Composition and Properties of Oil Deposits

E. V. BESHAGINA[1], N. V. YUDINA[1], I. V. PROZOROVA[1] and YU. V. SAVINYKH[2]

[1]*Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademicheskiy 3, Tomsk 634021 (Russia)*

E-mail: piv@ipc.tsc.ru

[2]*Vietsovpetro Enterprise, Le Loy str.105, Vung Tau (Vietnam)*

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Abstract

Composition and rheological behaviour of asphalt-resin-paraffin depositions that were excreted from high-wax oils under changes of temperature gradient of oil and adsorbing surface has been studied. An effect of petroleum composition and temperature on the quantity, composition, and rheological behaviour of oil sediments has been demonstrated.

INTRODUCTION

Complications that arise during production activity and transportation of high-wax oils, as a rule, are related to the formation of asphalt-resin-paraffin depositions (ARPD) on the walls of pipelines and process equipment. Thus far, there is no standard mechanism of the ARPD formation, and solving particular technological problems to control these depositions is still the main direction of scientific research [1–7].

The oil deposit is produced as a result of competitive collisions of the disperse particles with the capacity for Brownian motion, in a diffusive sublayer, boundary with the wall, with larger disperse particles that precipitate on the surface [8]. The primary factor that has influence on the fallout of a solid phase is a decrease of solubility of paraffin hydrocarbons (PH) in oil. In its turn, the PH solubility depends appreciably on the oil temperature. As it decreases, the crystals of PH being produced attach to each other and form a strong structural lattice, which worsens considerably viscous characteristics of oil, right down to the full loss of its fluidity.

The purpose of the work is to study the composition and properties of ARPD as a function of petroleum composition, its temperature, and the temperature of the adsorbing surface.

EXPERIMENTAL

Samples of high-wax oils of Verkhnesalatskoye, Archinskoye, and Festivalnoye fields (Tomsk Region) have been chosen as subjects of the research.

Mass fraction of the PH and resins was determined by chromatographic (column-adsorption) method, and the mass fraction of asphaltenes, by the "cold" Goldye procedure [9].

The studied samples of oils exhibit a significant content of paraffins and high temperatures of congelation (Table 1). Group content of Verkhnesalatskoye and Archinskoye oils, being identical in their PH content, significantly differs in their gum content and the content of asphaltenes. Accordingly, the samples of Verkhnesalatskoye oils are typified by a low content of aromatic hydrocarbons (AHC), resins and are completely absent from asphaltenes. The fraction of naphthenic hydrocarbons (NH) is insignificant in the group content of samples of Archinskoye oils. Festivalnoye oil is characterized by high gum content.

The quantitative estimate of the process of sludge formation in oil was conducted by the

TABLE 1

Physicochemical characteristics of the investigated oils

Deposits	Solidification point, °C	Content, mass %				
		P H	NH	AHC	Resins	Asphaltenes
Verkhnesalatskoye	12.0	10.5	79.9	8.2	1.4	–
Archinskoye	11.5	11.0	65.3	17.3	4.4	2.0
Festivalnoye	17.2	20.0	50.0	0.9	27.0	2.1

Note. PH – paraffin hydrocarbons, NH – naphthenic hydrocarbons, AHC – aromatic hydrocarbons.

“cold rod” method [6]. The temperature of the rod (the adsorbing surface) varied from 15 to 30 °C, temperature of oil – from 30 up to 70 °C. Rheological behaviour of deposits was analysed in a Reo-test 2.1 rotational viscometer with the use of a cone-plate. Individual composition of n-alkanes was determined by the high-temperature gas liquid chromatography method (GLC) in a HP-6890 chromatograph that was equipped with a direct sample injection on a NT-5 capillary column, 25 m in length. The assigned temperature schedule: from 50 °C the temperature was raised at a rate of 35 °C/min, from 150 °C – at a rate of 3 °C/min up to 410 °C, and further – the isothermal conditions over the course of 30–40 min.

