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Selection of depressor additives for transportation of high-viscositive Kazakhstan oils

By the «cold finger» method were deposited asphaltene-gum-paraffin deposits (AGPD) of Kumkol oil at different temperatures. Their quantity, composition and also efficiency of inhibition of AGPD by depressor additive Dewaxol TM was determined.

Key words: oil, asphaltene-gum-paraffin deposits, rheological properties, depressor additives.

The problem of fight against the asphaltene-gum-paraffin deposits (AGPD) of oil in world practice arose more than 120 years ago and till today remains actual. Due to the steady reduction of reserves of light crude, come to processing heavy oil, enriched with high-melting paraffin hydrocarbons, gum and asphaltene components now. Got in the territory of Kazakhstan oil are high-paraffinic, along with alkanes of a branched structure also contain a lot of normal structure paraffin. The last are characterized by higher values of temperatures of hardening, as defines deterioration of such properties as mobility and viscosity.

Oil deposits are the complex mixture of the high-molecular hydrocarbon compounds containing alkanes of 12–86 % (paraffin, naphthenes, ceresines), gums (1–20 %) and asphaltenes (0,5–45 %), oil oddments (33–41 %), water (0–80 %) and inorganic inclusions (0–37 %) (salt, sand) [1–4].

The improvement of rheological properties of oil under the influence of an additive allows solving the practical problems of a pipeline transportation. The main advantage of application of additives is stability of improvement of rheological properties of oil on all way of driving from a well face to oil refineries even in the composite climatic conditions. However, depressants and inhibitors, which are used now are not effective enough and do not possess the balanced properties. Besides, there are no generalizing recommendations about their application depending on physical and chemical characteristics and component composition of oils in literature.

The goal of this work is the research of rheological behavior of high-paraffinic oils (HPO) and selection of efficient polymeric depressor additives for prevention of AGPD sediment on internal walls of oil pipelines.

Experimental part

The Kumkol oil is characterized by high content of paraffin, and comparably low content of gum and asphaltenes. Therefore, the temperature of flowability loss (T_{lf}) of Kumkol oil, which is in charge of oil transition from free-dispersible in a bound and dispersible state, is high enough, which is caused by the high content of paraffin (Table 1).

Table 1

Component composition and rheological parameters of Kumkol oil

Density, kg/m^3 (at 20 ºC)	T_{lf}, ºC	Kinematic viscosity, mm/s^2 (at 20 ºC)	Paraffin, %	Gum, %	Asphaltenes, %
815–818	+6/+9/+12	8–13	12–14	5–6	to 1

Rheological characteristics of Kumkol oil (shear stress of τ, effective viscosity of η, dynamic ultimate strain of shift of τ_0, flowability coefficient K_f) are presented in Table 2.

From the data presented in table 2 follows that there is a direct dependence of values of shear stress, effective viscosity, dynamic ultimate strain of shift on temperature which is caused by reducing contents of paraffin in oil. Oil of a field Kumkol in temperature range 20–50 ºC keeps the Newtonian behavior though is in a free-dispersible state.

By chromatographic method we determined content of normal alkanes with number of carbon atoms from C_4 to C_{44}. It is revealed that the main share of *n*-alkanes in Kumkol oil is the share of group paraffin

C_{15}–C_{44}. Among this group in turn, the greatest percentage is the share of paraffin C_{15}–C_{19} (22,1 %) and C_{20}–C_{29} (32,4 %), and the least — of C_{30}–C_{44} (9,8 %).

Table 2

Rheological parameters of Kumkol oil

t, ºC	τ, Pa (D = 5 s^{-1})	η, Pa·s (D = 5 s^{-1})	τ_0, Pa	K_f, Pa·s
60	0,055	0,011	0	0,011
50	0,100	0,020	0	0,020
40	0,726	0,144	0,760	0,054
30	3,619	0,717	2,800	0,208
25	18,16	3,595	23,17	0,534

The process of selection of AGPD of petroleum crudes and the oil subjected to thermal treatment (TT), was investigated by means of the «cold finger» installation modeling of sedimentation process of AGPD on a long distance pipe line (Fig. 1).

