METHOD FOR CLEANING OF HEAVY OILS USING COORDINATION POLYMERS

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Abstract: *The effect of synthesized composite materials BAF-1 and BAF-2 (conditional names) based on coordination polymers on improving the rheological properties of oil was studied. The mechanism of action of nanostructured coordination polymers was studied by X-ray and electron microscopic methods. These composite materials form non-valent compounds with self-construction and self-organization due to their porous structure. When interacting with oil, they are capable to destroy the asphaltene-resin-paraffin deposits (ARPD), which ensures their equal distribution in oil. In this way, oil recovery from wells increases, and ARPD are effectively washed out of cavitation zones that form in the pipeline, which in turn ensures the cleaning of oil reservoirs from oil and oil product deposits.*
The proposed composites are capable of solving many problems associated with ARPD, in particular, they improve oil recovery from wells, reduce the viscosity of heavy oils and increase the transportation of such oils, i.e. the technology based on the indicated reagents is multifunctional.
Key words: *rheological properties of oil, coordination polymers, composite materials, reagent, asphaltene-resin-paraffin deposits, non-valent compounds.*
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Introduction

The oil industry is faced with a serious problem associated with the formation of large quantities of asphaltene-resin-paraffin deposits (ARPD), which increase the viscosity of oils and, consequently, reduce their fluidity. Crude oil stored in tanks is in liquid form and has some characteristic properties such as: dark black colour, intense odor (bisulfite), high viscosity, high flammability and low density greater than water. It consists of complex chains of heavy hydrocarbons and may also contain light hydrocarbons and other elements in smaller quantities. The main types of hydrocarbons that form crude oil are:

- Paraffins (saturated hydrocarbons-alkanes (e.g. octane));
- Olefins (unsaturated hydrocarbons-alkenes (e.g. pentene));
- Naphthenes or cycloparaffins (saturated hydrocarbons-cycloalkanes, e.g. cyclohexane);
- Aromatic hydrocarbons (arenes, e.g. benzene).

Despite the wide variety of methods for improving the rheological properties of oils, the problem is still far from being resolved and remains one of the most important in the domestic and foreign oil producing industries [1-5].

Therefore, the aim of this work is to study methods for improving the rheological properties of oils using the coordination polymers we synthesized and to clarify the mechanism of their action.

Results and discussion

In the course of this study, the structural and component composition of asphaltene-resin-paraffin deposits (ARPD) in crude oil samples collected from three different wells of the Siyazan oil field (Azerbaijan) was investigated.

The fractional composition of the samples was determined using the PAC OptiDist™ automatic distillation analyzer, which provided high-accuracy data on the boiling point ranges of various crude oil fractions.

The obtained results are presented in Table and demonstrate differences in the ARPD composition depending on the well, indicating the heterogeneity of the geochemical characteristics of the fluid even within the same oil field.

Table 1. Physicochemical properties of ARPD samples

Properties	Sample-I	Sample-II	Sample-III
Density, kg/m^3	977.4	933.1	987.3
Content. %			
paraffins	2.219	0.346	2.440
resins	8.34	1.384	4.04
asphaltenes	4.94	1.34	9.895
Fractional composition:			
boils at T. % mass., 150^{0}C	104.7	95.6	106.4
150-250^{0}C			
250-350^{0}C	14.2	21.0	13.0
350-400^{0}C	39.0	47.0	38.6
Remainder	16.6	8.1	15.8
	30.2	23.9	32.6

According to the results of the fractional composition analysis of the ARPD samples, it was established that they contain light fractions: up to a temperature of 350°C, approximately 51–53% of the mass of samples III and I evaporates, respectively, while for sample II, this indicator is 68%.

Thermogravimetric analysis of the ARPD samples was carried out in the temperature range of 25–600°C using a “Netzsch STA 449 F3” instrument, with a linear heating rate of 5°C/min.

The thermograms of the samples show a number of thermal effects accompanied by mass loss of the samples.