RESULTS AND DISCUSSION

The quantity of ARPD for the studied samples depends on the petroleum composition and on the gradient of temperatures of oil and cooled surface (Fig. 1).

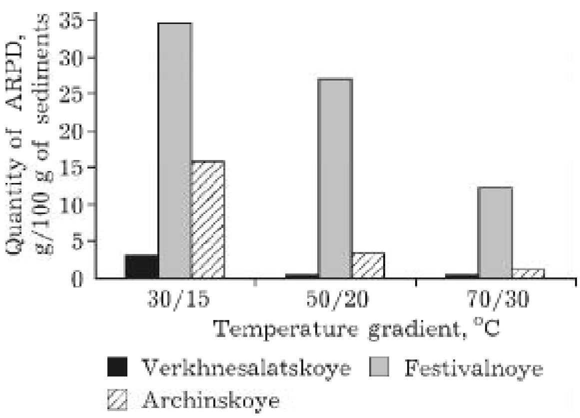

Fig. 1. Effect of the temperature gradient on the quantity of ARPD for paraffinaceous oils from various deposits.

Oil sediments are characterized by high values of specific boundary surface and thus by high values of superficial energy. In its turn, these factors promote passing of the processes that give rise to spatial structures and thermodynamic stability of these systems. The tendency of disperse particles to their association grows with an increase in the content of resins and aspartames in oil; meanwhile, their aggregation stability drops down [10]. The greatest quantity of ARPD is formed from the samples of Festivalnoye oil with the maximum content of paraffins and resins. Samples of Archinskoye and Verkhnesalatskoye oils that are characterized by the identical content of paraffins, by an insignificant fraction of resins and by absence from asphaltenes in the last-mentioned, strongly differ in the quantity of formed ARPD in the being investigated temperature range. It testifies that gum content and the content of asphaltenes in oil boosts the process of sludge formation. A decrease of temperature of the adsorbing surface also exerts influence on the process of the formation of ARPD, the maximum quantity of which is formed at a temperature close to the freezing point of oil (15 °C). Thus, the nature of ARPD excretion depends mostly on the temperature and the content of high molecular mass ingredients in oil.

Petroleum composition and the gradient of temperatures of oil and the cooled surface have a significant effect on the group content of ARPD (Fig. 2).

At the temperature of oil and the cooled surface 70 and 30 °C, the fraction of paraffin-naphthene hydrocarbons (HC) grows in ARPD samples of oils with close content of paraffins. Meanwhile, the ARPD samples from Verkhnesalatskoye oil exhibit an increase in their gum content, and the ARPD samples from Archin-

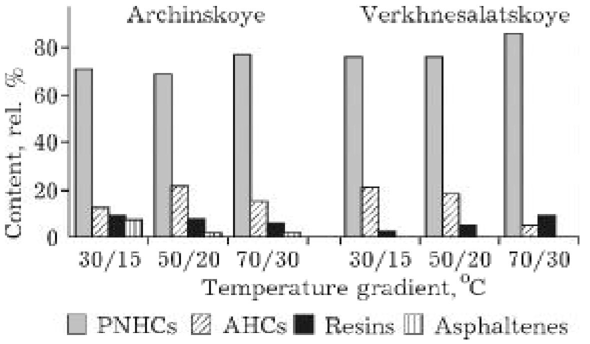

Fig. 2. Effect of temperature gradient on the group content of ARPD for paraffinaceous oils from various deposits.

skoye oil exhibit a decrease of their gum content and their content of asphaltenes. The quantity of aromatic HCs in the composition of sediments grows at a decrease of temperature of Verkhnesalatskoye oil and the temperature of the cooled surface. The maximum quantity of aromatic HCs in the composition of ARPD from Archinskoye oils is registered at the gradient of temperatures 50/20 °C.

The study of individual composition of n-alkanes by the GLC method has suggested that their molecular mass distribution (MMD) in oil deposits is also controlled by the petroleum composition and the temperature gradient (Fig. 3).

