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Using New Nanostructured Coordination Polymer Additives BAF-1 and BAF-2 in Crude Oils

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Abstract: Recently, there has been a steady trend towards an increase in the volume of oil transported. Thus, in order to solve the problem of increasing the volume of oil pumping, it is necessary to develop new or optimize the applied oil transportation technologies, taking into account their flow properties and operational characteristics of pipelines. Due to the urgency of the problem, the results of experimental studies of mixed oils by physico-chemical methods are of great interest. Our studies have shown that when mixing oils it is necessary to take into account the factor of the mutual influence of the composition of oils in order to estimate the unacceptable and optimal concentrations of individual components. Background Recently high-viscosity oil fields, where non-Newtonian crudes are met, are rapidly developed. Non-Newtonian viscosity dependence on the flow rate imposes certain requirements to the transportation of such petroleum. Aims and objectives to improve the rheological properties, the kinematic viscosity of the heaviest Azerbaijan oil from Muradhanla field, in particular, so that to facilitate pipeline transportation of the tank oil. Methods Laboratory experiments and analysis of the lab data. Conclision: Laboratory experiments and analysis of laboratory data proved the suitability of nanostructured coordination polymers for transporting high-viscosity oil from Azerbaijan Muradhanla and Sangachal oils. Transportation with coordination polymers involves injection of polymer and diesel alkaline waste (DSO) through hydrodynamic cavitator. This significantly reduces viscosity of heavy oil during transportation. Coordination polymer-based composites have been developed and tested. Use of composite solves a number of technological problems associated with the transport of high-viscosity oil.

Keywords: Disperse Systems, SNPX-2005, Resins, Asphaltenes, Viscosity, Paraffinization, Dynamic Viscosity, BAF-1 Reagents and BAF-2

1. Introduction

In recent years, a significant part of oil production has been provided by the inclusion of heavy, highly viscous oil fields in the development process. The production and transportation of such oils is difficult due to the high viscosity and freezing temperature, abnormal rheological behavior. Peculiarity of rheological properties of these oils is manifested in variability of their dynamic viscosity, depending on shear stress and liquid velocity [1]. During transport of high-paraffin oil there is intensive paraffination of pipelines, reduction of their throughput capacity, which significantly complicates operation and leads to increase of labor and material costs [2]. High-paraffinic oil at low temperatures show sharply expressed non-Newtonian (viscoplastic, viscoelastic, thixotropic) properties without which it is impossible to organize rational operation of wells, collecting, preparation and transport of oils.

When the pumping process is stopped, paraffin structures are formed, the strength of which depends on the content of paraffin fractions, the rest time of the oil, the conditions for the formation of paraffin structures and other factors. The resumption of the pumping process sometimes requires the creation of start-up pressures that are significantly higher than the operating pressures of pipelines, valves and equipment. [3].

Asphalt-resin-paraffin deposits (ARP) are still relevant in oil production and transportation, despite the fact that many different ways of their prevention and removal have already been developed. Practice has shown that the most promising way to prevent asphaltosmoloparaffin deposits remains the chemical method of acting on oil using additives (additives) for various purposes - depressant (reducing the freezing temperature of oil), inhibiting (preventing the occurrence of ARP), etc. A very large number of additives are used in the petroleum industry, but high molecular weight polymer compounds of various types have become most widespread. It should be noted that the existing additives - regulators of the rheological properties of oil are not devoid of shortcomings. In some cases, they show little or no regulatory effectiveness. Therefore, a relevant scientific and applied task is the development of new polymer compositions for controlling the viscosity-temperature properties of oils [4].

It is promising to share several methods of influencing petroleum dispersion systems, for example, the use of various versions of electric, electromagnetic, magnetic, vibration or acoustic fields. At the same time, effects corresponding to an increase or, conversely, a decrease in the ordering of the supramolecular structure of substances are relatively easily achieved. The fight against ARP provides for the implementation of measures in two areas - the prevention of precipitation and their removal. An important environmental and economic task is the collection, transportation, preparation, processing and disposal of ARP and oil sludge. Further progress in the field of transport and the preparation of problematic oils is associated with advances in the field of oil chemistry and the development of new approaches to the impact on oil dispersion systems [5].