A low-intensity endothermic effect at a temperature of 110°C can be attributed to the loss of residual adsorbed water (moisture), with mass loss in this range amounting to 5.4–7.2%. On the DSC curves, exothermic peaks are observed for all ARPD samples at temperatures of 318°C and 393–395°C. At this stage, mass loss occurs due to the evaporation of light organic fractions, the content of which reaches 45–48%.

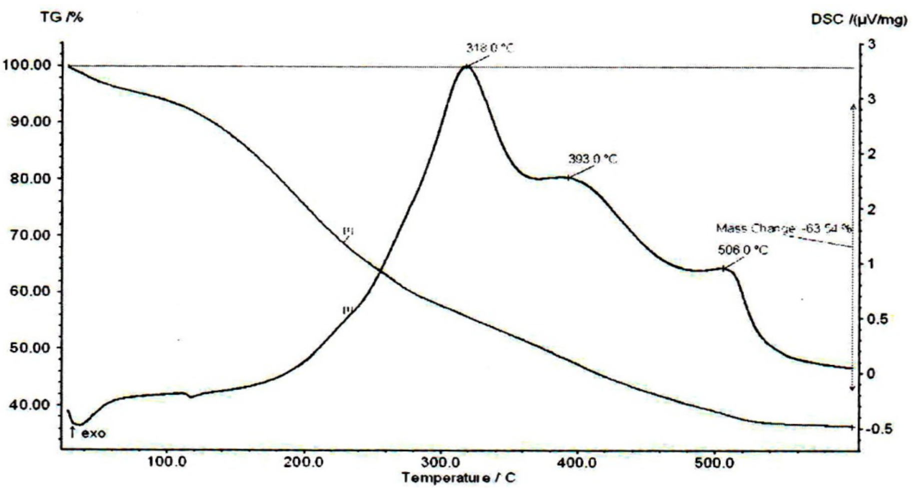

Fig. 1. DSC/TG analysis of sample I.

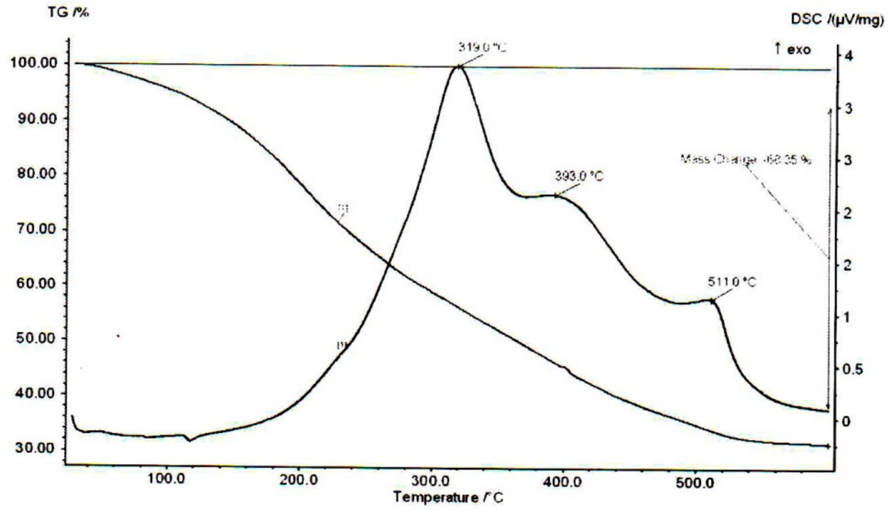

Fig. 2. DSC/TG analysis of sample II.

Thermograms of oil sludge samples show a number of thermal effects accompanied by a loss of sample mass.

