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Petroleum Resin Influence on the Relaxation Process of Petroleum Paraffin Solutions Treated in Ultrasound

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Abstract. This paper summarizes the experimental work done on the effect of petroleum resins on the process of relaxation the structural and rheological properties of petroleum paraffin solutions treated in ultrasonic field.

A combined treatment of petroleum paraffin solutions including 22 kHz ultrasonic exposure and addition of petroleum resins (0.3% 0.6% 0.9% by weight) was carried out. The addition of petroleum resins into the treated solution depresses the crystallization of hydrocarbons and favours the reduction of structural-mechanical characteristics of the system. The transition of the excited state of systems after the removal of the ultrasonic load to an equilibrium state occurs in time, and the nature of the change in the rheological characteristics and microstructure of paraffin crystals depends on the composition of the dispersion medium. It was revealed that trace amounts of resins introduced into paraffin oil systems treated with ultrasound will reduce their viscosity and improve transportation of hydrocarbons for 2 days at minimal cost.

1. Introduction

The increase in energy consumption worldwide and the decline of global light-oil reserves necessitates more attention to paraffinic oil reservoirs. Crude oils with a high content of high molecular n-alkanes and low content of resin-asphaltene components have high pour point. Lowering the temperature of the crude oil leads to a significant increase in viscosity due to formation of a dispersed phase. Formation of the dispersed phase is mainly associated with the presence of a multicomponent mixture of paraffin containing carbon atoms in the range of C₁₈-C₆₅ in oils. Such formations have a solid gel-like structure formed by three-dimensional (3D) network of interconnected paraffin crystals and occluded dispersion medium. Novel methods and techniques are of great importance to remove barriers and increase production from such reservoirs. Developing new methods in the field of heavy oil is an issue of great importance, as the large volume of these reserves can help meet the world's ever-increasing energy needs.

Currently, the possibility of using ultrasound technologies for the oil industry needs is being widely studied. Theoretical and experimental studies were successfully carried out in the field of ultrasonic cavitation. These studies allowed the development of new technological processes occurring under the influence of ultrasound [1-5]. Ultrasonic treatment (UT) is one of the most environmentally friendly methods of influencing oil disperse systems. Also worth noting are the advantages such as ease of operation, high manufacturability and low cost.



A review of scientific studies has shown that the structural and mechanical properties of different components of crude oils after treatment in an ultrasonic field do not change unambiguously. In this regard, to predict the properties of crude oil systems after ultrasound exposure, it is necessary to evaluate the effect of oil components on their behaviour.

It is known that the process of hydrocarbons crystallization in petroleum in the presence of resins is slowed down. Resins are natural depressors of viscosity-temperature parameters and inhibitors of sedimentation. Oil resins are high-molecular condensed heterocyclic systems, in the hydrocarbon part of which aromatic and naphthenic cycles, paraffin chains are contained. The resins form fairly strong associative complexes with an ordered structure while interacting with paraffin hydrocarbons, thereby preventing the aggregation of crystal nuclei [6].

Identifying of the behaviour of different component composition of highly paraffin systems in an ultrasonic field can be simplified by using model systems.

The purpose of this work is to study the effect of petroleum resins on the process of relaxation of petroleum paraffin solutions after ultrasonic treatment.

2. Experimental methods and materials

Resins were isolated from a highly resinous crude oil via liquid-adsorption chromatography. At first, asphaltenes were extracted from oil in a 40:1 excess of n-hexane and then the deasphalted oil (DAO) was separated into saturates and resins by chromatographic separation. DAO was charged to silica gel and extracted with solvents of increasing polarity. Silica gel activation proceeded at 250 °C for 2 h. The silica gel-DAO slurry placed in vacuum oven at 50°C for 24 h. Chromatography columns (1 x 50 cm with 150 ml solvent reservoir) were initially filled with a mixture of 95:5 hexane:toluene (v/v). Specially cleaned activated silica gel was added until the depth reached ~ 10 cm. Finally, silica gel with adsorbed DAO was transferred to the column until full. A solvent mixture contained 95% (v/v) hexane and 5% (v/v) toluene eluted saturates, mono-, di-, and triaromatics from the silica gel. Once the saturates and aromatics were extracted, a more polar solvent (50:50 toluene:ethanol) was applied to elute the resins. The resin-solvent mixture was filtered to remove any silica gel fines and rotary evaporated until dry. The resins were transferred to vials and placed in vacuum oven at 60 °C for 48 h or until completely dry.

