The use of esters as an inhibitor to prevent asphalt-resinous-paraffin deposits

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Abstract. This article discusses the problem of asphalt-resinous-paraffin deposits in production and tubing pipes. As a rule, these deposits help to reduce the debit of the well with the subsequent failure of the sucker rod or electric centrifugal pumps that are installed at the wellhead. For this reason, the fight against asphaltene-resinous-paraffin deposits is an urgent research task. We considered the chemical method of exposure to asphaltene deposits, in particular with the use of esters, which are part of inhibitors. Today, a wide range of varieties of inhibitors is known that are used as substances that slow down physicochemical processes; the word inhibitor itself comes from lat. “Inhibere”, which means “delay, slow down”. Of the currently available inhibitors, an ester-based inhibitor has been proposed that can be used initially to prevent the accumulation of asphaltene deposits.

1. Introduction

The development of oil and gas fields raises a wide range of issues, one of which is maintaining a constant flow rate of the well. The flow rate of the well is affected by the hydrodynamic parameters of the formation, the size of the drainage area, as well as the effectiveness of the hydraulic connection of the well with the formation [1]. The effectiveness of the hydraulic connection between the well and the formation mainly depends on the primary and secondary opening of the formation, as a result of which during the future operation most of the wells become imperfect. Therefore, their effective productivity loses its potential. In addition, during the development of oil and gas fields, the hydrodynamic parameters of the bottomhole formation zone, such as permeability and hydraulic conductivity, are constantly changing and, as practice shows, often are getting worse [2, 3]. Factors affecting the decline in well productivity are:

- physical and lithological;
- physical and chemical;
- thermobaric;
- mechanical.

Physicochemical factors that reduce well productivity include: emulsification, deposition of paraffin, salt and asphalt-resin substances on the surface of the rock skeleton. Thermobaric factors to reduce well productivity include changes in temperature and pressure in the reservoir, which leads to the activation of physico-chemical factors when the formation properties of rocks and fluids change. A decrease in temperature causes a sharp increase in oil viscosity, a decrease in its mobility and a decrease in well productivity. For this reason, questions about the expedient exploitation of an oil field...
and methodical and preventive work aimed at maintaining a constant flow rate of a well are an urgent research task [4-7].

2. Methods and material
Based on the analysis of literature data, we can state the fact that to prevent the formation of paraffin deposits in oil fields, a chemical method of protecting downhole equipment is used, based on the use of specially selected chemicals - paraffin inhibitors, which are ionic or non-ionic surfactants. Ionogenic surfactants are divided into cationic and anionic [8-10].

3. Method description and its evaluation
Anionic surfactants in water dissociate into ions (positively charged cation and negatively charged anion). A negatively charged anion has surface activity. The most typical representatives of anionic surfactants used in the oil industry are alkyl acryl sulfonates (sulfonols), alkyl sulfonates and alkyl sulfates [11, 12]. The structural formulas of the anionic surface-active agent are shown in Figure 1 (a).

Cationic surfactants also dissociate in water as ions, but unlike anionic surfactants, cations, positively charged ions, have surface activity. Examples of cationic surfactants: aliphatic amines - hydrochloric acid salts, imidazoline derivatives. The structural formulas of the anionic surface-active agent are shown in Figure 1 (b).

![Figure 1. Structural formulas of anionic surface-active agent: a, b -- structural formulas of anionic and cationic surfactants, respectively](image)

Currently, the following Russian patents are known to help prevent asphaltene deposits: (RF patent No. 2388785, published May 10, 2010), the potassium salts of hydroxyethylated alkyl phenol carboxymethylate, butyl alcohol, etc.; (RF patent No. 2027730, publ. 01/27/1995), which combines a surfactant and an aromatic solvent, an ester obtained by sequential addition of ethylene oxide and propylene to fatty alcohol acts as a surface-active agent, and as an aromatic solvent, aliphatic alcohol and aromatic hydrocarbons, etc. This list can be continued at least as long as you like. But, a drawback of the compositions of the above substances is the lack of certain components that make up the surface-active agent and their high cost [13, 14].

Having analyzed the experience and application of various surface-active agents for cleaning production casing and tubing pipes, it is proposed to use inhibitors to prevent asphaltene deposits at an early stage of field development. As an inhibitor, noniogenic surface-active agents are used in conjunction with polymer esters. To evaluate the effect of the inhibitor we proposed on asphaltene deposits, the “capillary” method was used, the qualitative characteristic of which is the flocculation coefficient. Flocculation is a two-stage process of particle sticking, as a result of which several large flocs are formed from many small particles of oil (Figure 2).
Figure 2. Flocculation Stages

The essence of the capillary method is to apply a drop of the solution through a narrow capillary to filtered paper, which traps large dispersed particles in the center of the spreading drop. From the appearance of spots on the paper after absorbing a drop of a solution, it is judged about the presence of aggregates of asphaltene particles in it. Uniform coloring of spots on the sheet indicates the absence of aggregates such as asphaltene deposits, and uneven color indicates the presence of asphaltene deposits. The flocculation coefficient \( k_f \) is determined by the formula:

\[
k_f = \frac{V_o}{(V_o + x_{\text{min}})}
\]

Where \( x_{\text{min}} \) is the minimum volume of ester, which must be added to the volume of the analyzed oil \( V_o \) to detect uneven color stains on filtered paper.

As an example, we examine degassed oil with a density of 917 kg/m³, a viscosity of 97.3 MPa·s, a tar content of 12.6%, paraffins - 3.5% and asphaltenes - 1.71%. In the course of the study, we obtain the following graph (Figure 3).

![Figure 3. Dependence of the flocculation coefficient of asphaltenes in oil on its content in various concentrations of non-ionic surface-active agent in combination with a polymer ester](image)

As can be seen from the graph obtained, when an inhibitor based on a non-ionic surface-active agent is added to the oil in conjunction with an ester, the flocculation coefficient decreases with increasing concentration of the inhibitor, which indicates a decrease in their particle size as a result of the dispersing effect of this reagent.

4. Conclusion

One of the most important and urgent tasks of the development and operation of oil and gas fields was considered and investigated, namely, the fight against asphalt-resinous-paraffin deposits and their prevention at the initial stages of the development process. It was found that it is necessary to deal
with asphaltene deposits at the initial stages of the development process, because the time-lapse of an event of this nature leads to a decrease in the well flow rate with the subsequent failure of the sucker-rod or electric centrifugal pumps. An analysis of methods to combat asphaltene deposits is carried out, and a chemical method based on the action of asphaltene deposits with surfactant inhibitors in combination with esters is proposed.

The results of the study showed that, from the point of view of technical and economic feasibility, the use of a surfactant-based inhibitor in combination with esters eliminates asphaltene deposits on pipes in small concentrations at the initial stage of development of oil and gas fields.

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