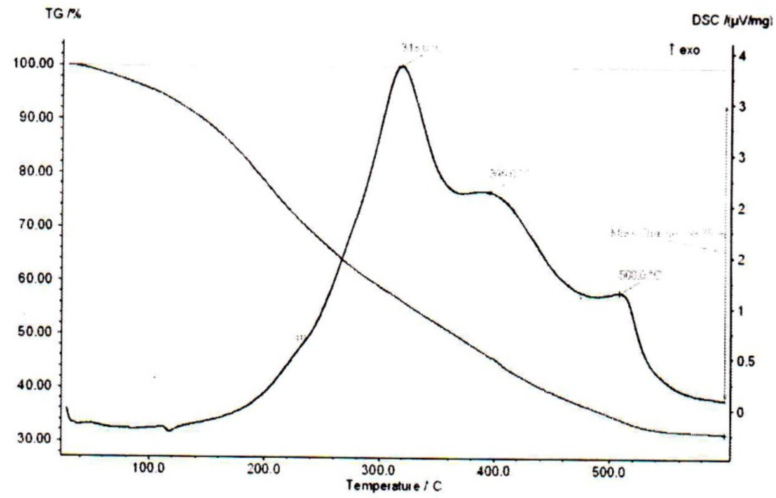

Fig. 3. DSC/TG analysis of sample III.

An exothermic peak in the range of 508–511°C is associated with the decomposition of the main structural fragments of asphaltene-resinous substances, resulting predominantly in low-molecular-weight volatile products and high-molecular-weight coke precursors. According to the TGA curve, the weight loss is 9.6%, 12.8%, and 12.1% for samples I, II, and III, respectively (figure 1,2,3). These data indicate that, compared to the other ARPD samples, sample II is the best resource for obtaining light fractions of oil-gasoline and diesel distillates [6-9].

Preliminary studies have shown that the coordination polymers we previously synthesized, conventionally named BAF-1 and BAF-2, improve the rheological properties of heavy oils—that is, they reduce viscosity, thereby facilitating transportation from the production site to the oil refinery or oil storage facility, and enhance oil recovery.

The BAF-1 and BAF-2 compositions were prepared based on waste from the diesel fraction-so-called diesel-alkaline waste (DAW), surfactants (SAA), and coordination polymers. Diesel-alkaline waste is a dark brown liquid, easily soluble in water, and is characterized by the following properties:

Boiling point: 135–210°C / 3 mm Hg, density d_4^{20} = 1.05 g/cm³, refractive index n_4^{20} =1.05, acid number=218 mg KOH/g. Average molecular weight–256. According to elemental analysis, the content is as follows: carbon–72.1%, hydrogen–11.1%, oxygen–16.8%.

This is a mixture of alkylcyclopentanecarboxylic acids with a small admixture of alkylcyclohexanecarboxylic acids.

The sodium naphthenates present in the waste from alkaline treatment of fuel fractions (14.0–18.0%) have the general formula $C_nH_{2n-1}COO^-Na^+$, and by their properties, they are water-soluble anionic surfactants. The aqueous solution also contains 2.0–2.5% of unsaponifiable compounds in emulsion form.

The coordination polymers, which form the basis of the BAF-1 and BAF-2 composites, are polycrystalline powders that are insoluble in water and neutral organic solvents, resistant in neutral and basic media, and salt-tolerant.

They have a porous polymer structure with pore sizes of 15–20 Å. The pores are through-type (open-ended). The BAF-1 and BAF-2 composites are prepared as 1% solutions of coordination polymers in diesel-alkaline waste (DAW). When these composites (BAF-1 and BAF-2) are added to oil samples, the changes in oil characteristics are shown in Table 2.

Table 2. Characteristics of the oil sample upon the addition of 140 mL of 1% BAF-1 composite

Characteristic	Before Addition	After Addition
Crude Oil, %	60.0	80.0
Density, kg/m³	878.0	889.0
Adsorbed Water, %	8.0	3.0
Viscosity, cSt	9.0	2.7
Resins, %	36.04	0.0
Mechanical Mixtures, %	32.0	17.0

X-ray and electron microscopic studies have been carried out to clarify the mechanism of effect of the reagents. For implementation of the research. 40 ml of a composite solution of the reagent was added to oil samples (300 ml each) taken from the same well and the other was left unchanged and distilled until a tar fraction was obtained.

As you know tar is a dry product of oil distillation at 450-600^{0}C temperature (depending on the nature of oil) under vacuum conditions and atmospheric pressure. It is also known that the chemical composition of oils does not change during atmospheric and vacuum distillation. Therefore, the results of analyzes obtained for dry oil products refer also directly to the oils themselves.