The composition of AFS has been studied by many authors, and to date there are fairly clear ideas on this issue. Solid hydrocarbons of oil and resin-asphaltenes (CAB) are the main part of high-molecular oil compounds. The composition of ARP varies widely depending on many factors in wells and oil collection systems, they contain (wt. %): paraffin - 12-86, resins - 0.8-20, asphaltenes - 0.3-45, oils - 6.3-50, inorganic inclusions - 0-37. Melting point of such deposits varies from 25 to 150°C [6]. According to modern ideas, ARP are not a simple mixture of asphaltenes, resins and paraffins, but are a complex structured system. The majority of ARP are paraffins. The monograph [11] contains data on chemical composition of solid limit hydrocarbons of oil: paraffin samples having a melting point of 40 to 60 °C are dominated by paraffins of a normal structure with a number of carbon atoms C_{24} - C_{30}; - the content of paraffin hydrocarbons of the isogenesis depends on the nature of the oil and can reach 25-30 wt. %, while low-branched paraffin hydrocarbons prevail; - with an increase in the molecular weight of solid hydrocarbons in their composition, the proportion of naphthenic and aromatic structures increases.

2. Materials and Methods

Resinous-asphaltenes are heterocyclic compounds of a complex hybrid structure, which include nitrogen, sulfur, oxygen and metals (Fe, Mg, V, Ni, Ca, Ti, Mo, Cu, Cr, etc.). Up to 98 wt. % of the surfactants are aromatic and naphthenic structures. Surfactants are concentrated in heavy oil residues - tar and bitumen. Depending on the nature of oil, CAS make up from 40 to 60-70 wt. % of heavy oil residue.

Table 1 [7] shows the percentage of resins and asphaltenes in various oils. Thus, the resinous-asphaltenes of oil make up the bulk of the so-called non-hydrocarbon compounds of oil. Depending on the content of paraffins (P), resins (R) and asphaltenes (A) and their ratio in the total mass of precipitation $\beta=(R + A)/P$, all AFS are divided into the following types: - asphaltenium, value $\beta \geq 1,1$; - paraffin, value$\beta \leq 0,9$; - mixed, value$\beta \approx 0,9–1,1$.

Table 1. *Content of resinous-asphaltenes in various oils.*

Field	Geographical area	Contents, Wt.%	
		Resins	Asphaltenes
Ellenberger	Municipality. Texas	4,2	0,24
Ragusa	Sicily	9	0,28
Grozny	RUSSIAN FEDERATION	8	1,5
Karami	China	14	1,8
Wilmington	California.	14	5
Belaim	Egypt	20	13
Baskan	Venezuela	29	18
Muradhanla	Azerbaijan	18,32	4,86

An analysis of the composition of ARP sampled at various depths of wells shows that at a depth of more than 1000 m there are more asphalt-resinous substances than paraffins [8]. Mechanical impurities at such depths are practically not involved in the formation of deposits (their content does not exceed 4-5 wt %). With a decrease in the depth of wells, there is a decrease in the content of asphalt-resinous substances in ARP, as well as an increase in the number of mechanical impurities and solid paraffins [9]. The closer to the well head, the more ceresins are in the ARP composition, and, accordingly, the higher the structural strength of the deposits. Although asphaltenes and resins are generally significantly lower than paraffins in the AFS composition, their presence in the oil can have a significant effect on both the kinetics of paraffin crystal formation and their structure by adsorption on the surface of paraffin crystals or co-precipitation. The resinous-asphaltenes may be present in the oil in the molecular dissolved, colloidal-dispersed state or in the form of macrophase [10]. The transition from one state to another may be due to changes in solvent composition and temperature.

