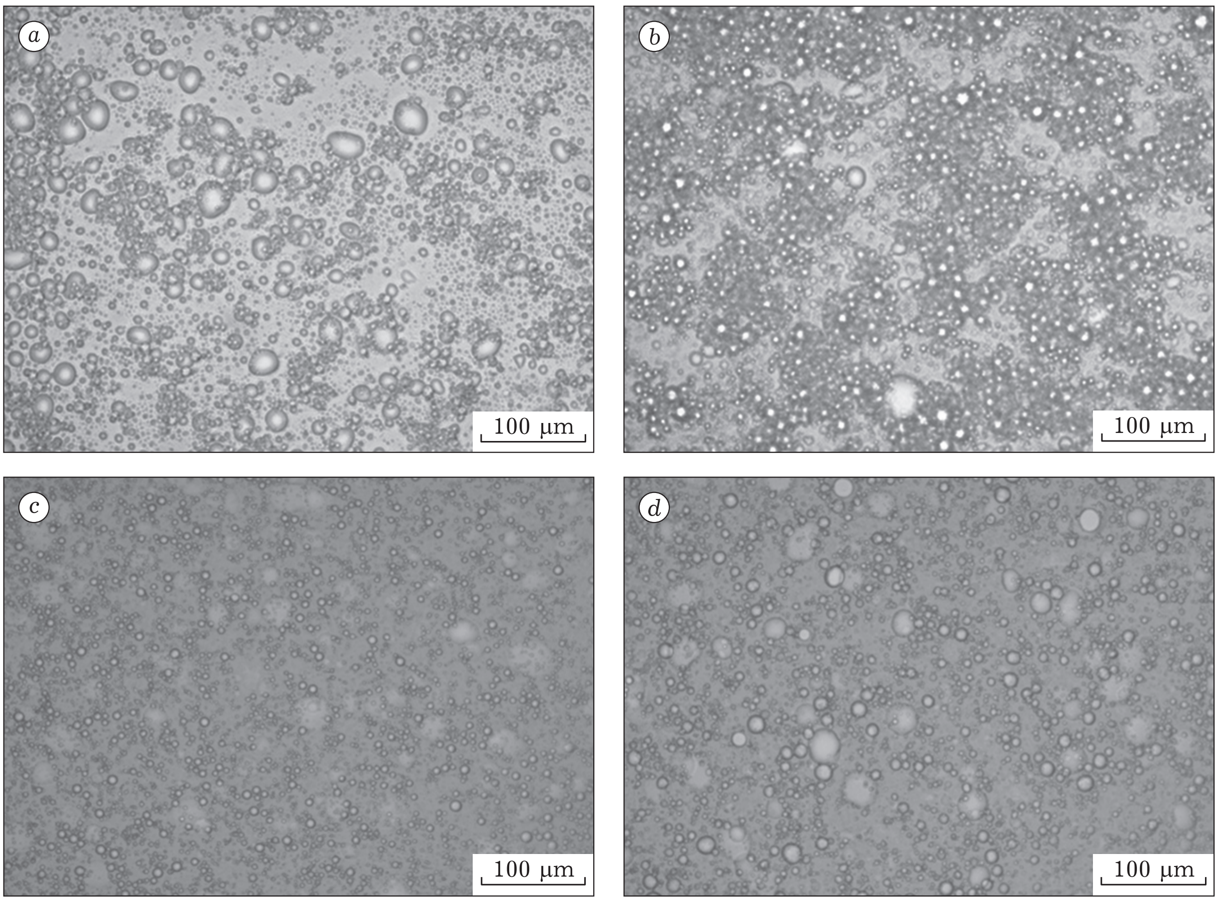


Fig. 1. Micrographs and average drop diameter ($D_{av}$) of the investigated samples of 30 % water-in-oil emulsion of Murmansk oil: *a* – initial, *b*–*d* – sediments. $D_{av}$, μm: 4.5 (*a*), 3.2 (*b*), 1.7 (*c*), and 3.6 (*d*).

the content of PHC is preserved in the deposits sampled in the presence of additives.

The minimum content of PHC characterises the 5 % sediment of the water-in-oil emulsion sampled in the presence of K-210 additive. The degree of inhibition of the additive therein is higher than that in the initial oil.

In oil sediments both with additives and without the latter, there is an increase in asphaltene fraction compared to the initial oil. Asphaltene fraction is decreased in deposits of water-in-oil emulsions without additives when the water content is increased.

The former in deposits of 5–40 % emulsions is almost twice higher when additives are introduced compared to the deposit of the initial oil. There is a slight increase in the resin fraction in deposits of 10–40 % emulsions with K-210 additive.

As exemplified by 30 % emulsion of Urmansk oil, the effect of additives on the dispersity of deposits of water-in-oil emulsions was considered (Fig. 1).

Compared to the initial emulsion, the average diameter of water drops in the deposit isolated from the water-in-oil emulsion without the additive is 1.4 and 1.8 times lower, being equal to 1.7 μm, without K-210 additive and with the latter, correspondingly. It is worth noting that the drop sizes in the sediment isolated in the presence of Flexoil additive are almost no different from the size of drops of the initial emulsion deposit.

Thus, there is a decrease in the water drop size in deposits of water-in-oil emulsions. That is likely to be explained by the fact that there is a reverse relationship between diffusivity coefficient and particle sizes. Therefore there is the diffusion of drops to the deposit-forming surface with a smaller size.