Considering the above dry products of oil samples were subjected to X-ray phase and electron microscopic studies. The obtained results are shown in Fig.s 4, 5, 6 and 7.

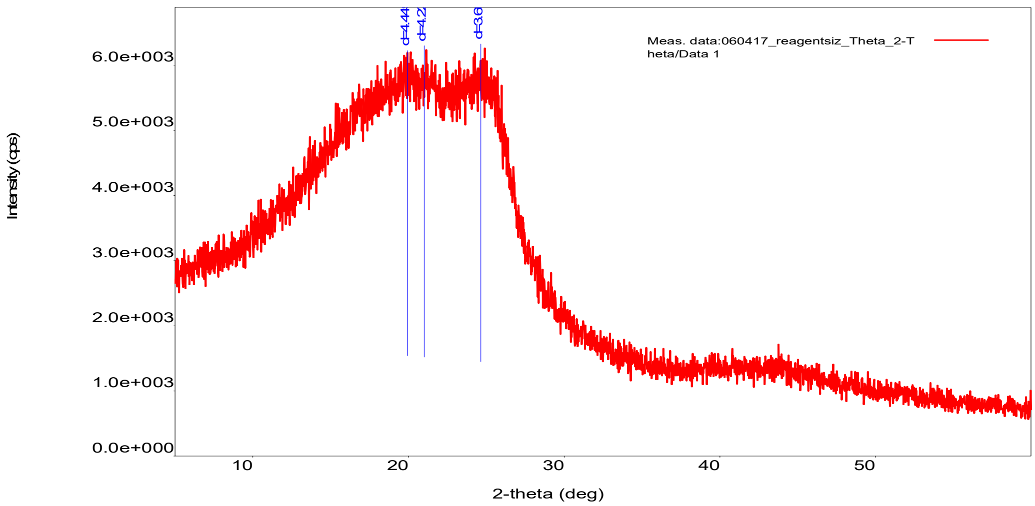

Fig. 4. X-ray diffraction pattern of dry non-reagent sample of the oil

As is seen from the X-ray diffraction pattern (Fig. 4) the sample of dry non-reagent product consists of three distinct phases with interplanar distances of 4.44; 4.22 and 3.64 Å.

On the X-ray diffraction pattern (Fig. 5) taken from a dry sample of an oil product with a reagent the third phase completely disappears and in the first two phases the maxima shift to small-angle sides that is the interplanar distances increase. This suggests that after the disappearance of the third phase the structure of the first and second phases changes and their crystallinity increases.

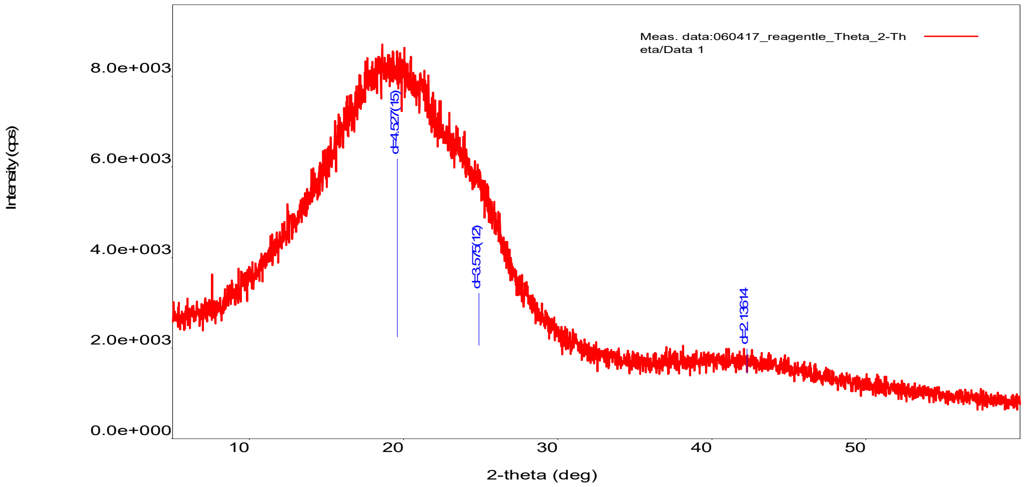

Fig. 5. X-ray diffraction pattern of dry oil sample with reagent

The results of the electron microscopic study of the non-reagent sample (Fig. 6) showed that in the dry residue there is an associate consisting of asphaltenes, resins and paraffins, which impairs the rheological properties of oils.