Two maxima are observed in the MMD curves of n-alkanes (see Fig. 3, *a*) for the ARPD samples from Verkhnesalatskoye oil that have arisen at the temperatures gradients of 70/30 and 50/20 °C. As the temperatures increase (70/30 °C), a shift of the second maximum (C_{45}–C_{49}) in the region of high molecular mass is observed. A monomodal distribution with a maximum that falls on C_{17}–C_{21} is recorded for n-alkanes from ARPD that have been excreted at a gradient of temperatures 30/15 °C.

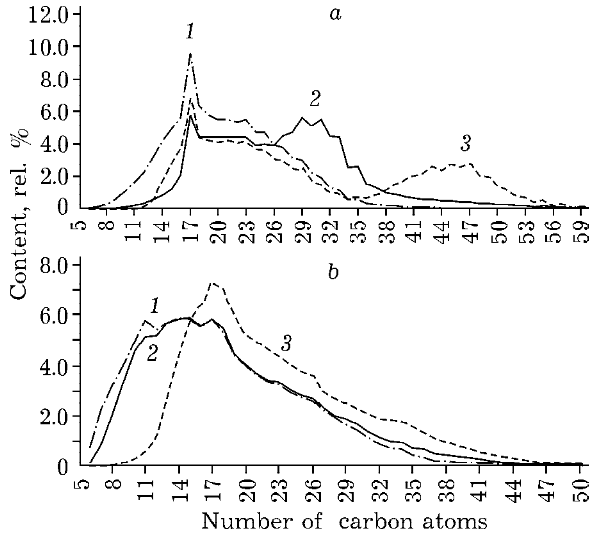

Fig. 3. Molecular mass distribution of n-alkanes in deposits of Verkhnyesalatskoye (*a*) and Archinskoye (*b*) oils at the temperature gradients of oil and the adsorbing surface, °C: 30/15 (*1*), 50/20 (*2*), 70/30 °C (*3*).

ARPD from the samples of Archinskoye oil that have arisen at the same gradients of temperatures are also typified by monomodal distribution of n-alkanes (see Fig. 3, *b*). Meanwhile, with an increase in temperatures of oil and the cooled surface, an insignificant shift of the maximum into the region of high molecular mass is observed.

From GLC data, the following indices have been calculated: the combined content of liquid paraffins (ΣC_7–C_{16}), of paraffinum durums (ΣC_{16}–C_{40}), of high molecular mass paraffins (ΣC_{40}–C_{70}); the ratio of the combined quantity of n-alkanes with an odd number of carbon atoms to the combined quantity of n-alkanes with an even number of carbon atoms (Table 2).

TABLE 2

Calculated indices for n-alkanes of oil deposits that have been excreted at various temperature gradients

Temperature gradient, °C	Content, mass %			ΣC_{41}–C_{49}/ΣC_{42}–C_{50}	ΣC_{51}–C_{59}/ΣC_{52}–C_{60}
	ΣC_7–C_{16}	ΣC_{16}–C_{40}	ΣC_{40}–C_{70}		
Verkhnesalatskoye oil					
30/15	7.3	30.4	0.2	1.5	1.3
50/20	1.5	41.3	3.0	1.2	2.1
70/30	3.1	34.2	16.4	1.1	2.1
Archinskoye oil					
30/15	10.0	11.5	0.2	1.2	1.6
50/20	9.0	12.5	0.5	1.3	1.7
70/30	2.9	14.3	0.7	1.2	1.5