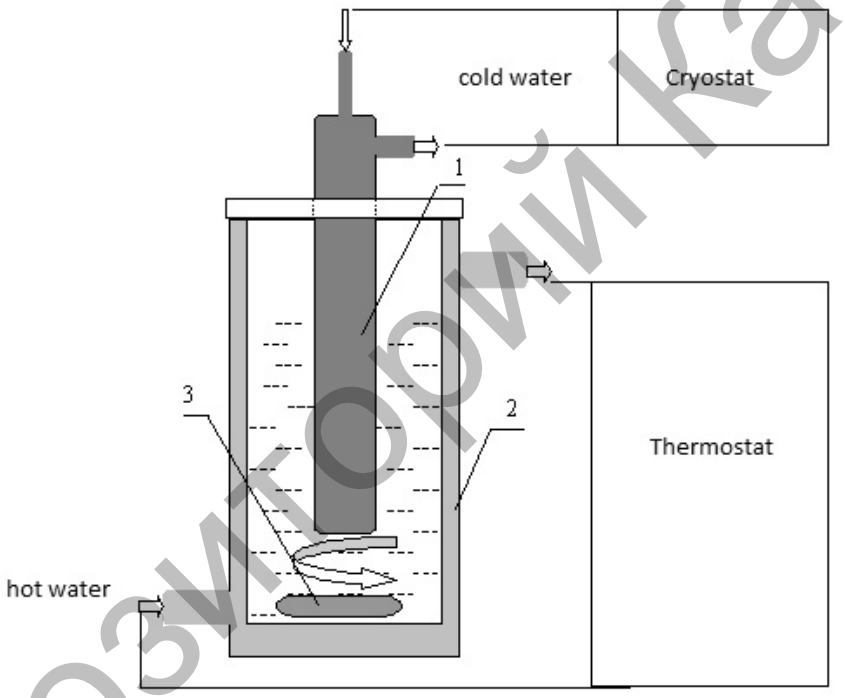


Figure 1. The scheme of the installation modeling of AGPD sedimentation

During the work a steel core cooled up to the temperature which is approximately 3 ºC lower than oil T_{lf}. In a glass 350 ml of the oil was poured with a temperature variation from 60 to 20 ºC. The AGPD, which have dropped out on a cold steel surface, were removed mechanically and analyzed on a chromatograph.

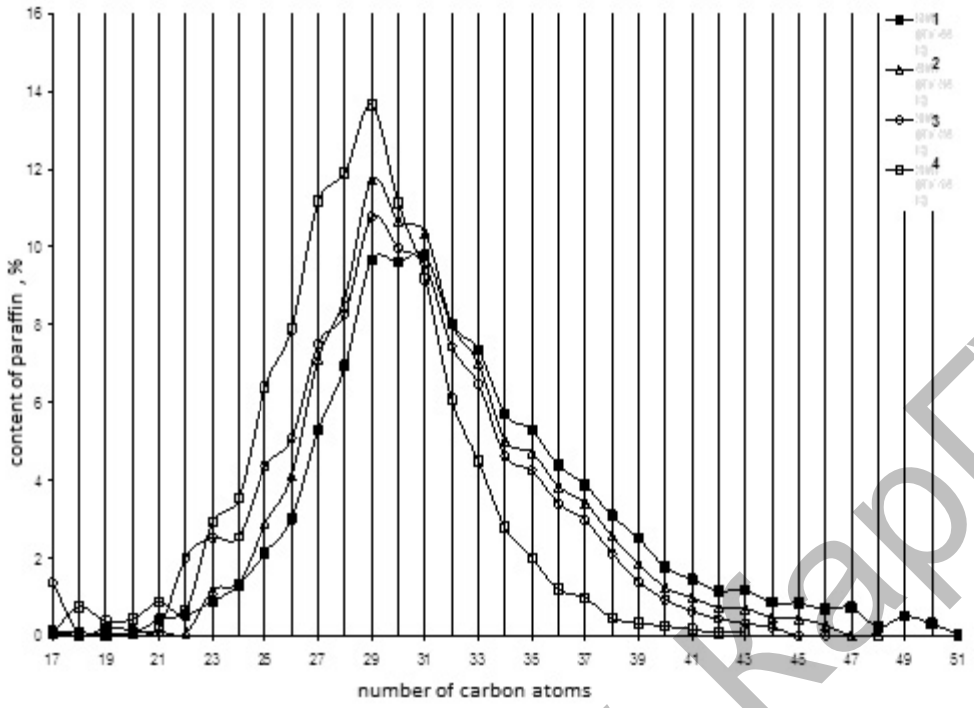
For a choice of efficient additives the screening of 11 reagents (additives) on ability to depress temperature of loss of flowability of Kumkol oil was carried out.