According to literature data, the presence of water in the oil system upon the formation of resistant reverse water-in-oil emulsions does not have a substantial effect on the mechanism of deposit formation [10 and 11]. It can be suggested that the effect of the reagent based on a polymer with amphiphilic properties (soluble in both the organic phase and aqueous one) in the oil system is not changed in the presence of water. The effect of the additive in both the anhydrous oil system and systems containing the aqueous phase consists in the dispersive interaction of hydrocarbon species of the polymer with oil PHC.

However, the polymer of the additive in water-in-oil emulsions interacts not with individual PHC agglomerates but with paraffins that are found in the surface of the water – oil phase boundary. Due to steric hindrances, the additive would mainly interact with PHC that are present on the phase boundary of larger size drops. Hence, smaller size drops are likely to take part in the process of deposit formation. Probably because of this, the drop size in the deposit sampled from the water-in-oil emulsion in the presence of K-210 additive (the degree of inhibition of which is over 68 %) is 1.8 times lower compared to the sizes of drops of deposits sampled from the initial emulsion and from that in

TABLE 3

Composition of paraffinic hydrocarbons in emulsion deposits of the investigated oils

| Deposits | Content, mass % | |
|---|---|---|
| | $\Sigma C_{12}–C_{16}$ | $\Sigma C_{17}–C_{40}$ |
| | *Urmanskaya oil* | |
| 5 % emulsion | 12.5 | 87.5 |
| Same + k-210 | 9.8 | 90.2 |
| 20 % Emulsion | 17.2 | 82.8 |
| Same + k-210 | 8.3 | 91.7 |
| 40 % Emulsion | 17.8 | 82.2 |
| Same + k-210 | 7.2 | 92.8 |
| | *Verkhne-salatskaya oil* | |
| 5 % Emulsion | 10.2 | 89.8 |
| Same + k-210 | 3.7 | 96.3 |
| 20 % Emulsion | 13.0 | 87.0 |
| Same + k-210 | 4.7 | 95.3 |
| 40 % Emulsion | 12.4 | 97.6 |
| Same + K-210 | 5.6 | 94.4 |

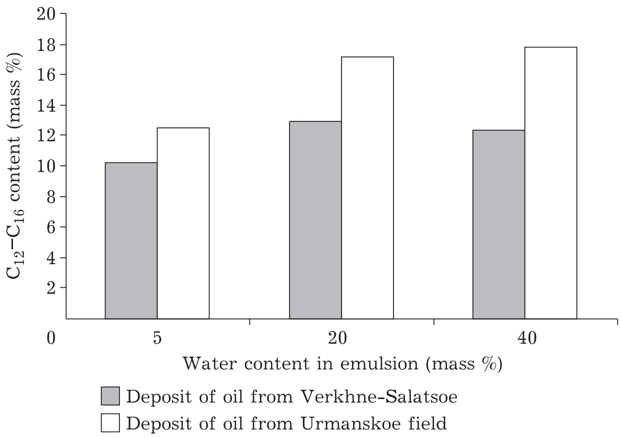


Fig. 2. Concentration of low-molecular-mass paraffin hydrocarbons ($\sum C = C_{12}-C_{16}$) as a part of deposits *vs* water content in emulsions.

the presence of Flexoil additive (a degree of inhibition of 13 %).

The interaction of additives with oil system PHC is accompanied by changes in the composition of *n*-alkanes in the resulting deposits of the investigated emulsions. The individual composition of *n*-alkanes in 5, 20 and 40 % emulsions and deposits of the latter was determined. The deposits were isolated from the investigated oil systems in the presence of the additive (Table 3).

As demonstrated by the composition analysis of PHC in oil emulsions, the initial emulsions are characterised by a relatively high content of solid paraffinic hydrocarbons (with a number of carbon atoms above 17) (see Table 3). There is an increase in the fraction of low molecular mass $\sum C_{12}-C_{16}$ species and a decrease in the concentration of solid $\sum C_{17}-C_{40}$ *n*-alkanes in the composition of PHC deposits for all investigated emulsions.

There is a symbatic increase in the fraction of low-molecular-mass *n*-alkanes when the content of the aqueous phase in emulsions is increased (Fig. 2). This trend is most apparent for paraffinic and resinous oils of the Urmansk field.

Precisely low-molecular-mass PHC are likely to be concentrated in the composition of the organic medium when the content of the aqueous phase is increased in emulsions, as solid hydrocarbons may be a part of the interphase shells of water droplets.

The use of the additive results in the redistribution of normal hydrocarbons in the resulting deposits. There is a significant reduction in the fraction of liquid PHC (by 2.2–2.7 and 2.2–2.5 times for the emulsion of the oil from Verkhne-Salatskoe and Urmansk fields, respectively).

It is noteworthy that the nature of changes in the composition of paraffin hydrocarbons of emulsion deposits matches with redistribution trends of PHC for deposited oil systems with inhibiting additives without water [12]. That may indicate the inalterability of the effect mechanism of additives when the aqueous phase appears in ODS.

## CONCLUSION

As demonstrated by the analysis of the data acquired, there is a decrease in the degree of inhibition of the additive till 68 % with an increase in water content to 20 % for emulsions of paraffinic and highly paraffinic oils from Urmansk and Verkhne-Salatskoe fields. A further increase in water content to 40 % does not have an effect on the degree of inhibition. It is worth noting that the fraction of low-molecular-mass paraffinic hydrocarbons for the oil from the Urmansk field is decreased in the composition of deposits sampled from water-in-oil emulsions in the presence of К-210 additive, whereas the former is increased for the oil from the Verkhne-Salatskoe field.

Thus, the inhibiting additive based on new ordered amphiphilic nitrogenous polymers has an effect on the process of deposit formation for emulsions of paraffinic and highly paraffinic oils leading to a significant decrease in deposit quantity in watered systems.

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