From the analysis of the GLC data it follows that liquid PH are constituents of ARPD, the maximum quantity of which excretes with a solid phase at the temperature gradient of 30/15 °C. As the temperature decreases, the structure of the liquid phase changes, and the regularity in the arrangement of molecules of the dispersed phase increases because of the decreased energy of thermal shocks from molecules of the dispersion medium. Complexes of previously oriented molecules form dense structured packing. Molecules of the liquid phase that form solvate shells around crystallization centres get in the sediment as a consequence of co-crystallization with the solid phase [11]. With a rise in the temperature, the content of paraffinum durums in ARPD grows together with their fraction of high molecular mass *n*-alkanes with the number of carbon atoms $C_{40}–C_{70}$. A combined quantity of *n*-alkanes with the number of carbon atoms $C_{40}–C_{70}$ in the deposit that arose at the respective temperatures of oil and cooling surface 70 and 30 °C is 80 times more as compared with that for ARPD that have arisen at the gradient of temperatures of 30/15 °C. In the region of low temperatures (30/15 °C), the combined content of odd *n*-alkanes with the number of carbon atoms $C_{41}–C_{49}$ shows a rise, and with an increase in temperatures (70/30 °C), so does the fraction of odd *n*-alkanes of composition $C_{51}–C_{59}$.

The combined quantity of *n*-alkanes and paraffinum durums in oil deposit from Archinskoye oil is 2-3 times lower in comparison with Verkhnesalatskoye oil. Their content depends also on the gradient of temperatures; however, the dependence manifests itself in a considerably smaller degree. At a constant temperature of the cooled surface (20 °C) and with an increase in the oil temperature, the growth of the total content of *n*-alkanes is observed, as well as the fraction of odd hydrocarbons in them. An increased temperature of the cooled surface and oil up to 30 and 70 °C, respectively, results in a decrease of the mentioned indices. ARPD samples from Verkhnesalatskoye and Archinskoye oils are dominated by odd *n*-alkanes that determine their crystalline modifications.

Structural-mechanical properties of ARPD depend on the concentration, molecular mass of ingredients and on their phase state [12]. At

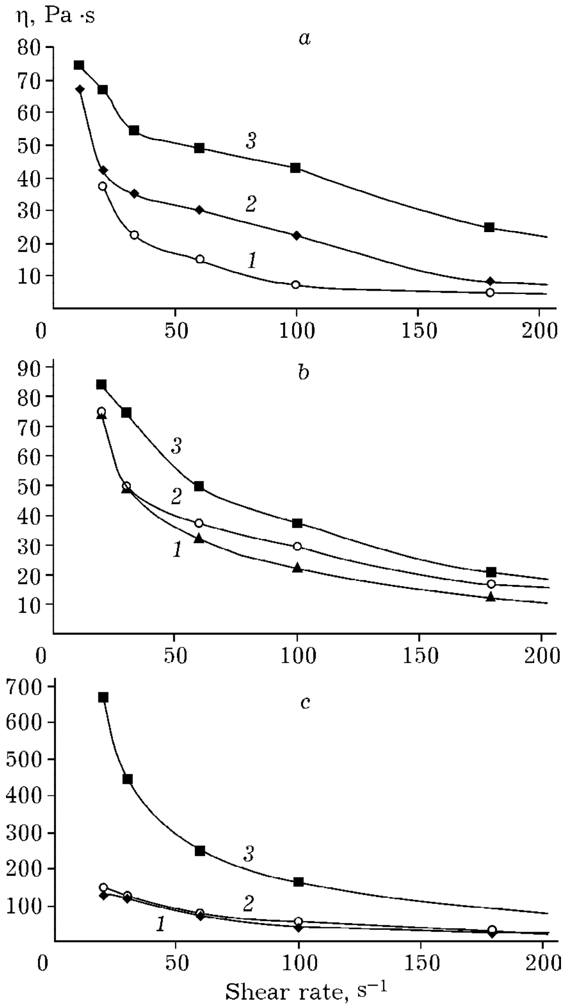

Fig. 4. Shear rate dependence of the dynamic viscosity of ARPD from Verkhnesalatskoye (*a*), Archinskoye (*b*) and Festivalnoye (*c*) oils at the temperature of 20 °C.

a temperature of 20 °C and at shearing rate of 15–4000 s^{-1}, the viscosity of ARPD from Verkhnesalatskoye oil is lower when compared to the viscosity of the deposit from Archinskoye oil (Fig. 4). An increase in the viscosity of the latter is caused by availability of asphaltenes and resins of a high molecular mass (2000 amu) in the deposit, together with a smaller content of paraffin HCs in it. High melting point paraffins, the fraction of which increases in the deposits that have been precipitated at a gradient of temperatures 70/30 °C, contribute to an increase in the viscosity of ARPD due to the formation of spatial crystal close-packed particle structures. A denser packing of disperse particles is possible only in the event that at the instant the liquid state (70 °C) changes to solid state, the particles show a sufficient mobility that would provide a regular arrangement of molecules.