Acoustic treatment of the samples was carried out for 10 min in a thermostatted cell using an UZDN ultrasonic disintegrator at an operating frequency of 22 ± 1.65 kHz, radiation intensity 18 W/cm².

The effect of resins and acoustic treatment on structural and mechanical properties was investigated using 6 wt.% petroleum paraffin solution in decane (PP-d).

The rheological parameters of the solutions were determined using a HAAKE Viscotester iQ rotational viscometer.

The process of changing the structure of paraffin particles was investigated by optical microscopy on an AXIO LAB.A1 Carl Zeiss microscope in transmitted light.

3. Results and Discussion

Petroleum resins isolated from petroleum were investigated in order to reveal the structural features of resins capable of decreasing viscosity values (figure 1). Structural-group parameters of petroleum resins were calculated based on the data of molecular weight, elemental analysis, and proton magnetic resonance spectroscopy. Structural and group characteristics of the petroleum resins under study are given in the article [7].

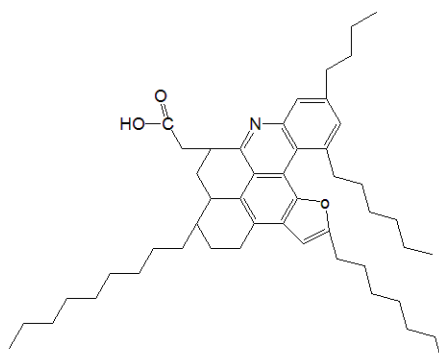


Figure 1. Structural formulas of petroleum resins.

Studies have shown that after ultrasonic treatment of the PP-d solution for 10 min, the viscosity increases 1.6-1.8 times, which is due to the intensive structuring of the system after removing the ultrasonic load. The viscosity of the treated sample reaches a maximum within two hours, and then relaxes to its initial value in 5 days (figure 2a).

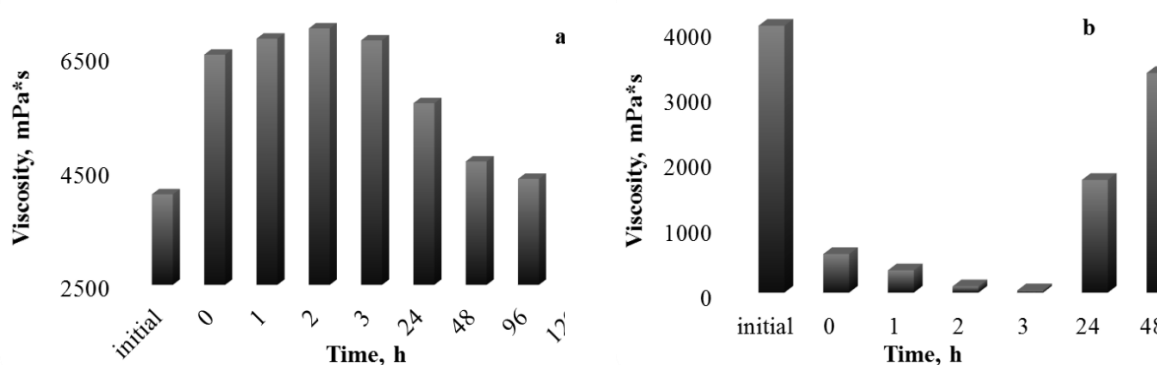


Figure 2. Effective viscosity of relaxing PP-d solutions: a - UT; b - UT + 0.3 wt.% resins.

Table 1 The effect of the petroleum resins concentration on the effective viscosity of the relaxing PP-d solution after ultrasonic treatment.

Concentration, wt. %	Relaxation time, h	Viscosity, mPa·s*
0	0	4085
	0	590
	1	341
0.3	2	96
	3	34
	0	10
0.6	1	8
	3	8
	0	5
0.9	1	4
	3	4

*shear rate 1 s^{-1}

A study of the effect of resins concentration that was injected into the solution of PP-d after ultrasonic treatment (table), on the viscosity of the relaxing system was made. Complex treatment in the presence of 0.3, 0.6 and 0.9 wt.% resins leads to a decrease in viscosity of 7, 408 and 817 times respectively.

Relaxation processes after complex treatment proceed differently in comparison with only ultrasonic treatment. The viscosity of the relaxing solution at a resin concentration of 0.3 wt.% continues to decline for 3 hours, and then increases on the second day to 3400 mPa·s, which, however, is lower than the initial value by 18 % (figure 2b). The viscosity of solutions containing 0.6 and 0.9 wt.% resins does not change for 3 hours.

The presented data on the viscosity of dispersed systems is possibly related to changes in the size and shape of the crystal structures formed when the temperature of the solution decreases.