The question of the role of asphaltenes in the processes of formation of ARP today has no definite answer. The crystallization of paraffins begins with the least soluble hydrocarbons having a relatively large molecular weight. The released paraffin crystals, joining together, form a strong structural grid, in the cells of which a liquid phase of oil is enclosed [12]. The growth rate of solid deposits on the pipeline wall due to molecular diffusion is determined by the Fick diffusion equation.

$$dG/dt=AD_m dC/dy,$$

where G is the total volume of paraffin deposits, A is the surface area, Dm is the molecular diffusion coefficient, dC/dy is a derivative of the volume fraction of paraffin particles dissolved in oil by distance from the pipe wall. It follows from the above equation that the intensity of formation of deposits is determined by the concentration of paraffin particles in a unit volume and the thickness of the diffusion layer [13].

To reduce the freezing temperature and improve the rheological characteristics of the produced oil in fields with heavy, highly viscous oil, oilmen use a number of technologies: thermal treatment and other methods of physical influence, dilution with light fractions of oil or various solvents, as well as the introduction of additives regulating viscoelastic properties of oil. To improve the rheological properties of high-paraffin oils, chemical methods of treating oils using depressant, inhibitory and detergent additives are used. Currently, a very large number of additives are used in the oil industry, but high molecular weight polymer compounds of various types have become most widespread [14].

The rheological properties of the oils are mainly affected by the resins and asphaltenes contained in them, and paraffin hydrocarbons, depending on the temperature factor.

Various types of additives (depressants) are added to control the effect of paraffins on the rheological properties of oils and increase the efficiency of transportation at low temperatures to the transported oil [15].

The observed and encountered technical difficulties in transportation show that the increase in viscosity of oils is directly related to the number of resins and asphaltenes when the temperature changes and from paraffins in its composition. To control efficient transportation through pipelines, oil is mixed in advance, compounded and selected by appropriate technological conditions, transported.

The purpose of the study:

The purpose of the present study is to study changes in the rheophysico-chemical properties of commercial oils using additives.

3. Results and Discussions

The effect of the reagent on highly viscous oils was checked on six samples of oil from the Neftchalinsky, Shirvansky, Karasuinsky, Muradkhanlinsky and Salyanskoye fields, the most similar in physical and chemical properties. In the composition of these oils, the amount of resinous and asphaltene hydrocarbons is more, and paraffin hydrocarbons are less and their freezing temperature is lower. Compared to these samples, Sangachalskaya oil differs in composition, so that in it asphaltene hydrocarbons average 0.36% (mass), paraffin hydrocarbons 9% (mass), and freezing temperature 18°. As part of the oil of the Muradhanlinsky deposit, asphaltene and paraffin hydrocarbons, respectively, make up an average of 4.86% (mass) and 6.21% (mass), freezing temperature 9° (Table 2). As already emphasized, the Muradkhanlinsky and Sangachalskoye oilfields show distinctive properties, therefore, the effect of the SNPX-2005 reagent has been checked on them.

Table 2. *Physicochemical properties of Muradkhanli and Sangachal oil fields.*

Indicators	Muradhanla	Sangachal	Test method
Density at 20°C, kg/m^3	876,7	856,3	GOST 3900
Viscosity, mm^2/cm^3 20°C	83,32	27,3	GOST 33
Content,% (w/w)			
Resins	18,32	8,94	Cromotakrafiya
asphaltenes	4,86	0,36	GOST 11858
paraffin	6,21	9,7	GOST 11851

Laboratory studies were carried out on a rotary viscometer (Reotest-2) with verification of changes in dynamic viscosity. For studies on the effect of the reagent on the dynamic viscosity of samples, the reagent was taken with a calculation of 0.8 kg/ton. Measurements of dynamic viscosity of oil samples were carried out in parallel for non-reactive and reagent samples of commercial oils at temperatures of 5, 10, 20°C C and 5°C, taking into account the additive of 1 kg/ton. The measurement results are shown in Tables 3 and 4.

The results of the analyses showed that the effect of the SNPX-2005 on the rheological properties of the Muradkhanlinsky and Sangachalsky oil samples is different, that is, as can be seen from the table, when using an additive taken taking into account 0.8 kg/ton at 20°C, their viscosity decreases by an average of 19.3% (wt), at 10°C -by 26.1% (wt), at 5°C - by 10.1% (wt). This suggests that at low temperatures, the additive weakly affects the rheology of oil. If the additive is taken taking into account 1 kg/ton at 5°C, the drop in dynamic viscosity is relatively increased. Tables 3 and 4 respectively show the trend of dynamic viscosity at temperatures of 5, 10 and 20°C without additive and with additive taking into account 0.8 kg/ton at different speed stages.