Abnormal change in the viscosity of oil systems as a function of the shear rate is caused by spatial structures that appear as a result of intermolecular interactions. An increase in the strain velocity brings about a decrease in the number of bonds of intermolecular interaction that disrupt during the force action. In so doing, the ARPD transform from bonded disperse to a free disperse state [13]. A sharp drop in the viscosity of sediments is evidenced in the flow curves at the shear rate below 50 s^{-1}, which is related to breaking down of permolecular structure, of associative bonds and to the orientation of molecules (Fig. 4). As the shear rate increases up to 300 s^{-1}, the viscosity of ARPD becomes a constant value.

The greatest values of the viscosity and the ultimate shear strain are typical for sediments that were excreted from samples of Festivalnoye oil. This fact is related to their high content of paraffins and alcohol-benzene resins. A maximum contribution of structural component to the magnitude of dynamic viscosity is typical for sediment that was excreted from samples of Festivalnoye oil at a gradient of temperatures of 70/30 °C. Analogous feature is also exhibited by an ARPD from Verkhnesalatskoye and Archinskoye oils, but with a less differences in the viscosity of these sediments.

To research the flow process of ARPD we used the equation of viscosity η *vs.* temperature [14]: $\eta = A\exp(-\Delta H/RT)$, where A is a preexponential coefficient that has only a weak dependence on temperature; ΔH is the heat of activation of viscous flow; R is the versatile gas constant; T is an absolute temperature. The experimental dependences of log η on $1/T$ for ARPD from Verkhnesalatskoye oil at certain temperature ranges can be approximated by a linear function (Fig. 5). The inflection point corresponds to the temperature of phase transitions. For an ARPD that has been excreted at a gradient of temperatures 30/15 °C, two linear sites are observed on the temperature dependence of viscosity: the viscosity of the system keeps constant up to the temperature of 5 °C, and the η magnitude sharply increases at 0 °C. Two inflection points are noted in the curve of the deposit that has been excreted at the gradient 50/20 °C, those at 10 and at 5 °C. The oil deposit that has been excreted at the gradient 70/30 °C is characterized by several phase states. The observed deviations from rectilinear temperature dependence of viscosity are attributable to the temperature effect on the free energy of activation of viscous flow that is consumed to destruct the intermolecular bonds [14, 15]. The heat of activation of viscous flow that is determined from a slope of the curves log η − $1/T$ is a measure of the strength of bonds in the associative complexes in each structural state of the ARPDs. Table 3 gives the values of the heat of activation for ARPDs that have been excreted from Verkhnesalatskoye oil samples. The acquired data (ΔH = 30 kJ/mol) are representatives of average effects of various kinds of intermolecular interactions. A deposit that has been excreted from oil at the gradient of 70/30 °C is made up mostly of paraffin-naphthenic hydrocarbons (80 mass %). The hydrocarbons are represented for 50 % by paraffinum durums with various crystallization temperatures. Apparently, this is associated with several phase transitions in the system. The ARPD that have been excreted at the temper-

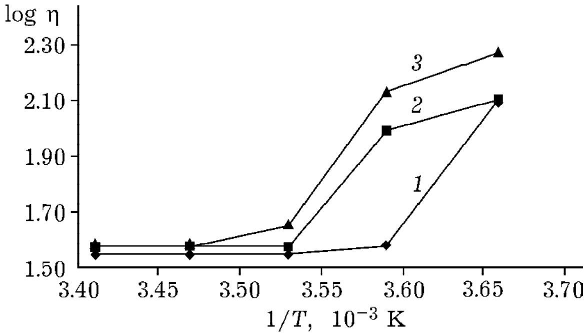

Fig. 5. Dependence of viscosity of ARPD from Verkhnesalatskoye oil on temperature (in Arrhenius coordinates). Temperatures gradient, °C: 30/15 (*1*), 50/20 (*2*), 70/30 (*3*).