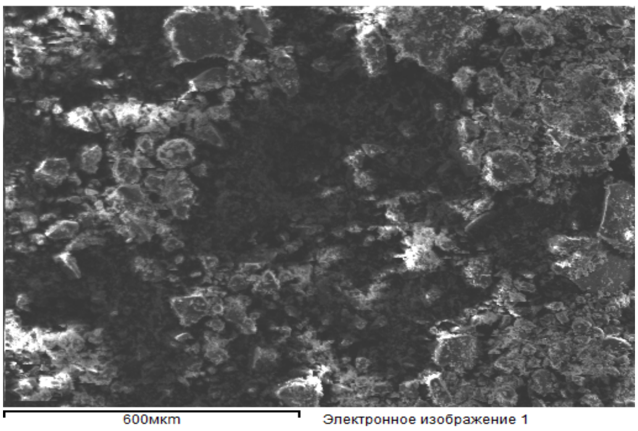

Fig. 6. Electron microscopic image of the dry non-reagent oil sample

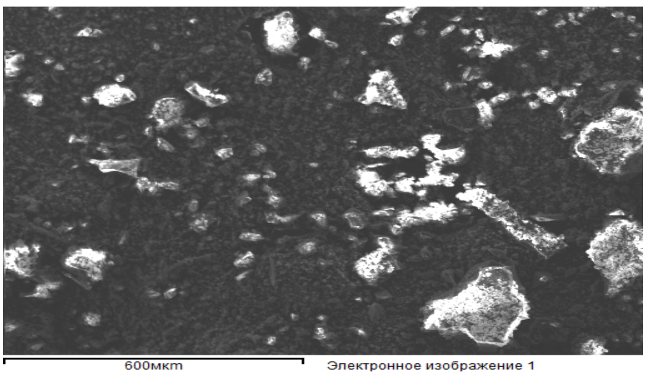

Fig. 7. Electron microscopic image of the dry oil sample with a reagent

The results of electron microscopic examination of the sample with the reagent (Fig. 7) indicate that the associate is in a fragmented form in the sample and is evenly distributed in the oil, that is, the associate is in the dissolved state.

The disappearance of the third phase (Fig. 5) with an interplanar distance (d = 3.60) shows that porous reagents (the pore size is approximately 20 Å BAF-1 and BAF-2) form non-valent compounds with the third phase via self-organization and self-construction (self-assembly) in other words when the reagent interacts with oil non-valent cracking interactions arise between porous coordination polymers and chromatic, heteroatomic macroassociates of the third phase. The first and second associates released from the third phase turn into small particles and dissolve in oil. Accordingly, the properties of oil were improved. At the same time an increase in the interplanar distance of the first and second phases shows that their structure is changing [10-12].

According to the results of electron microscopic analysis, it is also clearly seen that in a dry non-reagent product of oil ARPD associates are in a continuous mass and worsen its properties. And in the dry oil product with the ARPD reagent, the associates are fragmented into small particles, that is, they are evenly distributed in the oil and therefore rheological properties of the product are improved. This proves once again that reagents with chromatic heteroatoms form non-valent compounds.

Conclusions

1. The fractional composition of asphaltene-resin-paraffin deposits (ARPD) of heavy oils from the Siyazan oil field of Azerbaijan has been studied.
2. To improve the rheological properties of these oils, composites based on the coordination polymers synthesized by us have been proposed.
3. The mechanism of their action has been studied, and it has been shown that as a result of cracking interactions between coordination polymers and ARPD, the viscosity of the oil is reduced by 70%.

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