3.1. Results

The results of the conducted experiments showed that at a temperature of 20°C at various speeds, the dynamic viscosity of the taken samples of oils drops, and at temperatures of 10 and 5°C increases. The reason for what is happening, in our opinion, is the change in the aggregate state of paraffin hydrocarbons at low temperatures. The increase of dynamic viscosity values at low temperatures (10°C) is on average 33.8% (wt), and at 5°C-35.2% (wt). And for the oil of the Sangachal field at 5°C compared to the primary sample (without additive), the reverse process is underway. Thus, SNPX-2005 was added to the Sangachal oil sample with a calculation of 1 kg/ton and 0.8 kg/ton at 5°C and the dynamic viscosity was measured. The measurement results showed that with an increase in the amount of additive, the viscosity of oil drops from 35.2% (w/w) to 7.9% (w/w).

Table 3. *Change of dynamic viscosity of Muradkhanli oilfield oil samples, without and with addition of SNPX-2005 taking into account 0.8 kg/ton, 1.0 kg/ton additive.*

Speed stages	Dynamic viscosity without and with addition of 0.8 kg/ton SNPX-2005, cPz.									Dynamic viscosity without and with addition of 1.0 kg/ton of SNPX-2005, cPz.		
	20°C			10°C			5°C			5°C		
	Comme-rcial oil	Oil with additive	Average viscosity reduction, %	Comme-rcial oil	Oil with additive	Average viscosity reduction, %	Comme-rcial oil	Oil with additive	Average viscosity reduction, %	Comme-rcial oil	Oil with additive	Average viscosity reduction, %
1a	652,3	563,4	14,3	939,0	751,2	27,0	1234,5	1233,8	0,04	1234,5	1038,0	7,9
2a	397,0	332,0	16,4	626,1	469,6	25,0	678,3	626,1	7,7	678,3	533,0	21,4
3a	247,0	195,0	21,1	397,5	288,0	21,3	406,9	375,6	7,7	406,9	336,0	17,4
4a	128,0	88,0	31,3	243,6	156,6	21,4	261,0	208,8	20,0	261,0	197,0	24,5
5a	80,0	62,0	22,5	135,6	83,5	15,3	177,3	114,8	35,3	177,3	116,0	34,6
6a	49,0	33,0	32,7	81,2	52,2	14,3	104,3	69,6	33,3	104,3	58,0	44,4
7a	27,8	13,0	53,2	48,7	34,8	14,4	69,5	41,7	40,0	69,5	38,3	44,9
8a	15,4	13,5	12,3	30,9	19,3	18,8	44,4	28,97	34,8	44,4	25,1	43,5
9a	13,9	8,2	41,0	19,7	11,6	17,8	31,3	19,7	37,1	31,3	17,4	44,4
10a	7,7	4,5	41,6	12,2	7,1	15,6	18,7	13,5	27,8	18,7	11,6	38,0
11a	5,8	3,1	46,6	7,7	5,8	19,5	10,8	8,5	21,3	10,8	6,4	41,0
12a	4,1	2,4	14,3	5,4	3,2	20,4	7,1	5,4	23,9	7,1	3,8	46,7
Dynamic viscosity, sPz	136,1	109,8		212,3	156,9		244,7	220,0		244,1	198,1	
Average viscosity reduction,%			19,3			26,1			10,1			30,1

Table 4. *Change of dynamic viscosity of Sangachal oilfield oil samples, without and with addition of SNPX-2005 taking into account 0.8 kg/ton, 1.0 kg/ton additive.*