Precipitation was isolated from PP-d solutions and their crystal structure was investigated using optical microscopy. In the sediment separated from the solution treated in the acoustic field (P_1), paraffin crystallizes in two modifications: needles with a length of 20-50 μm and spherulite formations with a diameter of 22-50 μm (figure 3). After relaxation for 24 hours, rhombic lamellar crystallites with a longitudinal diagonal of 40-80 μm and with a transverse diagonal of 30-65 μm are formed, and parallel-oriented needle-like crystals and spherulites of larger size are present in comparison with similar structures in the freshly treated solution.

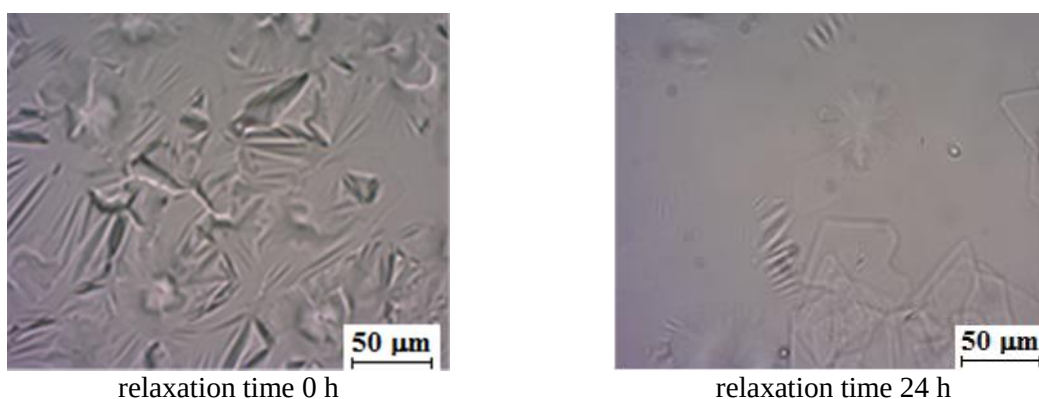


Figure 3. The crystal structures micrographs of sample P_1 .

After complex treatment of the PP-d solution, a precipitate is formed (P_2), the microstructure of which is represented by single crystals (figure 4). In the process of relaxation for 24 hours, the precipitate is recrystallized with the formation of needle-like crystalline formations with a length of 20-60 μm .

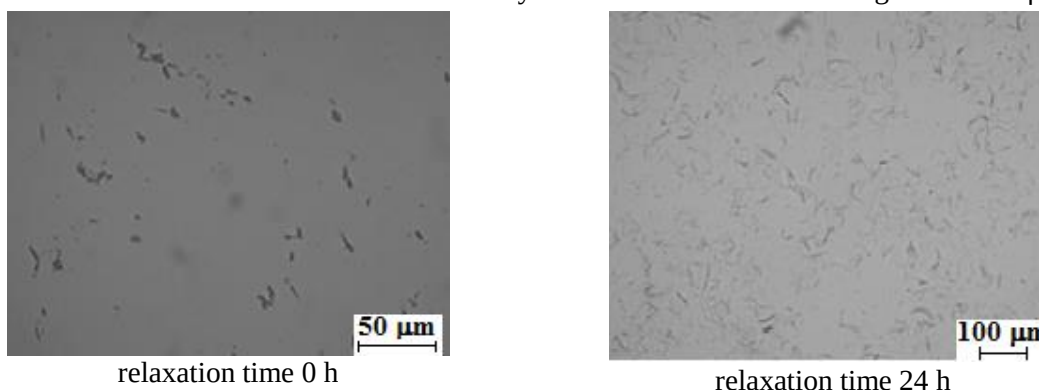


Figure 4. The crystal structures micrographs of sample P_2 .

4. Conclusion

Thus, the transition of the excited state of systems after the removal of the ultrasonic load to an equilibrium state occurs in time, and the nature of the change in the rheological characteristics and microstructure of paraffin crystals depends on the composition of the dispersion medium. The

introduction of resins in a paraffin-containing dispersed system, treated with ultrasound, leads to a decrease in viscosity after removing the acoustic load, and the depressant effect has prolonged nature. A significant effect of resins on the relaxation process is due to the inhibition of crystallization processes in paraffin-containing systems, which prevents the formation of a continuous crystalline network. Trace amounts of resins introduced into paraffin oil systems treated with ultrasound will reduce their viscosity. In this case, hydrocarbons are transported for 2 days at minimal cost.

Acknowledgments

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