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RESEARCH

INFLUENCE OF CHEMICAL REAGENTS AND SURFACTANTS ON RHEOLOGICAL PROPERTIES OF RODINO AND BAKLANOVO CRUDE OILS

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The influence of surfactants on the structural and rheological properties of crude oils containing resins, asphaltenes, and paraffin hydrocarbons in various concentrations is studied. The basic functional groups of the chemical reagents are identified by IR spectroscopy.
Key words: crude oil, rheology, surfactants.

Of late, high-viscosity oil fields are being developed to broaden the feedstock base of the oil refining industry. High viscosity of such oils renders their extraction and transportation difficult. To improve the rheological properties of high-viscosity crude oils, use is made of chemical reagents [1], surfactants [2, 3], dispersing additives [4, and magnetic field [5, 6].

The rheological properties of the oils were investigated on a Rheotest-2 rotary viscometer in the 20-60°C range at shear rates from 3 to 1312 sec^{-1}. Oils from Rodino wells 1200 (specimen *I*) and 306 (specimen II) and Baklanovo fields (specimen III) were investigated. The physicochemical properties of the oils are adduced in Table 1. As evident from this table, the oils are distinguished by high content of aromatic hydrocarbons, resins, and asphaltenes.

In order to improve the rheological properties of the oils, we used the reagents Neonol AF 9-12, Reapon IF, SNPKh 4880 D2, ETN-7r-14, IPG-12, Laprol, Sonpar, and copolymer of ethylene with vinyl acetate (vinyl acetate 26-30%). The IR spectra of the reagents were obtained on a Shimadzu spectrophotometer. The main functional groups of the reagents are characterized in Table 2.

The stretching vibration bands of hydrogen bonds of hydroxyl and nitrogen-containing groups are noticed in the 3300 cm^{-1} region. The absorption band in the 1250 cm^{-1} region is attributed to the presence of C-O-C valence bonds. The absorption band in the 1600 cm^{-1} region is referred to stretching vibrations of C-C bonds in aromatic

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Table 1

Indices	Oil Specimen		
	I	II	III
Density at 20°C, kg/m^3	928.5	–	956.7
Pour point, °C	– 4	–	0 – 5
Content, wt. %			
water	5	0	1
solid paraffins	4.0	4.7	3.0
Group composition, wt. %			
paraffinic–naphthenic	28.7	27.7	18.7
aromatic, including	56.0	56.4	60.1
monocyclic	15.1	9.0	8.9
bicyclic	5.4	6.0	5.6
polycyclic	35.5	41.4	45.6
resins			
benzene	5.8	4.3	6.7
alcohol–benzene	7.7	9.6	11.3
asphaltenes	1.8	2.0	3.2

Table 2

Reagents	Absorption band in the region, cm^{-1}				
	1600	380	1460	1250	3300
	skeletal C=C bonds in aromatic ring	C-H deformation vibration bonds in CH_3 group	C-H deformation vibration bonds in CH_2 and CH_3 groups	stretching vibrations of C-O-C group	stretching vibrations of O-H bond
Laprol 600	0.39	3.27	3.21	2.45	1.30
Sonpar	0.80	2.90	2.63	1.85	2.90
Reapon IF	0.62	2.30	2.00	1.82	1.00
SNPKh 4880 D2	0.54	1.40	1.70	1.10	2.00
Neonol AF 9-12	0.79	1.22	1.70	1.70	1.22
ETN-7r-14	0.72	0.92	1.40	-	0.44
IPG-12	0.57	0.57	0.72	-	0.70