Speed stages	Dynamic viscosity without and with addition of 0.8 kg/ton SNPX-2005, cPz.									Dynamic viscosity without and with addition of 1.0 kg/ton of SNPX-2005, cPz.		
	20°C			10°C			5°C			5°C		
	Comme-rcial oil	Oil with additive	Average viscosity reduction, %	Comme-rcial oil	Oil with additive	Average viscosity reduction, %	Comme-rcial oil	Oil with additive	Average viscosity reduction, %	Comme-rcial oil	Oil with additive	Average viscosity reduction,%
1a	657,3	525,8	20,0	751,2	1126,8	-50,0	1126,8	1126,8	0,0	1126,8	1154,8	-28,0
2a	401,8	313,1	22,1	469,6	547,9	-16,7	626,1	678,3	-8,3	626,1	652,2	-26,1
3a	219,1	156,5	28,6	288,0	322,4	-11,9	375,6	406,3	-8,3	375,6	391,3	-15,7
4a	144,4	99,2	31,3	156,6	194,9	-24,5	208,8	261,0	-25,0	208,8	226,2	-8,4
5a	73,02	46,9	35,8	83,5	120,0	-43,7	114,8	177,3	-54,4	114,8	156,5	-36,3
6a	40,6	26,1	35,7	52,2	75,4	-44,4	69,6	104,3	-49,9	69,6	92,7	-33,3
7a	27,8	24,3	12,6	34,8	48,7	-39,9	41,7	69,5	-66,7	41,7	46,9	-12,6
8a	13,5	9,7	28,1	19,3	30,9	-60,1	28,97	44,4	-53,3	28,97	25,1	13,3
9a	6,96	7,0	-0,6	11,6	19,7	-69,8	19,7	31,3	-58,9	19,7	17,4	11,7
10a	3,9	3,9	0	7,1	11,6	-63,4	13,5	18,7	-38,5	13,5	11,0	18,9
11a	2,3	2,7	-17,4	5,8	7,1	-22,4	8,5	10,8	-27,1	8,5	7,3	13,7
12a	1,3	1,5	-15,4	3,2	4,7	-46,9	5,4	7,1	-31,5	5,4	4,9	8,6
Dynamic viscosity, sPz	132,1	101,4		155,4	209,2		219,9	244,7		219,9	232,8	
Average viscosity reduction,%			15,1			-33,8			-35,2			-7,9

An experiment was also performed to compare our reagent with the SNPX-2005 reagent. The results of the studies are shown in Table 5.

Table 5. *Analysis results.*

Indicators	Volume of composite in 300 ml						
	0	10	20	30	40	50	60
Kinematic viscosity, mm^2/sec, 20°C	83,37	70,24	57,65	45,59	40,98	58,31	69,77

3.2. Results Analysis

It can be seen from the table that with the addition of 40 ml of reagent, the viscosity of the marketable oil of the Muradhanlinsky deposit decreases to 40.98 mm^2/s. Further addition of the reagent again increases the kinematic viscosity of the oil.

Graphic dependence of oil viscosity on reagent quantity is given in Figure 1.

The dependence of kinematic viscosity on temperature was also studied. Table 6 shows the results of the studies in 50°C. Figures 2 and 3 show the graphical dependencies of kinematic viscosity on the amount of composite at 50°C. The table and graphs show that the temperature adversely affects the properties of the reagent.

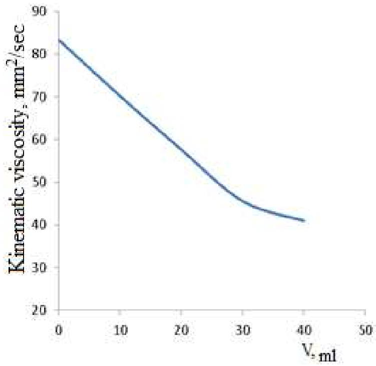

Figure 1. *The graphical dependence of the kinematic viscosity of oil on the volume of the composite (composition of the composite: 1g reagent - 98 g technical water - 1 drop of sulfanol).*

Table 6. *Results of kinematic viscosity change depending on the amount of composite at 50°C.*

I		II	
Amount of composite in oil, ml	**Kinematic viscosity of oil, mm^2/sec.**	**Amount of composite in oil, ml**	**Kinematic viscosity of oil, mm^2/sec.**
0	83,32	0	83,46
10	74,31	10	75,43
20	58,72	20	58,89
30	47,87	30	49,68
40	46,28	40	48,72

i {Diesel alkaline waste; Nanoreagent} ii {Diesel alkaline waste; Sulfanilic acid; Nanoreagent}