The experiment made as follows:

Oil of a field Kumkol was heated to the temperature of 60 ºC and thermostated within 30 minutes, then entered into oil heated solution of an additive (concentration of the active substance 200, 500 and 1000 ppm) and again thermostated oil within 20 minutes. Then, the oil was cooled on air and the temperature of loss of flowability was measured.

Results and discussion

Results of the researches ASPO allocated from oil without processing and after processing with additives are presented in Tables 3–4 and in Figure 2.



Oil temperature, ºC: *1* — 50; *2* — 40; *3* — 30; *4* — 20

Figure 2. The molecular-mass distribution of paraffin in the allocated AGPD on a «cold» core (core temperature 6^0C) from Kumkol oil

Table 3

Quantity of AGPD allocated from Kumkol oil (without processing)

№	T_{oil}, ºC	T_{finger}, ºC	ΔT, ºC	Mass of AGPD, g	Amount of paraffinum durums in AGPD, %	Appearance
1	60	6	54	6,6	23,4	Solid, dense, compact-grained
2	50	6	44	4,8	19,9	Solid, dense, compact-grained
3	40	6	34	7,8	13,7	Solid, friable, coarse-grained
4	30	6	24	7,2	11,1	Solid, coarse-grained
5	20	6	14	7,8	8,6	Friable, fluid at room temperature

The depressor activity of additives was compared to the activity of an additive DMN-2005 (a depressor, copolymer of ethylene with vinyl acetate of production of NPF of «Neftehimtekhnology» Kemerovo).

From the number of studied reagents the Dewaxol TM can be distinguished as a depressor additive. Its 200 ppm input in Kumkol oil was accompanied by fall of temperature of loss of flowability of oil to 0 and –3 ºC.

The selection of AGPD of Kumkol oil, wrought at 60 ºC with addition of the depressor additives DMN-2005 and Dewaxol TM, investigated by means of the «cold core» installation.

Results of research are presented in Table 4.

Table 4

Change of AGPD quantity from Kumkol oil after processing by additives

Sample	Change of AGPD quantity, g				
	1 day	3 day	5 day	10 day	20 day
Kumkol oil TT 60^0C (500 ml) + DMN (0,1 ml or 200 ppm of active substance)	4,7	4,7	5,0	5,3	5,5
Kumkol oil TT 60^0C (500 ml) + Dewaxol TM (0,1 ml or 200 ppm of active substance)	4,9	5,0	5,5	5,5	5,8

These additives showed the following values of inhibiting power:

Depressor additive DMN-2005: $I_{DMN\text{-}2005} = 27$ %.

Depressor additive Dewaxol TM: $I_{Dewaxol\ TM} = 25$ %.

Therefore, the additive Dewaxol TM on value of inhibiting power slightly concedes to the additive DMN-2005.

Thus, the usage of depressor additive Dewaxol TM (produced by Mirriko company, Kazan), consisting of nonionic surface-active substances and polymeric compounds in alcohol-aromatic solvent can be suggested. Inhibiting action of this additive is explained by blocking of crystal growth of paraffin in phase boundary model system — a «cold» core at the expense of what considerably decreases quantity of paraffin sediments, chill point and improvement of rheological behavior.

