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## Multifunctional Additive for Paraffinic and High-Paraffinic Oil

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### Abstract

Regulation of the transport characteristics of oil is often implemented with the help of depressor and inhibiting additives. A characteristic feature of new developments in the area of oil additives is the composite nature (two or more components of the active substance), which provides their multifunctional action. Results obtained in the investigation of the effect of complex additives based on polyalkylacrylate (PAA) and petroleum-polymer resins modified through nitration (N-PPR) on the chilling temperature and viscosity of paraffin and high-paraffin oils of West Siberia, as well as on the amount and composition of asphaltic resinous paraffin sediments (ARPS) are presented. It is established that, in comparison with the additive based on PAA, the complex additive causes a decrease in the amount of ARPS (by 10 % as average), a two-fold increase in the depression of oil chilling temperature and a decrease in its dynamic viscosity. The efficiency of the complex additive was revealed to depend on the method of N-PPR preparation. The best results with respect to all parameters are demonstrated by the additives for which the N-PPR were synthesized by means of ion and initiated polymerization. It was shown in the evaluation of the surface activity of resinous asphaltene oil components and the components of the developed compositions that among the studied samples N-PPR are characterized by the lowest surface tension. The resins of oil kinds under investigation differ from each other in surface tension only insignificantly. Among all components, asphaltenes are characterized by the highest surface tension. A new complex additive based on PAA and modified PPR was proposed, which may be used to reduce the chilling temperature and viscosity of paraffin and high-paraffin oil, as well as the amount of ARPS formed in them.

**Keywords:** oil polymer resins, modification of oil polymer resins, asphaltic resinous paraffin sediments, polymer additives, resinous asphaltenic components

### INTRODUCTION

The fraction of heavy highly paraffinic oil in the produced hydrocarbon raw material has recently increased. Its transportation inevitably involves the formation of asphalt-tar-paraffin sediments (ATPS) in the pipeline, which causes a decrease in the pipeline capacity, higher wear of the equipment and an increase in the cost of oil transportation [1]. In oil-producing regions of West Siberia, this problem is additionally complicated by low-temperature climatic conditions. This explains the necessity to choose efficient

multifunctional additives possessing inhibiting and depressor action.

Development of the integrated-action additives based on high-molecular polymers in combination with low-molecular compounds with oxygen- and nitrogen-containing functional groups is of relevant importance [2]. Special interest as the low-molecular component of the complex additives (CA) hold polymeric petroleum resins (PPR) synthesized from liquid pyrolysis products. It is known that the residual products of oil processing, such as goudron, cracking residues, indene-coumaric resin and so on possess depressor prop-

erties. In particular, it is necessary to mention publications [3, 4] in which the oxidized PPR synthesized from the heavy resin of pyrolysis (boiling point above 300 °C) showed itself as a good additive decreasing the solidification temperature of oil and oil products. Moreover, under the conditions of progressing import substitution PPR are an economically profitable version for the development of additives because they are distinguished by relatively easy synthesis method and available stable inland raw material basis [5].

Relying on the above-listed factors, the goal of the present work is to investigate the effect of modified PPR within CA on the viscosity and temperature-related characteristics of paraffinic and high-paraffinic oils and the amount of ATPS formed in them.

## EXPERIMENTAL

Oil from the Ust-Tegus deposit (UT) was chosen as an example of the paraffinic oil, and oils from the Festivalnoe (FS) and Archinskoe (AR) deposits were chosen as the high-paraffinic oil. These oil kinds differ from each other in the content of paraffinic and resinous-asphaltenic components (RAC), which noticeably affect their chill points (Table 1).

Chill temperature  $T_z$  and dynamic viscosity  $\eta$  of oil were determined with the help of the Kristall device (Russia) measuring the low-temperature parameters of oil products (MLPO). The quantitative estimation of ATPS formation was made by means of the coldfinger test [6]. The group composition of oil samples was determined using the cold Holde's method and by means of column adsorption on ASK silica gel [7]. The surface tension of the toluene solutions of samples under investigation was measured with a du Ноу tensiometer [8].