TABLE 3

Data on the activation energy of viscous flow of ARPD from Verkhnesalatskoye oil, kJ/mol

Temperature gradient, °C	Interval of temperatures, °C 0–5	5–10	10–15
70/30	8.2	32.8	5.5
50/20	6.4	28.7	n/d
30/15	31.0	n/d	n/d

Note. n/d − not determined.

ature gradients of 50/20 and 30/15 °C, along with a decrease in their content of paraffinum durums, show an increase in their fraction of aromatic HCs that make a significant contribution to the intermolecular interactions.

CONCLUSIONS

1. Quantity of ARPD is controlled by chemical nature and by the proportion of basic ingredients in the dispersed phase of oil, primarily by the gum content and the content of asphaltenes. The group content of oil sediments depends on the oil temperature and on the temperature of cooled surface.

2. With an increase of oil temperature and of the temperature of cooled surface, the fraction of liquid paraffins in the composition of *n*-alkanes decreases, while the content of solid high molecular mass paraffins increases.

3. Rheological behaviour of ARPD is controlled by the content, by composition of high molecular mass ingredients and by their phase state. A jump in the viscosity of ARPD at a decrease of temperature is attributable to the phase transition and to the precipitation of a solid phase. Distinctions in temperature dependences of viscosity point to different structural types.

REFERENCES

1 B. A. Mazepa, Zashchita neftepromyslovogo oborudovaniya ot parafinootlozheniy, Nedra, Moscow, 1972.
2 G. A. Babalyan, Bor'ba s otlozheniyami parafina, Nedra, Moscow, 1965.
3 A. Z. Bikulov, A. I. Shamazov, K mekhanizmu obrazovaniya neftyanykh otlozheniy v trubakh, 3 Mezhdunar. konf. po khimii nefti (Proceedings), Tomsk, 1997, vol. 2, p. 43.
4 V. P. Tronov, Mekhanizm obrazovaniya smoloparafinovykh otlozheniy i bor'ba s nimi, Nedra, Moscow, 1969.
5 K. T. Zhazykov, P. I. Tugunov, *Neft. Khoz-vo*, 1 (1985) 80.
6 R. N. Mukhametzyanov, L. Kh. Kayumov, S. G. Safin, *Neftepromysl. Delo*, 1 (1992) 13.
7 S. G. Agaev, Z. N. Berezina, A. N. Khalin, G. V. Kravchenko, *Izv. Vuzov. Neft' i Gaz*, 1 (1997) 89.
8 A. Z. Bikulov, A. I. Shamazov, *Ibid.*, 5 (1998) 100.
9 N. N. Abryutina, Sovremennye metody issledovaniya, Nedra, Leningrad, 1984.
10 I. Z. Mukhametzyanov, Strukturnaya organizatsiya makromolekulyarnykh assotsiatov v neftyanykh sredakh, Khimiya, Moscow, 2003.
11 L. P. Kazakova, Tverdye uglevodorody nefti, Khimiya, Moscow, 1986.
12 S. G. Agaev, E. O. Zemlyanskiy, A. N. Grebnev, *Zh. Prikl. Khim.*, 79 (2006) 1373.
13 V. E. Dreval, Vsesoyuz. konf. po reologii (Treatises), Novosibirsk, 1987.
14 A. N. Ratov, *Ross. Khim. Zh.*, 39, 5 (1995) 106.
15 A. N. Ratov, *Neftekhim.*, 36 (1996) 195.