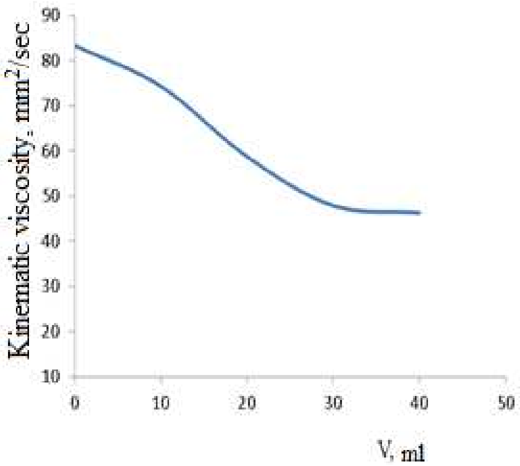

Figure 2. *Graphical dependence of the kinematic viscosity of oil on the amount of composite at 50°C (composition of the composite: 198 g purified DSO; 2 g - nanoreagent).*

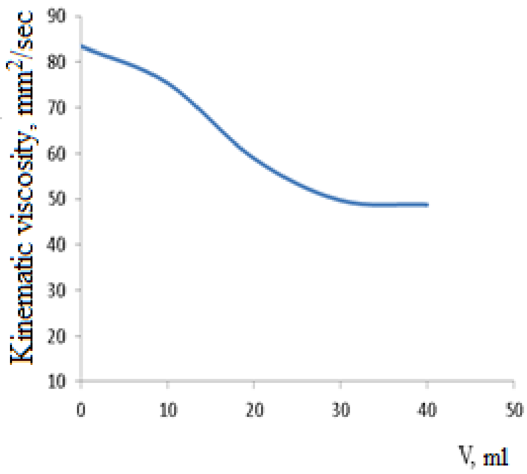

Figure 3. *Graphical dependence of kinematic viscosity of oil from the amount of composite at 50°C (composition of the composite: 95 ml of DSO, 103 ml 0.3% sulfanilic acid solution, 2 g nanoreagent).*

The table and graphs show that the temperature adversely affects the properties of the reagent. Also studied is reduction of kinematic viscosity from the amount of surfactant. The results of the experiments showed that an increase in the amount of surfactant adversely affects the decrease in the kinematic viscosity of hydrocarbons. Despite the fact that there is no pattern between the amount of surfactant and the kinematic viscosity of the hydrocarbon, but, ultimately, the latter decreases.

Thus, the experiments conducted show that the composites of BAF-1 and BAF-2 about half (51%) reduce the viscosity of the highly viscous mixed oils of the Muradkhanli field. As is known, the viscosity of various oils mainly depends on the percentage of resins and asphaltenes in the oil composition [11]. It is also known that resins and asphaltenes consist of heteroatoms with different molecular weights (from 450 to 1500).

The mechanism of action of reagents on the rheological properties of oils, in our opinion, is due to the formation of non-valent compounds between the reagent and heteroatoms of resins and asphaltenes with self-organization and self-construction, since the coordination polymers we use have sufficiently large crystallographic pores (20 Å) available for heteroatoms. When reactant interacts with oil, nonvalent skecking of interaction occurs between porous coordination polymers and chromatic, heteroatomic macroassociates contained in oil and break them into small fragments, which ensures reduction of viscosity.

Thus, the results of the study showed that when using the additive BAF-1 and BAF-2 (at a ratio of 1:1), taking into account 0.400 kg/ton, the dynamic viscosity of the marketable oil of the Muradkhanli field at 20°C decreases by 43.88%. This means that the small amount (0.4 kg/ton) of said reagent is 2.7 times stronger than SNPX-2005.

4. Conclusion

The results show that the reagents BAF-1 and BAF-2 are not only effective in comparison with SNPX-2005, but in general are effective reagents for reducing the viscosity of heavy commercial oils and have exceptional high technical and economic parameters.

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