Polyalkylacrylate (PAA, chain length  $R = C_{16} - C_{20}$ ; the number mean molecular mass  $M_n =$

20 600, the mass mean molecular mass  $M_w = 55 600$ ) was used as the major high-molecular component of CA. The PPR of the aromatic fraction  $C_9$  of liquid pyrolysis products synthesized *via* initiated, thermal or ion polymerization and modified through nitration (N-PPR) were chosen as the low-molecular component of the additive. The oil polymer resins synthesized by thermal (PPR<sub>therm</sub>) and initiated (PPR<sub>init</sub>) polymerization were obtained from the Angarskaya Neftekhimicheskaya Kompaniya LLC. The oil polymer resin synthesized through ion polymerization (PPR<sub>ion</sub>) was obtained according to the procedure described in [9].

Polymeric petroleum resins was modified using a standard procedure, taking into account the fact that PPR of the  $C_9$  fraction is composed of 75 % of styrene units, and every third unit of the polymer chain is subjected to nitration [10]. A 50 % solution (by mass) of PPR in chloroform was used for nitration; concentrated  $HNO_3$  in the concentration of 30 % of PPR mass was used as a nitrating agent. Nitration was carried out at 70 °C for 3 h. The solvent and unreacted hydrocarbons were isolated from the reaction mass at reduced pressure.

According to the data of elemental analysis, N-PPR is in comparison with initial PPR samples have increased contents of nitrogen and oxygen. This is the evidence that nitration also involves oxidation processes (Table 2).

## RESULTS AND DISCUSSION

The following optimal CA composition was determined, providing the most efficient decrease in chill temperature of oil disperse systems (ODS) and the amount of ATPS formed in them, mass %: polyalkylacrylate (PAA) 49.80, N-PPR 0.15, toluene 50.05.

It was demonstrated in the investigation of the effect of the composition in 0.05 mass % concentration on the viscosity-temperature charac-

TABLE 1  
Characteristics of oil under study

| Deposit | Content, mass %                        |        |             | Chill temperature, °C |
|---------|--|--------|-------------|-----------------------|
|         | Petroleum oils (paraffin hydrocarbons) | Resins | Asphaltenes |                       |
| AR      | 85.3 (7.0)                             | 13.1   | 1.6         | +6.5                  |
| FS      | 82.0 (20.0)                            | 15.9   | 2.1         | +18.0                 |
| UT      | 71.1 (4.5)                             | 25.7   | 3.2         | -5.0                  |

TABLE 2  
Elemental composition of PPR

| Sample                | Elemental composition, mass % |     |     |     |      |
|-----------------------|-------------------------------|-----|-----|-----|------|
|                       | C                             | H   | N   | S   | O    |
| PPR <sub>init</sub>   | 83.1                          | 6.9 | 0.1 | 0.0 | 9.9  |
| PPR <sub>term</sub>   | 83.5                          | 7.7 | 0.1 | 0.0 | 8.7  |
| PPR <sub>ion</sub>    | 81.9                          | 7.0 | 0.2 | 0.0 | 10.9 |
| N-PPR <sub>init</sub> | 68.3                          | 5.1 | 4.1 | 0.0 | 22.5 |
| N-PPR <sub>term</sub> | 68.1                          | 4.5 | 3.8 | 0.0 | 23.6 |
| N-PPR <sub>ion</sub>  | 68.8                          | 5.2 | 4.0 | 0.0 | 22.0 |

teristics of oil kinds under study (Table 3) that the amount of precipitate obtained in the presence of CA decreases by 10 % on average in comparison with the amount of precipitate collected from oil in the presence of PAA alone. Depression  $T_z$  of the samples of oil from the Archinskoe and Festivalnoe deposits in the presence of CA is 8–14 °C on average, which is 2 times more than the depression  $T_z$  in the presence of PAA. In addition, a decrease in the dynamic viscosity of oil (approximately by a factor of 1.3) is observed. With the use of CA, a minimal depressor and inhibiting effect was observed for oil from the Ust-Tegus deposit, which is characterized by increased RAC content. It should be stressed that the best results over all the parameters are demonstrated by the additives containing M-PPR<sub>init</sub>