The molecular-mass distribution of paraffin in the allocated AGPD studied by method of the gas chromatography is presented in Figure 2. From the presented schedules correlation between results of chromatography and laboratory analyses is visible. For investigated oils the following tendency is characteristic — reduction of a difference between oil temperature and temperature of a steel surface of a core in the course of allocation of AGPD on a «cold» core leads to change of the contents long-chain and short-chain paraffin in AGPD. So, the contents in AGPD is short-chain (to C_{30}) alkanes increases with reduction of temperature of investigated oil. In samples of AGPD allocated from oil at high temperature long-chain paraffin prevails (C_{30} above).

Visual supervision and the analysis of component composition showed that the sample of AGPD is nonuniform on a consistence and is divided into firm and friable components. The firm part which is densely linked to a core differs in lack of mechanical impurity and the low maintenance of asfaltenes and gums.

The content of paraffin in firm part of AGPD is lower, in comparison with a friable component. However, according to a chromatogramm, in firm part the greatest content of long-chain C_{27}–C_{48} paraffin is observed. This paraffin also drops out first of all on a core surface, forming the firm, difficult deleted layer. AGPD samples which are dropping out on an internal steel surface of the pipeline consist from dense it is difficult for the deleted part and more friable and easily deleted part.

Conclusion

Thus, if to consider the obtained data within real process of transportation of oil, it is possible to draw the following conclusions:

Loss the long-chain paraffin crystallizing at high temperatures happens at the initial stage especially in case of a big difference between temperature of oil and a wall of a pipe. Thus the quantity of AGPD will be small, but these deposits will represent dense hard-to-remove mass.

For the prevention and decrease in loss of such AGPD it is possible to recommend, not to allow receipts in the oil pipeline with high temperature (50–60 ºC) without having achieved decrease in temperature to 30–40 ºC.

At a small difference between temperature of oil and a wall of a pipe there is a loss of bigger quantity of AGPD. Data of AGPD will represent more friable easily deleted deposits (owing to the high contents the of short-chain paraffin and asphaltene-gum substances and rather low content of long and chain paraffin). For the prevention and decrease in loss of such AGPD the depressor additive combining qualities of inhibitor of paraffin deposits [5] can be used.

It is established that application of the depressor additive Dewaxol TM by quantity of 200 ppm allows reducing the quantity of AGPD by 25 %, and allows Kumkol oil to behave as the Newtonian liquid at subzero temperatures. It is defined that the effect from the additive Dewaxol TM remains the for long time after the input. It is also observed both for values of temperature of loss of flowability, and for rheological parameters. Effectiveness of an additive remains 10 days, then, the slight deterioration of cold-fluid properties is observed. The high difference between temperature of oil and temperature of a steel surface (more than 30 ºC) promotes the formation of dense, difficult deleted APPD on a metal surface. For decreasing the mass of AGPD formed at transportation of high-paraffinic oils on steel pipelines, and increasing of a share in them friable, easily deleted sediments, it is recommended to support a difference between temperature of oil and a pipeline wall no more than 20 ºC and a turbulent mode of a current.

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Жоғары тұтқыр қазақстан мұнайын тасымалдау үшін депрессорлық қосымдар таңдау

Мақалада «суық ши» әдісімен Құмкөл кен орны мұнайының құрамындағы асфальтен-шайыр-парафинді шөгінділердің (АШПШ) мөлшері мен құрамы әр түрлі температурада зерттелді. Сондай-ақ Dewaxol ТМ депрессорлық қосымының АШПШ ингибирлеу тиімділігі анықталды.

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Подбор депрессорных присадок для транспортировки высоковязкой казахстанской нефти

В статье методом «холодного стержня» были осаждены асфальтено-смоло-парафиновые отложения (АСПО) нефти месторождения Кумколь при различных температурных режимах. Были определены их количество и состав, а также эффективность ингибирования АСПО депрессорной присадкой Dewaxol TM.