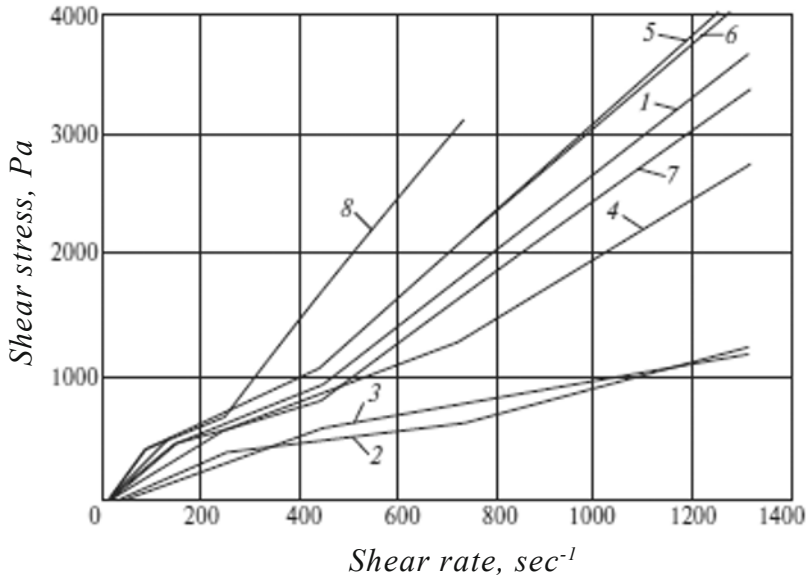

Fig. 1. Shear stress versus shear rate at 20°C for crude oil *I* (curve 1) and its blends with 0.05% of various reagents: 2 - Sonpar, 3 - Laprol, 4 - Neonol, 5 - Reapon, 6 - ETN-7r-14, 7 - IPG-12, and 8 - SNPKh 4880 D2.

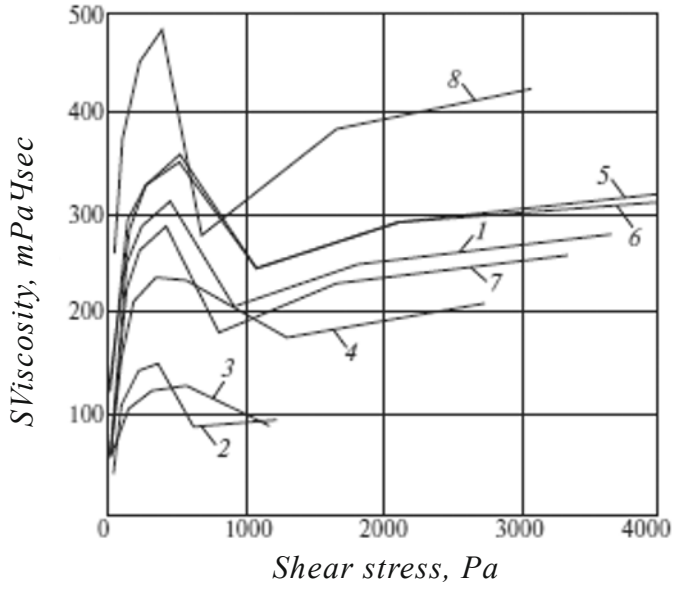

Fig. 2. Viscosity versus shear stress at 20°C for oil *I* (curve *1*) and its blend with 0.05% reagents: *2* - Sonpar, *3* - Laprol, *4* - Neonol, *5* - Reapon, *6* - ETN-7r-14, *7* - IPG-12, and *δ*- SNPKh 4880 D2.

rings. The appearance of the absorption band at 1380 cm^{-1} is associated with terminal methyl groups. The absorption band at 1460 cm^{-1} corresponds to the asymmetric deformation vibrations of CH_2 and CH_3 groups. As will be seen from Table 2, Laprol, Sonpar, and Reapon contain the maximum number of terminal methyl groups. Unlike the other reagents, Sonpar and SNPKh 4880 D2 contain more functional groups of heteroatoms.

In Fig. 1, the shear rate is plotted against the shear stress at 20°C for crude oil *I* and its blends with 0.05% of various reagents. On the flow curves, three typical segments are distinguishable: the first segment