TABLE 3  
Structural-rheological characteristics of oils under investigation in the presence of the additives of different compositions

| Oil system                        | $T_z$ , °C | Inhibition degree, % | $\eta$ at 5 °C, mPa · s |
|-----------------------------------|------------|----------------------|-------------------------|
| <i>Archinskoe (AR) deposit</i>    |            |                      |                         |
| AR                                | +6.5       | –                    | 503                     |
| AR + PAA                          | +0.3       | 50.1                 | 210                     |
| The same + N-PPR <sub>init</sub>  | –7.9       | 73.7                 | 198                     |
| The same + N-PPR <sub>therm</sub> | –5.6       | 63.4                 | 201                     |
| The same + N-PPR <sub>ion</sub>   | –8.5       | 76.7                 | 200                     |
| <i>Festivalnoe (FS) deposit</i>   |            |                      |                         |
| FS                                | +18.0      | –                    | 703                     |
| FS + PPR                          | +8.3       | 60.7                 | 356                     |
| The same + N-PPR <sub>init</sub>  | +0.1       | 72.4                 | 325                     |
| The same + N-PPR <sub>therm</sub> | +2.4       | 65.6                 | 340                     |
| The same + PPR <sub>ion</sub>     | –0.5       | 78.0                 | 310                     |
| <i>Ust-Tegus (UT) deposit</i>     |            |                      |                         |
| UT                                | –5.0       | –                    | 423                     |
| UT + PPR                          | –10.8      | 50.6                 | 159                     |
| The same + N-PPR <sub>init</sub>  | –13.3      | 70.5                 | 142                     |
| The same + N-PPR <sub>therm</sub> | –11.4      | 64.4                 | 154                     |
| The same + PPR <sub>ion</sub>     | –15.6      | 72.3                 | 130                     |

or N-PPR<sub>ion</sub>, in which nitrogen content is  $\geq 4.0$  mass % (see Table 2).

Analysis of the composition of precipitates in oils under study, obtained in the presence of the additives of different compositions, showed that in the case of N-PPR the content of asphaltenes and paraffin hydrocarbons in the precipitate increases (Table 4).

Most probably, the efficiency of CA effect on the viscosity-temperature characteristics of paraffinic and high-paraffinic oils under investigation is also due to the properties of their RAC. In this connection, we studied their surface properties.

Evaluation of the surface activity of oil RAC and CA components revealed that N-PPR samples are characterized by the lowest surface tension (~26 mN/m) among the studied samples; the surface tension values of the resins of oil kinds under study differ from each other (resins of oil from the Archinskoe deposit have lower values); asphaltenes have the highest surface tension (40–45 mN/m) among all components. So, the surface activity of the molecules increases as a sequence N-PPR → PAA → oil resins → asphaltenes (Table 5).

Z. I. Syunyaev with co-authors determined that under the conditions of crystallization, complicated structural units (CCU) are formed in ODS, with their nuclei composed of paraffin hydrocarbons [10]. These CCU possess excess sur-