Table 3

Composition	Viscosity (mPa × sec) at shear rate, sec^{-1}			
	27	48.6	81	145.8
Oil *I* with no additive	153	243	285	313
Oil I with 0.05% of reagent				
Laprol	-	37	80	106
Sonpar	-	61	110	142
Neonol	66	146	212	236
Reapon	197	292	329	356
ETN-7r-14	186	280	329	354
IPG-12	121	219	263	288
SNPKh 4880 D2	373	451	483	115*
Oil II with no additive	132	183	235	250
Oil II with 0.05% of reagent				
Laprol	22	91	128	156
Sonpar	33	122	161	189
Neonol	44	110	143	166
Reapon	175	226	278	293
ETN-7r-14	88	159	190	215
IPG-12	197	268	314	337
SNPKh 4880 D2	44	134	183	207
Copolymer of ethylene with vinyl acetate	44	128	150	177

Note. * Determined in two steps

corresponds to crude oil flow without destruction of the structure, the second, to highly plastic flow, and the third, to crude oil flow under high shear stresses whereupon the structure is completely destroyed and the oil exhibits Newtonian properties. At higher temperatures the oil flow becomes Newtonian. Similar mechanisms are typical for other blends of the oil as well.

The viscosity of oil *I* and its blends with reagents is plotted against the shear stress in Fig. 2. At low shear stresses the viscosity is high perhaps because of phase transition in the asphaltene associates.

The influence of the reagents on the rheological properties of the crude oils is shown in Tables 3 and 4. It can be seen that Laprol exerts the best modifying effect on the oils. Reapon IF, ETN-7r-14, and SNPKh 4880 D2 raise viscosity of oil *I*. In terms of effectiveness of oil viscosity reducing action, the additives can be put in the following order: Laprol > Sonpar > Neonol > IPG.

Laprol is the best additive for oil *II* as well. The effectiveness of the reagents in this regard declines in the order: Laprol > Copolymer of ethylene with vinyl acetate > Neonol > Reapon > Sonpar.

The surface activity of the modifiers depends on the chemical nature of the side groups and the rate of their rearrangement along the main chain of the modifiers. Alkyl groups create steric hindrances, which hinder growth of paraffin crystals, their close contact, and formation of spatial structure. The inhibiting efficiency of

Table 4

Composition	Viscosity (mPa × sec) at shear rate, sec^{-1}			
	5.4	9	16.2	27
Oil *III* with no additive	10524	4968*	7418*	8592*
Oil III with 0.05% of reagent				
Laprol	7125*	1242*	3795*	5175*
Sonpar	9866	4347*	6556*	7763*
Neonol	8770	3416*	5520*	6832*
Reapon	8770	4347*	6038*	7039*
ETN-7r-14	4140*	7453*	9489*	10144*
IPG-12	2072*	5590*	8281*	9316*
SNPKh 4880 D2	11904*	14906*	16562*	16252*
Copolymer of ethylene with vinyl acetate	7235	1863	4140*	5486

Note. * Determined in two steps.

paraffin wax deposits rises with increase in the number of methyl and methylene groups. Perhaps because of this, Laprol exerts the maximum modifying effect on the test crude oils. Note that the other functional groups in the reagent molecules were not found to have specific influence on the rheological properties of the oils.

Thus, the investigations conducted revealed that the maximum decrease in the dynamic viscosity of the test crude oils occurs in the presence of Laprol. The alkyl groups inverted to the hydrocarbon medium facilitate adsorption of the modifiers on the paraffin crystal surface. The more numerous they are, the stronger their modifying effect.

REFERENCES

1. S. A. Ifutina, L. K. Khvatova, V. A. Ezrets, et al., *Neftepromyslovoe Delo i Transport Nefti*, No. 9, 22-24 (1985).
2. R. N. Shiryaeva, F. Kh. Kudasheva, and R. N. Gimaev, *Neft. Khoz.*, No. 8, 124-125 (2007).
3. R. N. Shiryaeva, F. Kh. Kudasheva, and R. N. Gimaev, *Khim. Tekhnol. Top. Masel*, No. 3, 31-33 (2008).
4. A. N. Ratov, *Neftekhim.*, 36, No. 3, 195-208 (1996).
5. Yu. V. Loskutova, I. V. Yudin, and S. I. Pisareva, *Ibid.*, 48, No. 1, 50-54 (2008).
6. Yu. V. Loskutova, N. V. Sizova, N. V. Yudina, et al., *Ibid.*, 45, No. 2, 146-150 (2005).