TABLE 4

Composition of precipitates of oil kinds under study, obtained in the presence of the additives of different compositions

| Oil systems in which precipitates were obtained | Fraction content in precipitate, mass % |        |             |
|---|---|--------|-------------|
|   | Petroleum oil (paraffin hydrocarbons)   | Resins | Asphaltenes |
| <i>Archinskoe (AR) deposit</i>                  |   |        |             |
| AR  | 80.7 (9.2)                              | 13.6   | 2.7         |
| AR + PAA  | 76.4 (11.0)                             | 14.2   | 3.4         |
| The same + N-PPR <sub>therm</sub>               | 76.6 (13.4)                             | 12.6   | 4.8         |
| The same + N-PPR <sub>init</sub>                | 76.2 (10.3)                             | 11.6   | 3.2         |
| The same + N-PPR <sub>ion</sub>                 | 75.8 (13.9)                             | 11.9   | 3.3         |
| <i>Festivalnoe (FS) deposit</i>                 |   |        |             |
| FS  | 80.3 (22.9)                             | 16.7   | 3.0         |
| FS + PAA  | 78.9 (23.6)                             | 17.2   | 3.9         |
| The same + N-PPR <sub>init</sub>                | 77.9 (24.0)                             | 17.9   | 4.2         |
| The same + N-PPR <sub>therm</sub>               | 80.0 (23.2)                             | 16.9   | 3.1         |
| The same + N-PPR <sub>ion</sub>                 | 77.9 (24.3)                             | 17.8   | 4.3         |
| <i>Ust-Tegus (UT) deposit</i>                   |   |        |             |
| UT  | 70.1 (7.5)                              | 25.9   | 4.0         |
| UT + PAA  | 70.9 (8.0)                              | 24.8   | 4.3         |
| The same + N-PPR <sub>init</sub>                | 74.1 (8.7)                              | 21.4   | 4.5         |
| The same + N-PPR <sub>therm</sub>               | 71.2 (7.8)                              | 24.8   | 4.0         |
| The same + N-PPR <sub>ion</sub>                 | 74.1 (9.1)                              | 21.2   | 4.7         |

face energy, so solvate shells composed of paraffin hydrocarbons and oil components are formed around them.

The use of inhibiting additives may cause weakening of intermolecular interactions (IMI) between the components of the solvate layer of CCU and RAC of the oil system [11]. Associative complexes formed due to the IMI between the solvate layer of CCU and polar groups of the polymers in the additive are formed in the volume of the oil system.

A direct dependence between the degree of inhibition of the proposed additives (see Table 3) and the surface activity of the components of the additive (see Table 5) attracts attention. The low-

er is the surface tension of the additive, the easier may IMI with paraffin hydrocarbons of ODS arise, thus holding *n*-alkanes within the volume of the oil system.

Thus, the additives should be characterized by lower surface tension values than the resinous and asphalteneous components of ODS, which will allow them to form more stable associates with the solvate shell of CCU of the oil system. If we take into account the fact that asphaltene is the most polar component in the oil system, their surface tension would be always higher than that of inhibiting additives. Then one may assume that asphaltene does not have any noticeable effect on the efficiency of inhibiting additives [12].

TABLE 5

Values of surface tension of RAC of oils of AR, FS and UT deposits, N-PPR and PAA

| Sample        | Surface tension, mN/m | Sample                | Surface tension, mN/m |
|---------------|-----------------------|-----------------------|-----------------------|
| AR resins     | 30.5                  | N-НПС <sub>ион</sub>  | 26.3                  |
| FS resins     | 35.1                  | N-НПС <sub>иниц</sub> | 26.2                  |
| UT resins     | 32.4                  | N-НПС <sub>терм</sub> | 27.1                  |
| AR asphaltene | 43.6                  | ПАА                   | 31.2                  |
| FS asphaltene | 45.4                  |                       |                       |
| UT asphaltene | 40.8                  |                       |                       |

The surface tension of the solutions of resinous components and inhibitors are most close to each other, so the maximal influence on the efficiency of inhibiting additives will be that caused by the resinous components of the oil system.

#### CONCLUSION

According to the results of the investigation, a new complex additive based on PAA and modified PPR is proposed. It may be used to lower the chill temperature and viscosity of paraffinic and high-paraffinic oils, as well as ATPS formed in them.

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